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Kinetics and stage transitions of graphite for lithium-ion batteries

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Kinetics and stage transitions of graphite for lithium-ion batteries

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Kinetics and stage transitions of graphite for lithium-ion batteries

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Michael Heß
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What is the limit you are able to reach?*

\[ \lim_{n \to \infty} \text{your}^n \]

If you know ZERO the answer is clear. If you work alONE you will also not get much out. But if you have a good team which you can discuss and learn from and have a lot of ideas and knowledge your possibilities are almost infinite.

* adapted from flyer of Boston Consulting group (2010)
Abstract

Graphite is one of the most common used materials for the negative electrode of current lithium-ion batteries. However, it is one of the limiting factors for the recharge rate capability in a battery. Therefore, this work focused on the separation of the different limitations of the material itself. The influences of diffusion, surface reactions and ohmic potential drops could be separated with the help of a newly developed thin-layer electrode technique.

Furthermore, the difference between a standard electrode response of graphite similar to a real application and the actual rate capability of the material itself are evaluated. It shows clearly, that the electrolyte diffusion limits medium and high rate capability. The morphology of particles determines the shape of the pores and connections between them. Thus, spherical particles seem to perform better in standard electrodes than flake-like ones.

The evaluation of the rate-limiting influences of graphite leads to the chemical modification of graphite to enhance the recharging rate capability. Two different approaches are investigated. First, a titanate-coating on potassium-intercalated graphite has been synthesized to introduce a surface stress. Second, chemical pillaring of the graphite bulk has been performed using partially-disproportionated graphite-oxide GOpd. The expansion of the interlayer distance leads to enhanced charge rate capability compared to standard graphite while the specific charge could almost be doubled. This material would be a break-through for high-power batteries if the severe aging in the first 70 cycles can be overcome.

The investigation of the thermodynamic phase transitions in graphite revealed new insight initiated by mean-field modeling. The stage transitions at low state-of-charge could be refined in situ for the first time since the first investigation on the Li-graphite system in 1975. Both in situ x-ray and neutron powder diffraction showed a continuous transition of stage 4L, 3L and 2L. The solid-solution regime could be determined and parameterized crystallographically. This can explain the long-known paradox about the continuous c-axis shift reported in literature although distinct stages are formed. Additionally, the sloppy potential profile in the low state-of-charge region can be explained.

Based on the findings, different mechanisms could be proposed. First, a model about the diffusion pathway is proposed forming annuli in the graphite particle which propagate with different diffusional velocity into the particle center. Second, a mechanism about the chemical pillaring in GOpd and the aging mechanism could be proposed. Last, the stage transitions could be described in more detail based on the new findings based on the diffraction techniques. These results might guide future research and might help to improve todays batteries based on graphite.
**Kurzfassung**


Motivation and goal of the PhD work

During my studies I got in contact with graphite where some problems occurred that I could not solve. Despite the rich literature some details on kinetics and thermodynamics of graphite are still missing where some new hypotheses about this material could be developed.

One of these hypotheses concerns the diffusion of lithium in graphite. A very high diffusion coefficient was predicted by density-functional-theory but graphite seemed to be a rather medium-fast battery material as reported in literature. Therefore, the first goal of this thesis was the proof of fast diffusion kinetics in graphite.

The second idea concerned a change of the elastic energy which needs to be overcome during the lithiation of graphite. An idea was developed theoretically which aimed to introduce a stress on the material to expand the distance between the graphene sheets in graphite. These modifications lead to novel features of graphite.

During the modeling of the phase diagram of the Li-graphite system, inconsistencies at very low state-of-charge were recognized. Therefore, in situ diffraction techniques were applied to graphite to elucidate the phase-transitions in this regime.

These developments let to further work to calculate the phase-boundary alignment in graphite during a two-phase coexistence. The combination of the results led to sketches how lithium-ions diffuse and organize in graphite.

On the one hand, these results help to understand the bottlenecks of graphite in lithium-ion batteries and, on the other hand, offer solutions to overcome these limitations (chemical modification, electrode engineering). The results might contribute to enhance the understanding of lithium intercalation in graphite and may help to improve some applications where this technology is used, e.g., laptops and smartphones where the current recharge capability is very limited.
1. Introduction

Lithium-ion batteries are currently used in many electronic devices like laptops, smartphones, tablets, mp3-players and other portable devices. In these gadgets the recharging time of the used lithium-ion battery is allowed to be more than two to three hours which is mostly done overnight. But today the field of application is expanding to the transportation sector. Hybrid electrical vehicles and full electrical vehicles enter the market as an alternative to the combustion engine. Besides the need of a high specific energy and good volumetric energy density also aspects of aging, thermal management, safety, control systems and costs play a significant role.

But one aspect which is also very crucial concerns the recharging rate capability. When an electrical vehicle “runs out of fuel”, meaning that the state-of-charge (SOC) of a battery is too low to deliver enough power, a recharge is necessary. In contrast to the portable electronic devices, recharging for two to three hours at the electrical recharging station is inconvenient when one wants to overcome long distances. The duration for recharging is mainly limited by the negative electrode which is graphite in most cases of today’s lithium-ion batteries. The high specific charge of graphite and very negative potential close to metallic lithium is the key to a very high energy density of the battery [1]. However, this very negative potential also limits the recharging of the graphite electrode because very limited kinetic overpotentials can be applied to fill the particles with lithium-ions. This limits the rate drastically.

Other materials like titanates substitute graphite for high-power applications because titanates have a less negative potential and possess three-dimensional solid-state diffusion thus allowing higher overpotentials and rates. But the main disadvantages of these titanates are the lower energy density which is often less than half of cells with graphite (Li$_4$Ti$_5$O$_{12}$ possesses a theoretical specific charge of 175 mAh/g at ~1.55 V [2]). Therefore, one sacrifices energy density and battery voltage for the possibility to recharge more rapidly.

But what if one can improve the rate capability of graphite and still use all other advantages? This could help to overcome the recharging problem for electrical vehicles while keeping a high energy density which is a prerequisite for the application in the transportation sector. Therefore, this work will focus on the identification of the bottlenecks during recharging of a graphite electrode and possible methods to overcome these bottlenecks by chemical modifications.
2. Fundamentals of batteries

To understand the system under investigation, both the concept and the mathematical equations governing the battery have to be described.

2.1 Concept of electrochemical energy storage systems

Both batteries and electrochemical double-layer capacitors belong to the group of electrochemical energy storage systems. Batteries can be further classified by their used material or exchanged ion which is used to transport the electric current via ions between the positive and negative electrode. Some of these battery types are lead acid batteries which are often used in cars, nickel-metal-hydride batteries still used for low energy portable applications and lithium-ion batteries for high energy applications. In contrast to these storage systems, there are several energy conversion systems like the fuel cell and the internal combustion engine which transform chemical energy in electrical and mechanical energy, respectively. To compare these systems the Ragone plot can be adducted which relates the specific power with the specific energy [3] as shown in Figure 1. For high power applications super capacitors are appropriate while for storing high amounts of electrical energy batteries are more suitable. In general, energy conversion systems have higher specific energy but have the problem to require a certain system size to operate which excludes them for electronic portable gadgets. In comparison, also the requirements for electric and hybrid-electric vehicles have been included in Figure 1 by Cairns and Albertus [4] which indicates that further research is necessary to develop electrochemical energy storage systems being able to reach the needed specifications for electric vehicles.

![Ragone plot](image-url)  

Figure 1: Ragone plot of several electrochemical energy storage and energy conversion systems (internal combustion (IC) engine, fuel cells) compared to the requirements of electrified vehicles (electric, plug-in electric and hybrid vehicles (EV, PHEV, HEV)) [4, 5].
To reach the goal for electric vehicles, improvements on the battery system seem to be most promising. In general, batteries can be classified in primary and secondary batteries where the former can only be discharged once while the latter system can be charged and discharged for hundreds of cycles. Such secondary batteries are in the focus of current research because they are more environmentally friendly compared to primary systems due to the reusability and can become more cost efficient over long-term cycling although their initial costs are high. Primary batteries are for example the Leclanché cell based on manganese oxide. Secondary batteries are e.g. the lead-acid battery, nickel-metal-hydride, nickel-cadmium, zinc-air, sodium-sulfur and lithium-ion battery.

2.2 Lithium-ion battery

Lithium-ion batteries work on a simple principle. Lithium-ions are often intercalated into layered structures of transition-metal oxides (e.g. LiCoO$_2$) on the positive electrode and graphite at the negative electrode as depicted in Figure 2. During charging of the battery lithium-ions diffuse and migrate from the positive electrode to the negative one where the intercalation host is reduced. The ions are stored in the interslabs of the layered material. During discharge these ions are extracted from the material in the negative electrode and diffuse and migrate through an electrolyte to the positive electrode where the lithium-ions get intercalated into the layered oxide. The transition-metal oxide gets reduced during the lithium insertion. The half-cell reactions can be formally written as:

\[
\begin{align*}
Li^+ + e^- & \xrightleftharpoons{\text{charge}} \xleftarrow{\text{discharge}} LiCoO_2 \\
Li^+ + e^- & \xrightleftharpoons{\text{discharge}} \xleftarrow{\text{charge}} LiC_6 \\
\Delta G &= -zFU
\end{align*}
\]  

The driving force for charge and discharge depends on the electrical potential difference \( U \) between the materials which is related to the difference in the free energy of the system as shown in eq. (2.3). During charge the electrical potential difference of the electrodes in the cell increases and the system has to be forced externally. During discharge the cell potential decreases and the released energy can be used. Figure 2 shows the scheme of this process. Figure 3 shows schematically the composite porous electrode including the main parts of a lithium-ion battery. On the left hand side in Figure 3 one can find the copper current collector for the negative electrode. Copper is used because of its stability to lithium metal at very negative potentials, because the Cu-Li binary phase diagram shows no intermediate phase at room temperature [6]. Only at temperatures above 480°C a Cu$_2$Li$_3$ binary phase was calculated [7].
For the positive electrode, aluminum can be used as a current collector which is a preferred metal due to its low mass density, stability due to surface passivation and rather low costs. In general, the main task of the current collectors is the homogeneous distribution of electrons across the electrode guaranteeing a low ohmic resistance. Additionally, they possess good mechanical stability which supports the porous electrode.

The porous electrode is directly coated on the current collector. It consists of particles of active material, binder, conductive filler and pores filled with electrolyte. The active material differs for the negative and positive electrode and will be described in the next sections. The binder is needed to get a mechanical adhesive connection between the particles in the electrode. The binder can consist of polyvinylidenefluoride PVDF, polytetrafluoroethylene PTFE [8], carboxymethylcellulose CMC or other organic polymers. All of them have different properties and electrochemical stability regions. In general, PVDF is stable at potentials negative to 4.5V and PTFE above 1V both vs. Li⁺/Li which leads to their use in either the negative or positive electrode, respectively.
Conductive fillers are often added in small quantities to increase electronic conductivity in the electrode especially for insulating active materials like LiCoO$_2$ [9] or LiFePO$_4$ [8]. Sometimes, even a carbon coating on the active material surface is added to enhance the conductivity [10, 11]. Several different conductive additives can be used mainly on the base of carbon soot like acetylene black [8], carbon black [11] or SuperP.

The remaining part of the electrode is porosity which is filled with electrolyte. Due to very negative potentials and a large potential window ranging from circa -3 to +2V vs. the standard hydrogen electrode (0 to +5V vs. Li$^+/\text{Li}$), organic electrolytes have to be used in lithium-ion batteries. Alkene-carbonates play an important role among several other solvents like e.g. ethylene carbonate, propylene carbonate, dimethyl carbonate and diethyl carbonate [12, 13]. Various lithium salts can be mixed with the organic solvents to create the electrolyte. One of the main salts used today is LiPF$_6$ but also other salts can be utilized like LiClO$_4$, LiAsF$_6$, LiBF$_4$ [12, 13] and in rare cases also lithium methide LiC(CF$_3$SO$_2$)$_3$ [14].

The separator is also soaked with electrolyte and is located between both electrodes. The main task of the separator is the electronic insulation of both electrodes to each other while guaranteeing a good ionic conductivity. This can be fulfilled by using e.g. fiber cloth with porosity between the fibers for the electrolyte, a polymer electrolyte or solid electrolytes. Examples for fiber cloth are glass fiber and polyethylene fibers. Polymer electrolytes are generally consisting of a solid polymer like polyethylene oxide or polyacrylonitrile. Solid electrolytes are often made of an inorganic ceramic which conducts ions like e.g. Li$_{10}$GeP$_2$S$_{12}$ which exhibits an ionic conductivity of 12 mS/cm at room temperature similar to organic liquid electrolytes [15].

The composite porous electrodes can be e.g. spiral-wound in a cylindrical casing which is displayed in Figure 4 [4], be assembled in a pouch-cell or other geometrical forms. One can also

Figure 4: Cylindrical, spiral-wound battery designed like a standard 18650 cell of dimensions 18x65 mm [4].
see parts of the safety system of a cell in Figure 4. A resistor with a positive temperature coefficient PTC is indicated which increases its resistance during short-circuit in the cell to prevent a thermal runaway of the cell. Additionally, there can be a vent which opens if a high gas pressure evolves within the closed cell preventing explosion.

The casing and insulating parts of this standard cell are contributing to the overall mass of a battery. This composition in weight percent (wt%) is presented in Figure 5. The active materials in the negative (anode) and positive (cathode) electrode take only 42 wt% of the total mass in an 18650 cell. In contrast, all inactive materials like the current collectors and the casing take approximately 58% of the total mass. This shows clearly that also the system engineering can improve the overall energy and power density drastically.

### 2.3 Materials for the positive electrode of Li-ion batteries

Active materials for the positive electrode are generally layered transition-metal oxides where the transition-metal changes its oxidation state during lithiation and delithiation. But besides these layered materials, there exist also various other intercalation hosts like spinel type structure, e.g. LiMn$_2$O$_4$, or olivine type hosts, e.g. LiMPO$_4$ (M=Fe, Mn, Ni, Co). Some of the most utilized positive electrode materials are summarized in Table 1.

Some materials for the positive electrode were already found in the beginning of the 1970’s and are based on layered dichalcogenides and trichalcogenides. Some candidates are LiTiS$_2$ [16, 17], LiNbSe$_2$ [18], and even other hosts are known like AgTaSe$_2$ and AgTiS$_2$ [19]. LiNbSe$_2$ and Ag-TiS$_2$ undergo stage transitions during lithiation and delithiation which can be stage 1, 2 and 3 for LiNbSe$_2$ [18] and stage 1 and 2 for AgTaSe$_2$ and AgTiS$_2$ [19]. In contrast, LiTiS$_2$ has a sloppy potential profile between 1.8-2.5V and a continuous c-axis expansion of the lattice [16].

![Figure 5: Mass composition of an 18650 cell [courtesy of Dr. Wohlfahrt-Mehrens, ZSW].](image-url)
Vanadium pentoxide, V₂O₅, is another early material for the positive electrode [20, 21]. Several phase transitions with a corresponding potential plateau are observed during the first cycle which changes to a sloppy charge-potential curve in the following cycles. Also other vanadates were investigated like V₆O₁₃ [22] and Li₃V₃O₈ made from H₂V₃O₈ [23].

LiCoO₂ was the first commercially available material for a full-cell [24]. It possesses a theoretical specific charge of 274 mAh/g, however, is restricted to a delithiation to circa 0.5 Li per unit formula due to the phase transitions occurring at potentials positive to 4.2 V vs. Li⁺/Li [9, 25]. LiCoO₂ crystallizes in hexagonal R-3m space group where the transition metal resides in octahedral side corner-sharing with three unit cells stacked above one another per unit cell (O3) [9]. At extraction of 0.5 Li per unit formula, a monoclinic phase occurs [25] which is an intermediate structure. At very positive potentials the structure becomes unstable and the transition-metal-oxide layers collapse forming a so-called O1-phase where the cobalt-ions are still in octahedral sites but are shifted to a face-sharing structure [9]. This process is to a very high extent irreversible so that only a practical specific charge of 145 mAh/g can be delivered in a potential range up to 4.2 V. The energetically interesting potential range up to 4.6 V cannot be accessed due to stability reasons [9, 25]. Additionally, cobalt is toxic and expensive which pushes research towards other transition-metal-oxides.

Another candidate is LiNiO₂ which is isostructural to LiCoO₂ with a theoretical specific charge of 274 mAh/g. However, it delivers only ~240 mAh/g in the first cycle and ages rapidly [26]. During the cycling three hexagonal and one monoclinic phase occur with a strong lattice expansion which often results in micro-cracks in the structure [27]. Additionally, a Li⁺ and Ni²⁺ ex-

Table 1: Selected active materials for the positive electrode in lithium-ion batteries.

<table>
<thead>
<tr>
<th>Material</th>
<th>Theor. specific charge [mAh/g]</th>
<th>Potential vs. Li⁺/Li [V]</th>
<th>Energy density vs. Li⁺/Li [Wh/kg]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiTiS₂</td>
<td>225</td>
<td>1.8-2.5</td>
<td>480</td>
<td>[16]</td>
</tr>
<tr>
<td>Li₃V₂O₅</td>
<td>397</td>
<td>1.5-3.7</td>
<td>1030</td>
<td>[21]</td>
</tr>
<tr>
<td>LiCoO₂</td>
<td>274</td>
<td>3.8-4.2</td>
<td>1096</td>
<td>[9]</td>
</tr>
<tr>
<td>LiNiO₂</td>
<td>274</td>
<td>3.5-4.2</td>
<td>1070</td>
<td>[26]</td>
</tr>
<tr>
<td>LiMnO₂</td>
<td>285</td>
<td>3.0-4.0</td>
<td>630</td>
<td>[28]</td>
</tr>
<tr>
<td>LiMn₂O₄</td>
<td>118</td>
<td>4.0-4.1</td>
<td>480</td>
<td>[29]</td>
</tr>
<tr>
<td>Li(MₙNiₙCoₙ)O₂</td>
<td>170</td>
<td>3.9-4.3</td>
<td>700</td>
<td>[30]</td>
</tr>
<tr>
<td>LiMnO₃+NMC</td>
<td>280</td>
<td>3.8-4.5</td>
<td>1150</td>
<td>[31]</td>
</tr>
<tr>
<td>LiFePO₄</td>
<td>170</td>
<td>3.47</td>
<td>590</td>
<td>[32]</td>
</tr>
<tr>
<td>LiMnPPO₄</td>
<td>171</td>
<td>4.04</td>
<td>690</td>
<td>[33]</td>
</tr>
<tr>
<td>LiNiPO₄</td>
<td>167</td>
<td>5.07</td>
<td>850</td>
<td>[33]</td>
</tr>
<tr>
<td>LiCoPO₄</td>
<td>167</td>
<td>4.73</td>
<td>790</td>
<td>[33]</td>
</tr>
<tr>
<td>LiFeSO₄F</td>
<td>151</td>
<td>3.6</td>
<td>540</td>
<td>[34]</td>
</tr>
</tbody>
</table>
change in the lattice can occur due to similar ion radii of these two ions. Ni$^{2+}$-ions in the interslab hinder the diffusion of lithium-ions which results in lower rate capability [26, 27]. Therefore, this electrode material also possesses severe disadvantages which seem to be reduced by fluoride doping and Lithium excess in Li$_1.08$Ni$_{0.92}$O$_{1.9}$F$_{0.1}$ [26].

LiMnO$_2$ is another material which could be isostructural to LiCoO$_2$. However, the pure form of LiMnO$_2$ is metastable in the R-3m space group and changes to Pmnm [35]. Only doping with Ni, Co [35], Al or Cr [28] can stabilize the structure. The doping combination Li$_2$MnO$_3$+LiCrO$_2$, i.e. Li[Li$_{0.2}$Cr$_{0.4}$Mn$_{0.4}$]O$_2$ [28] can lead to a more stable cycling where more than 180 mAh/g can be extracted during the first cycles [28]. But a formation of a spinel phase is often observed after a few cycles [35]. These problems have prohibited the use in commercial applications so far.

Manganese spinel, LiMn$_2$O$_4$, is a very fast intercalation host due to its three-dimensional diffusion channels in the Fd3m space group [36]. The profile of the open-circuit potential consists of three potential plateaus at circa 4.1, 4.0 and ~2.8 V vs. Li$^+$/Li due to the different phase transitions [37]. The phase transition at ~ 2.8 V leads to an irreversible destruction of the material so that only 0.8 Li can be excessive in the first two potential plateaus. Modeling confirmed a high diffusion coefficient [29, 38, 39] which makes this material one of the fastest cathode materials known today. But its low specific charge urges to use blended electrodes made out of a high specific charge material combined with LiMn$_2$O$_4$ for high power applications.

A combination of the previously mentioned layered transition-metal-oxides LiMO$_2$ (M= Co, Ni, Mn) being Li(M$_{x}$Ni$_{y}$Co$_{z}$)O$_2$ (NMC) combines most of the advantages of each single compound. A specific charge of 170 mAh/g can be extracted reversibly in the potential range from 3.9- 4.3 V [30]. Overlithiated NMC with composition Li$_{1.1}$(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)$_{0.9}$O$_2$ shows no transition from O3 to O1 phase even at potentials positive to 4.5 V but release oxygen at very positive potentials [40]. Today, the stoichiometric NMC has been further improved by using a Li$_2$MnO$_3$ stabilized NMC which shows specific charges of 280 mAh/g between circa 3.8- 4.5 V [31]. In the first delithiation a plateau is observed which was attributed to the activation of Li$_2$MnO$_3$ with partial oxygen release from the structure [31, 40]. This material is of particular interest because of its high energy density and stable cycling.

LiFePO$_4$ was first developed by Padhi et al. in 1997 [32]. Although it was firstly thought to possess a low diffusion coefficient and electronic conductivity [8, 32] it is widely used today. Carbon coating [10, 11, 41] improved the cycling performance significantly although too thick carbon layers lead to a reduction of the LiFePO$_4$ to Fe$_3$P$_2$ [11]. Also its low initial kinetics were overcome with nanosizing [42] or doping of 1 wt% of Niob [43]. In general, LiFePO$_4$ is a two-phase separating material [44, 45] in which the phase boundary aligns in (100) direction if de-
fects are present [46] and in (101) direction for coherent interfaces with partial phase-separation at the surface [47]. This was first clarified by modeling of Cogswell and Bazant [48]. The diffusion of lithium-ions in the olivine structure is along the y-direction in Pnma space group [49].

LiFePO₄ is one of the most studied materials today and reveals many interesting features like an extended solid-solution with 1 wt% Niob doping [43], a pure solid-solution reaction if nanosized below 20 nm [47, 50], a partial solid-solution reaction after deep discharge [51] and a surface coating of pyrophosphates as a shell around LiFePO₄ can improve rate capability to rates up to 80C in a standard electrode [52-54]. Additionally, overpotentials might drive the pure phase-separation mechanism to turn into an intermediate amorphous phase in a certain overpotential regime and particle size [55]. This aspect is still discussed controversially in literature but recent modeling predicts a kinetic-driven solid-solution when high current densities are applied [56]. An electrode of LiFePO₄ could be assembled by biological viruses which dock to the LiFePO₄ and attach it to single-walled carbon-nanotubes [57, 58]. Furthermore, recent improvements to observe at atomic-scale resolution with annular-bright-field scanning transmission electron microscopy showed a staging at the interface between LiFePO₄ and FePO₄ similar to stage 2 as also observed in TiS₂ and graphite [59, 60].

Additionally, the modeling of LiFePO₄ needs to be described in more detail because it can be used as a model electrode for other phase-separating materials. In 2004, Srinivasan and Newman developed a shrinking-core model [61] which was further developed to give a history dependence [62]. But experiments [46] and calculations [63] showed that this isotropic approach is not valid for the one-dimensional defined diffusion channels for LiFePO₄. Therefore, the domino-cascade model was developed [64] and further improved by information about the phase-separation mechanism with a Cahn-Hilliard approach [65]. Additionally, it was predicted that defects blocking the (010) diffusion channels lead to severe limitations of the propagation of the phase boundary [66] and that a distribution of the particle size of LiFePO₄ leads to a mosaic instability meaning that small particle phase-separate before bigger ones [67]. A hysteresis was found to be due to the spinodal-decomposition of the LiFePO₄ particle-by-particle [68]. These findings can guide research for other phase-separating materials and will be used for reference.

Other olivines LiMPO₄ (M = Mn, Ni, Co) also crystallize in the Pnma space group and have much higher redox potentials with up to 5.07 V vs. Li⁺/Li for LiNiPO₄ [33]. But all of them suffer under kinetic limitations which limits the extracted specific charge significantly. Also silicates show very positive redox couples positive to 4.5 V [33]. Another recently discovered material is LiFeSO₄F which is also two-phase-separating like LiFePO₄ but at slightly more positive potential but lower specific charge [34].
2.4 Materials for negative electrodes of Li-ion batteries

Some materials which store lithium in the negative electrode are summarized in Table 2. The highest charge density can be stored for pure lithium-metal negative electrodes [13, 68]. On the surface of the lithium-metal, the organic electrolyte gets reduced forming a solid-electrolyte-interphase SEI with different inorganic and organic decomposition products of both the salt and organic solvents from the electrolyte [13]. These surface films increase the resistivity during charge and discharge significantly [69, 70]. But a more severe challenge concerns the dendrite formation during lithium deposition on the metal electrode during charge of the battery system which can be followed by NMR [71] and was also modeled to be of needle-like shape during growth [72] with many branches [73]. These dendrites might lead to short-circuits if they grow through the separator to the positive electrode which would a significant safety and life-time issue. Therefore, pure lithium-metal is used only in primary batteries commercially due to the avoiding of lithium deposition during recharging in secondary batteries.

Graphite is another material for the negative electrode in lithium-ion batteries. The specific charge for the lithiated graphite with formula LiC₆ is 372 mAh/g [1] which is attained at potentials very close to metallic lithium. This results in a relatively high energy density (with respect to the redox potential of LiFePO₄/FePO₄) in a full cell as shown in Table 2. The graphene sheets in graphite are bonded by van-der-Waals forces [74] and undergo several phase transitions during lithiation/delithiation. Graphite has a hexagonal lattice with ABAB stacking of the graphene layers but can also contain the metastable rhombohedral phase with ABCABC stacking [1].

<table>
<thead>
<tr>
<th>Material</th>
<th>Theor. specific charge [mAh/g]</th>
<th>Potential vs. Li’/Li [V]</th>
<th>Energy density vs. LiFePO₄ [Wh/kg]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-metal</td>
<td>∞ / 3861</td>
<td>0</td>
<td>∞ / 13400</td>
<td>[13]</td>
</tr>
<tr>
<td>Graphite</td>
<td>372</td>
<td>0 – 0.3</td>
<td>1240</td>
<td>[1]</td>
</tr>
<tr>
<td>Coke</td>
<td>~200</td>
<td>0 – 1.0</td>
<td>610</td>
<td>[1]</td>
</tr>
<tr>
<td>Hard-carbons</td>
<td>~1500</td>
<td>0 – 1.5</td>
<td>4080</td>
<td>[1]</td>
</tr>
<tr>
<td>TiO₂ anatase</td>
<td>168</td>
<td>1.78</td>
<td>280</td>
<td>[75]</td>
</tr>
<tr>
<td>TiO₂(B)</td>
<td>235</td>
<td>1.6</td>
<td>440</td>
<td>[75]</td>
</tr>
<tr>
<td>TiO₂ brookite</td>
<td>~165</td>
<td>1.7</td>
<td>290</td>
<td>[75]</td>
</tr>
<tr>
<td>TiO₂ rutile</td>
<td>315</td>
<td>0.1-3.0</td>
<td>530</td>
<td>[75]</td>
</tr>
<tr>
<td>Li₄Ti₅O₁₂</td>
<td>175</td>
<td>1.55</td>
<td>340</td>
<td>[2]</td>
</tr>
<tr>
<td>Li₂Ti₃O₇</td>
<td>198</td>
<td>1.4 – 2.3</td>
<td>350</td>
<td>[76]</td>
</tr>
<tr>
<td>Li₁₃Si₄</td>
<td>3101</td>
<td>0 – 1.0</td>
<td>9210</td>
<td>[77]</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>375</td>
<td>0 – 3.0</td>
<td>740</td>
<td>[78]</td>
</tr>
<tr>
<td>SnO₂</td>
<td>711</td>
<td>0 – 3.0</td>
<td>1400</td>
<td>[79]</td>
</tr>
</tbody>
</table>
During lithiation the stacking order rearranges to a final AA stacking with lithium-ions in every interslab in LiC₆ structure [80]. All phase transitions will be explained in detail in the next section. It also forms a solid-electrolyte-interphase similar to the one on lithium-metal [13]. The medium material costs, relative safe cycling compared to lithium-metal and reasonable specific charge made it the most used negative electrode material used commercially up to date.

Other carbon derivatives can also be used. Coke delivers circa 200 mAh/g between 0-1 V vs. Li⁺/Li [1] while some hard carbons can store lithium up to specific charges of 1500 mAh/g [1]. There the lithium can reside in both covalent and ionic sites next to each other [81]. Also other sites were proposed for the storage of the lithium-ions [1]. But hard-carbons often show a very high irreversible specific charge in the first cycle due to the solid-electrolyte-interphase formation and suffer from severe aging which makes it unappealing for applications. Some special carbons like graphitized carbon nanobeads also intercalate lithium with ~200 mAh/g [82]. Carbon nanofilaments give circa 400 and 220 mAh/g if heat-treated at 1000°C and 2800°C, respectively [83] and electrospun carbon nanofibers with specific charges is the same range as the filaments have also been reported [84].

Several titanates exist which can be used for electrochemical storage of lithium-ions. TiO₂ can occur in the form of anatase, brookite, rutile, TiO₂(B) [75]. Anatase shows a phase-separation plateau at ~1.78 V with ~0.5 Li reversible exchanged [75]. TiO₂(B) cycles at ~1.6 V with Li₀.₉¹TiO₂ giving a specific charge of up to 305 mAh/g in the first cycle and ~0.7 lithium in subsequent cycles [75]. Brookite cycles at ~1.7 V with 160-170 mAh/g specific charge while the rutile TiO₂ can be cycled if nanosized between 0.1-3 V delivering circa 315 mAh/g [75]. It was shown that an addition of surfactants improves rate capability of titanates due to a better particle dispersion in the slurry [85]. Additionally, the titanium-spinel, Li₄Ti₅O₁₂, is widely used which can insert three lithium-ions to form Li₇Ti₅O₁₂ at a potential of ~1.55 V giving 175 mAh/g [2]. Also the ramsdellite, Li₂Ti₃O₇, can be cycled giving the theoretical specific charge if doped with carbon to stabilize the structure [76] inserting two lithium-ions between 1.4 to 2.3 V vs. Li⁺/Li. In general, the disadvantages of a more positive potential and a lower specific charge for all titanates can be compensated by an increased safety and higher charge rate capability especially for the titanate spinel which is often used for high-power (but lower energy-density) applications.

Materials undergoing an alloying in the presence of lithium are able to deliver very high charge. The most common material used is silicon which crystallizes as Li₂₂Si₅ in the fully lithiated form [86, 87]. However, this phase is often believed to be inaccessible electrochemically. The alloy Li₁₃Si₄ seems to be formed with a theoretical specific charge of 3101 mAh/g which is
consistent with specific charges found experimentally [77]. The large volumetric changes of silicon during lithiation (~300 vol% between Si and Li$_{22}$Si$_5$) lead to a pulverization of almost any micrometer sized particle. Therefore, nanosizing and very porous silicon in the range of a few nanometer can solve this issue partially [77]. However, the high irreversible specific charge in the first cycle to form the SEI and its nanosizing which increases reactivity of the Li-Si alloy drastically have prohibited the broad commercial application so far. Tin, aluminum and antimony can also be used to alloy with lithium but suffer from similar volumetric expansions causing fracturing of the particles.

Last, conversion materials can be used where the lithium reacts e.g. with oxides or fluoride compounds by an ion-exchange in the structure which often leads to an extrusion of the cation in the starting material. Examples are CuO where the stored specific charge is highly dependent on particle size and the back-conversion is believed to end at Cu$_2$O [78]. Also SnO$_2$ can be used and cycled reversibly when embedded between graphene layers which can accommodate the strain during the volumetric expansion while keeping the electronic network intact [79]. These materials also suffer from drastic volume changes during cycling and a high surface area due to nanosizing which increases the irreversible specific charge. Therefore, conversion materials are still under research and have not been applied widely.

2.5 Thermodynamic stage-transitions in graphite

As mentioned in the previous section, graphite undergoes several phase transitions during lithiation and delithiation [88]. Figure 6 sketches all known phase transitions at room temperature. The dashed lines indicate the solid-solution regime which was approximated roughly from the experimental phase diagram of the Li-graphite system [89]. The galvanostatic lithiation and delithiation response at C/7 rate is indicated in the top of Figure 6. 1C corresponds to a full charge or discharge in one hour. This means that a C/7 rate takes seven hours to fully lithiate or delithiate graphite. The open-circuit potential is somewhere between the charge and discharge curves, the pseudo-open-circuit potential reflects the mean of the charge and discharge potential at a certain state-of-charge. The regimes where only a single phase exists are indicated by the dashed lines while the region between these single phases corresponds to the phase transition regime with a phase-coexistence. These transitions can be of different character. For example, the stage 1L to stage 4L, stage 2L to 2 and stage 2 to 1 transition undergo phase separation while the transitions of stage 4L to 3L and 3L to 2L might be of different origin because x-ray diffraction data suggests a continuous shift of the c-axis parameter which would indicate a solid-solution phase transition mechanism [88, 90, 91]. The different phases in graphite are called stages because of their ordering of the lithium-ions in every $n^{th}$ interslab. The different stages are shown in Figure 7.
The lithiation starts from pure graphite in Figure 7a) and continues to stage 1L which is not a new phase but reflects the miscibility of lithium in pure graphite at 300 K [89]. At zero kelvin the miscibility is zero and hence no stage 1L exists [89, 92]. But the name stage 1L has been used in literature to describe the disordered (liquid-like, L) lithium-ion intercalation in every interslab. In this work stage 1L will be also called graphite solid-solution since it captures the origin of this lithium-ordering more precisely and would be consistent with all other solid-solutions of the pure stages as indicated in Figure 6.

A phase transition occurs from graphite solid-solution to stage 4L, where lithium-ions are intercalated in every fourth interslab in a liquid-like manner (disordered). The subsequent transitions from stage 4L to stage 3L followed by the transition from stage 3L to 2L is still under debate but it is clear that lithium-ions are ordered in every third and second interslab in a liquid-like manner [90, 91]. The average in-plane density of these liquid-like stages varies in literature [93]. The transitions of these liquid-like stages have many interesting features. For example, Monte Carlo simulations by Kirczenow [94] showed that the transitions between the stages can have mixtures of stage 3, 2 and 1 where these stages can merge and separate during the transition. At the end of the simulation a mixture of 3% stage 1, 82% stage 2 and 15% stage 3 were coexisting where stage 3 was mainly located at the surface of the simulated particle [94]. The Daumas-Herold domains which are local islands of intercalation formed very late in the transition process [94]. Kirczenow [95] also simulated that during the transition from stage 3 to 2 an intermediate

![Figure 6: Phase transitions of graphite during lithium intercalation with solid-solution and phase-transition regions derived from the phase diagram at ~300K [89], cycling at C/7 vs. Li⁺/Li, small irreversible charge shifts phases to slightly higher state-of-charge as also shown by Dahn [88].](image)
disorder mixing exists between these pure stages which he suspected to be very difficult or almost impossible to observe with diffraction techniques. They should only decrease peak intensity of the pure stages [95]. The transition to stage 2L was also shown to have very slow reaction kinetics and takes three days to form starting from a mixed ordered stage 3 and stage 2 when heated from 240 K to 300 K [96]. A lithium-ion battery usually cycles around 298 K which might lead to a kinetic suppression of stage 2L during cycling (low rates of C/20 are only five to six hours in the regime of stage 3L-2L-2 transition). Dahm [88] also observed only slight peaks of stage 2L. Additionally, no coexistence of stage 4L and 3L was found and only continuous c-axis shifts were observed [88, 97].

The next transition from stage 2L to stage 2 keeps the same c-axis ordering but the in-plane density changes from the disordered stage 2L to the ordered LiC₆ in-plane density where the empty layer decreases from 3.35 Å for standard graphite to 3.245 Å [90].

Figure 7: Staging of graphite during lithium intercalation with a) graphite, b) stage 4L, c) stage 3L, d) stage 2L, and both e) stage 2 and f) stage 1 with LiC₆ in-plane order.
The last stage transition transforms stage 2 to stage 1 with every interslab filled with lithium-ions and LiC₆ in-plane ordering [80, 88, 90] as shown in Figure 7f). The stage 2 to 1 transition can deliver most of the specific charge as shown in Figure 6 and is also the best understood one.

An exceptional phase of Li-graphite intercalation compound Li-GIC is observed at very high pressures of 50-60 kbar and 280°C which corresponds to LiC₂ with lithium-ions in every hexagon [98]. The lithium-ion distance to each other is smaller than in lithium-metal [98]. This structure would be highly favorable for lithium-ion batteries due to three times the specific charge compared to stage 1 LiC₆ but decomposes via several intermediate phases at ambient pressure [98].

The lithium-graphite intercalation compounds Li-GIC can be compared to other alkali and earth-alkali metal intercalation compounds but shows an ordering of the lithium-ions in columns in stage 1 and 2. Potassium [99], rubidium [100] and caesium [100] can also intercalate in graphite, however, form a helix-like ordering of the ion in stage 1. In contrast, sodium can only intercalate in very low amounts (NaC₆₄ with ~ 25 mAh/g) [101] which was attributed to a lattice mismatch of the sodium-ion to the hexagonal structure of graphite [100]. These GICs show additional or complementary properties to the Li-GIC. For example, potassium and rubidium can have the fractional stage 3/2 which is a mix of stage 2 and 1 stacked above one another with an ordering of CmCCmCmCCm at pressures between 15-19 kbar for K-GIC [102, 103] and 20 kbar for Rb-GIC [104]. For K-GIC stages up to stage 8 have been reported [100]. Additionally, it could be proven by diffraction techniques that K-GIC has stage mixing for stage ≥2 [105]. For example at the state-of charge of expected pure stage 5 only 71% are attributed to stage 5 with contributions of 19% of stage 4 and 10% of stage 6 packages [105]. Expected stage 4 consists of 94% stage4, 4% stage 5 and 2% stage 3, (accuracy ±1%) [105]. Stage 3 in K-GIC is maximum 98% pure and stage 2 is only pure shortly before its transition to stage 1 [105]. Such an investigation would shed more light on the higher stage transitions in Li-GIC but was not found in literature. This mixing seems to be less during deintercalation in K-GIC [106]. But mosaic spread seems to increase with continuous vapor potassiation and depotassiation from 0.8 to 5 to 8° during the first three cycles [106]. These observations might also be present in Li-GIC and might have to be considered although they have not been reported for Li-GIC explicitly.

These stage transitions can be also seen from a crystallographic point of view. Graphite crystallizes in hexagonal P63/mmc space group where the graphene layers are stacked in ABAB sequence above one another [92, 107]. Additionally, a metastable rhombohedral phase, R-3m, can exist reflecting an ABCABC stacking found already by Debye and Scherrer [108, 109] but is removed during heat-treatment at temperatures above 2800°C [110-113]. Figure 8 shows the
structure of graphite with the different facets being basal and prismatic surfaces where prismatic ones can be further divided in zig-zag and arm-chair surfaces. The ordering of stage 4L is unknown so far but a repeated distance of 13.76 for oxidation and 13.9 Å for reduction was found [97]. XRD refinements with electron density calculations suggest [ABA|ACA|] stacking, however, contribution of [ABA|ABA|] stacking are probable for stage 3L [91]. The ordering of stage 2L in Li-GIC is [AB|BA|] stacking of the graphene layers with no in-plane Li-ordering [90, 93] and therefore different to all other alkali-metal GICs which have [AB|BC|CA|] stacking [89, 93].

Finally, dense stage 2 and 1 have an [AAα] [80, 90, 93] and [Aα] [80, 90, 93] stacking where the graphene layers are congruent to each other [80, 89, 93] with lithium-ordering in columns with LiC₆ in-plane density as shown in Figure 9a. Both dense stages, stage 1 and 2, crystallize in P6/mmm space group but with 3.706 Å and 7.065 Å in c-direction [80]. This is in contrast to the other alkali-metal GICs which order in C₆-structure with a helical stair type in CaCβCγCδCa stacking for K, Rb and CaCβCγCα for Cs [114]. Also the earth-alkali metals, CaC₆, SrC₆, BaC₆, and even Lanthanides, EuC₆, SmC₆ and YbC₆ order their ions in [CaCβ] stacking in P6₃/mmc space group which is due to coulombic repulsion of the cations within the dense structures [115-118]. Therefore, LiC₆ crystallizes in an unusual column stacking which is contrary to the known coulombic repulsion and has to be treated as an exception [100, 115].

All found crystallographic data on Li-GICs is summarized in Table 3. The stages ≥ 2 do not fill one interslab completely while leaving the other ones empty. They order in local domains, the so called Daumas-Herold domains [119]. These domains have a local ordering of a certain stage which can shift after an islands length as shown in Figure 9b. Additionally, the experimental phase diagram of the Li-graphite system is given in Figure 9 [120] which summarizes work of many researchers [80, 89, 93, 96, 102, 121].

![Graphite structure](image)

Figure 8: Graphite structure with AB-stacking of the graphene layers and different facets being basal and prismatic surfaces, zig-zag and arm-chair belong to prismatic surfaces (original in [1]).
Some small features of Li-GIC which are observed during electrochemical cycling are also worth mentioning. A small hysteresis of 10 mV has been reported for lithium-GIC and a galvanostatic-intermittent-titration technique can resolve the pseudo-open-circuit potential better than a galvanostatic C/800 charge/discharge [88, 97]. Further, special care has to be taken when graphite is cycled to very positive potentials because anion intercalation can occur for ClO$_4^-$ [122], PF$_6^-$ [122, 123] and other anions.

Also modeling reveals interesting features of graphite. In the beginning of graphite modeling mainly two different aspects of GICs were investigated which were either of electrostatic or elastic origin. The first approach to model the phase diagram of graphite was done by Safran [124] who was able to capture the staging process of GICs by a Hamiltonian which used attractive in-plane and repulsive interplane forces. But also fractional stages occurred which are not observed at ambient pressure. This approach was developed further by including a strong-screening effect which removed the fractional stages [125, 126].

Elastic approaches started by modeling the lattice expansion of GICs during ion intercalation. Modeling of the lattice expansion in c-direction by a spring-plate model captured the lattice expansion quiet well [17] but was shown to be insufficient [92]. Another attempt by Kirczenow was able to model the attraction and repulsion at the domain boundaries in the Daumas-Herold domains [119]. He showed that a domain distance of less than 7.7 Å results in an attraction in the case of Li-domains while higher distances lead to repulsion between the Li-GIC-domains. A first

a) LiC$_6$ in-plane ordering [1] 

b) Sketch of Daumas-Herold domains [119]

c) estimated phase diagram of Li-graphite [120]

Figure 9: Graphite ordering during lithium intercalation a) LiC$_6$ in-plane order in stage 1 and 2 (taken from [1]), b) sketch of Daumas-Herold domains with local islands of stage 2 (adapted from [119]), c) estimated Li-GIC phase diagram (from [102, 120]).
combination of elastic and electrostatic effects by Hawrylak [127] was able to model all stage transitions in K-GIC without the strong-screening effect which has no physical validation. The elastic energy deleted the fractional stages although stage 3/2 could be modeled consistent with experiments [103]. Other approaches like the modeling of stage 2L in the Li-GIC phase diagram [128] and rotation of intercalation islands [129] were later meant to be not close to reality [92].

The bending energy model of Kirczenow was further developed by Hawrylak et al. [130] for higher stages where he showed that the amount of islands should depend on the stage number leading to longer equilibration times for higher stages. Additionally, elastic energy should be independent of coherency which means that little defects do not alter the total free energy of the system [130] which will be important for phase boundary calculation in section 5.4. Additionally, the even stage numbers are more stable and lead to pure stages while odd ones can produce fractional stages [130].

A following work by Hawrylak et al. [131] used the Landau-Ginzburg theorem (similar to the Cahn-Hilliard approach [132-135]) showing that the intercalation proceeds via the formation and migration of islands of intermediate stages while they combine previous elastic [17] and electrostatic [124] work. He predicted the fractional stages and an island wave length of 20 Å and a diffusion coefficient of $10^{-6}$ cm$^2$/s for GICs which is very close to DFT calculation 20 years later.

Table 3: Summary of crystallographic data for the lithium-graphite-system at room temperature

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>Parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite (2H)</td>
<td>P63/mmc</td>
<td>a = 2.460(2) c = 6.704(5)</td>
<td>[107]</td>
</tr>
<tr>
<td>Graphite (3R)</td>
<td>R-3m</td>
<td>(a = 3.635) (alpha = 39.49)</td>
<td>[109]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a = 2.456 c = 10.039</td>
<td>[109]</td>
</tr>
<tr>
<td>Stage 4L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c_{ox} = 13.76$, $c_{red} = 13.9$</td>
<td>[97]</td>
</tr>
<tr>
<td>Stage 3L</td>
<td></td>
<td>a = 2.4684 c = 10.408 (c = 2x3.33+3.748)</td>
<td>[91]</td>
</tr>
<tr>
<td>Stage 3L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c_{ox} = 10.401$, $c_{red} = 10.473$</td>
<td>[97]</td>
</tr>
<tr>
<td>Stage 2L</td>
<td></td>
<td>a = 2.4725 c = 7.065 (c = 3.33+3.735)</td>
<td>[90]</td>
</tr>
<tr>
<td>Stage 2L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 7.055 ±0.005</td>
<td>[93]</td>
</tr>
<tr>
<td>Stage 2</td>
<td>P6/mmm</td>
<td>a = 4.2867 c = 7.025 (c1 = 3.245)</td>
<td>[90]</td>
</tr>
<tr>
<td>Stage 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>P6/mmm</td>
<td>$c_{ox} = 7.043$, $c_{red} = 7.072$</td>
<td>[97]</td>
</tr>
<tr>
<td>Stage 2</td>
<td>P6/mmm</td>
<td>c = 7.024 ±0.005</td>
<td>[93]</td>
</tr>
<tr>
<td>Stage 2</td>
<td>P6/mmm</td>
<td>a = 4.288 ±0.002 c = 7.065 ±0.01</td>
<td>[80]</td>
</tr>
<tr>
<td>Stage 1</td>
<td>P6/mmm</td>
<td>a = 4.316 c = 3.703</td>
<td>[97]</td>
</tr>
<tr>
<td>Stage 1</td>
<td>P6/mmm</td>
<td>a = 4.305 ±0.002 c = 3.706 ±0.01</td>
<td>[80]</td>
</tr>
<tr>
<td>Stage 1</td>
<td>P6/mmm</td>
<td>a = 4.305 c = 3.706</td>
<td>[90]</td>
</tr>
</tbody>
</table>
Additionally, the mixing of high stages shown experimentally [105] could be modeled [137]. Ulloa and Kirczenow [138] showed that domain wall energy determines the difficulty of ion intercalation so that Li can intercalate easily because it needs to overcome a low energy barrier for matching domain walls while ions like Na and Ca have a high symmetric and asymmetric energy barrier so that these ions do not intercalate easily. These calculations are consistent with experimental findings 20 years later for Ca-GIC [115]. These models should guide experimentalists and consider elastic energies like crystal strain, graphene bending, matching domains and also electrostatics like Coulombic repulsion between cations for the evaluation of their experiments.

2.6 Experimental methods

2.6.1 Electrochemical measurement techniques

a) Galvanostatic cycling

Charging and discharging under constant current condition is called galvanostatic cycling where the change in electrochemical potential is measured. Since the total specific charge can often not be extracted fully during galvanostatic charge/discharge, especially at higher rates, a constant potential step can follow which holds the electrode potential and measures the decreasing current. The difference of the measured potential during galvanostatic measurement and the open-circuit-potential is the so-called overpotential which drives several kinetic processes like the surfaces reactions, migration and is also partially due to ohmic resistances.

b) Potentiodynamic sweep/cyclic voltammetry

When the potential-difference of an electrochemical system is changed at a certain sweep rate, e.g. 10 mV/s, the current response is measured and can help to identify redox potentials of electrochemical reactions. But the overpotential can change drastically because the applied current can change by several orders of magnitude which can change contributions from the linear ohmic resistance drastically.

c) Galvanostatic-intermittent-titration technique

This measurement technique applies galvanostatic currents for a certain time period which is followed by an open-circuit period for a few hours in which the potential of the material can relax. The relaxation time includes many kinetic processes which try to relax back close to the equilibrium. Some of these processes involve diffusion in the solid and electrolyte. The relaxation time needs theoretically infinite to reach the equilibrium; however, experiments have to be stopped after a certain period of relaxation. Ohmic potential drops can be seen instantly after cur-
rent shut-off if they are not connected to a capacitance or coil where they would form a RC or RL time-constant of first order (for more information see transfer function theory). From this technique the pseudo-open-circuit-potential can be extracted. Often the potentiostatic-intermittent-titration technique is used where the diffusion coefficient can be extracted applying the Cottrell equation \[139\].

d) Electrochemical impedance spectroscopy

Also alternating current can be applied to electrochemical systems. During electrochemical impedance spectroscopy the current response to an alternating potential-difference is measured which gives information about amplitude and phase of the electrochemical impedance. These data can be divided in real and imaginary contributions and are commonly plotted as Bode or Nyquist plots. Additionally, a Fourier transform + filtering + back transformation can be applied to extract the time constants of the electrochemical system \[140, 141\]. The experimental can often be fitted by resistance and capacitance elements and help to extract information about the system \[142\]. To be able to fit the impedance response with linear RC-elements, the amplitude of the mostly sinusoidal excitation of the EIS has to be restricted to the linear regime of for the processes in the system. This restricts the amplitude of the applied potential-difference to be normally much less than 30 mV which is the beginning of the Tafel-regime for a surface reaction. Very small amplitudes suffer from noise. Therefore, often amplitudes of 10 mV are applied \[142, 143\].

2.6.2 Diffraction techniques

Diffraction is a widely used technique for material analysis. It can be applied to single-crystals and powder by the use of x-rays, neutrons, electrons or other electromagnetic waves. From the Bragg reflexes one can be extract the distance of crystallographic planes which fulfill the Bragg equation:

\[ n\lambda = 2d \sin \theta \quad (2.4) \]

where \( \lambda \) is the wavelength of the incident beam, \( d \) is the distance between the crystallographic planes and \( \theta \) is the angle of the incident beam. The Bragg equation describes the additional distance a coherent beam has to travel between two parallel crystallographic planes. X-rays scatter on the electron cloud of atoms which means a better scattering for elements with many electrons.

Generally, light atoms like H, He, Li almost do not diffract x-rays while Pb, Au, Ag diffract very well. Neutrons scatter on the nuclei of elements and therefore show different scattering profiles for different isotopes of the same element. Neutrons can also scatter on light atoms and can often be used as a complementary diffraction technique to x-ray diffraction (XRD). Especially,
hydrogen has a strong neutron cross-section which can lead to diffuse scattering. Therefore, hydrogen has to be often replaced by deuterium which possesses a much smaller cross-section. Another feature of neutron diffraction concerns the transition-metals Ni, Mn, Co which have very similar scattering in x-rays but can be differentiated more easily in neutron diffraction. But neutrons interact very weakly with matter which necessitates larger amounts of material in the beam while x-rays diffract already at very low quantities of the material of interest.

Both ex situ and in situ diffraction can be applied. “In situ” is derived from Latin “at the place, locally” which means essentially that the measurement is done directly at the same location where the battery is cycled. In situ measurements often decrease or prevent problems like relaxation of the phases, transitions of metastable phases or contamination during sample preparation. However, in situ measurements are often more difficult to perform experimentally compared to ex situ diffraction of a sample which shows often much less parasitic diffraction from other materials like the current collector or cell parts. This is one of the challenges in situ cells have to overcome.

From the diffractogram one can extract the space group and refine the crystallographic parameters of the unit cell by Rietveld refinement. For refinement of the diffractogram, many programs can help to refine these parameters and atomic positions, e.g. Fullprof [144]. Further information on structure of matter and crystallography can be obtained from De Graef [145].

2.6.3 Other methods

a) Scanning electron microscopy

Scanning electron microscopy uses a focused electron beam to scan the surface of a material of interest. The electron beam interacts with electrons at the surface of the investigated material and delivers information about morphology. The lateral resolution can be in the nanometer range while different detectors can be used including the secondary electron and back-scattering detector. Secondary electrons are electrons from the material itself which were excited by the incident electron beam giving different intensity depending on the tilt of the measured surface. Back-scattering electrons originate from elastic scattering of the beam electrons on the surface of the material and travel back to a detector. They contain often more information of the material composition since they interact with the material directly. Additionally, they can often deliver a more topographic image of the surface when they are measuring from the side of the sample. In general, the material needs to be conducting. Otherwise, local charging can occur creating an electric field thus decreasing the resolution drastically. Conductive additives like carbon or gold sputtering onto insulating materials can help to overcome this challenge.
b) X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy XPS uses the outer photo effect and measures the kinetic energy and number of excited electrons which have been activated by x-rays. This technique can measure the composition and valence state of the outer surface in the range of ~1-10 nm. X-rays can penetrate much deeper into the material, however, the excited electrons deeper in the material are mostly trapped in excited states of the material again and do not leave the material to be detected. The binding energy of the electrons are determined from

\[ E_{\text{bond}} = E_{\text{photon}} - E_{\text{kin}} - \Phi \]  

where \( E_{\text{bond}} \) corresponds to the binding energy which is the difference of the energy of the x-ray photons \( E_{\text{photon}} \), the measured kinetic energy of the detected electrons \( E_{\text{kin}} \) and the work function of the spectrometer \( \Phi \). The measured number of electrons can be plotted versus the measured binding energy giving element specific features. To measure the composition close to the surface below 10 nm, sputtering can be applied. However, the material is often strongly distorted by physical sputtering so that the results have to be interpreted carefully. XPS necessitates ultrahigh vacuum because the detector is often up to 1 m away from the sample.

2.7 Theoretical description of batteries

Electrochemical energy storage systems have been long known and were approached from a modeling point of view from several perspectives including kinetic models describing mainly diffusion, ohmic potential drops and surface reactions [143, 146, 147], thermodynamic models to described phase separation [65-68, 131], elastic models [17, 130] or finite-element-method (FEM) of a previously tomographed battery electrode [148]. This section will shortly describe the fundamentals of a set of, herein called, kinetic equation and is partially taken from Heβ and Novak [149].

Starting from the equation system described by Newman et al. [146, 147] for a porous electrode, the equations for the potential drop in the electrolyte \( \nabla \Phi_e \) and electrolyte diffusion can be described as [146]:

\[
\nabla \Phi_e = \frac{-i_e}{\kappa} + \frac{2RT}{F} (1 - i^0) \left( 1 + \frac{d \ln f_{i^0}}{d \ln c_e} \right) \nabla \ln c_e 
\]  

\[
\varepsilon \frac{\partial c_e}{\partial t} = \nabla \cdot \varepsilon D_e \left( 1 - \frac{d \ln c_0}{d \ln c_e} \right) \nabla c_e + \frac{i^0_{ne} \nabla \cdot i_e + i_e \cdot \nabla i^0_{ne}}{F} 
\]  

(2.7)
where the potential in the electrolyte $\Phi_e$ is a function of the current density in the electrolyte $i_e$ divided by the electronic conductivity $\kappa$ of the electrolyte which corresponds to the linear ohmic part in eq. (2.6). The universal gas constant $R$, temperature $T$, Faraday constant $F$, transference number $t$, activity coefficient $f$ and concentration of the salt in the electrolyte $c_e$ model the concentration gradient dependent part of the potential drop in the electrolyte. Note that the current density in the electrolyte $i_e$ has to be normalized to its area fraction in the porous separator and electrode.

The electrolyte diffusion equation (2.7) is a sum of the diffusion described by Fick’s second law which is adapted for porosity $\varepsilon$ and the influence of the transference number [146]. The diffusion coefficient in the electrolyte $D_e$ and concentration of the solvent $c_0$ determine the Fickian part while the transference number of the anions $t^0_{\text{ne}}$ and current in the electrolyte account for the conditions in concentrated solutions [147].

The equations governing the electrode kinetics of the negative and positive electrode include the surface reactions which can be described by the Butler-Volmer equation (2.8) for each electrode material in an electrolyte where the overpotential $\eta$ in eq. (2.9) is described to be the difference of the potential in the solid $\Phi_s$, the potential in the electrolyte at the surface of the solid particles $\Phi_e$ to the open-circuit potential of the material $U_{\text{OCP}}$. Additionally, ohmic potential drop in the solid-electrolyte interphase can be accounted by a resistivity $R_{\text{SEI}}$ and the normalized current density through the SEI [146].

\[
I = i_0 e^{a_c \frac{zF}{RT} \eta} - i_0 e^{a_a \frac{zF}{RT} \eta} \quad (2.8)
\]

\[
\eta = \Phi_s - \Phi_e - U_{\text{OCP}} - R_{\text{SEI}} i_n \quad (2.9)
\]

where the superficial current density $I$ is a function of the exchange current density $i_0$ with an exponential dependence on the overpotential $\eta$ times an anodic and cathodic charge transfer coefficient $a$. In the case of a one-electron transfer process and assuming that the transfer coefficient describes the symmetry of the energy barrier of the surface reaction one can simplify eq. (2.8) by $a_a + a_c = 1$ [150]. One of the limitations of this modeling approach is the determination of the open-circuit potential which is usually very difficult to measure precisely (see section 2.6.1 for GITT). However, it is often necessary to model the OCP to understand several thermodynamic effects as e.g. shown for LiFePO$_4$ [65].

The diffusion of lithium ions in the solid can be represented by Fick’s second law in equation (2.10) where the concentration change of lithium ions in the solid $c_S$ with time $t$ is a function of the diffusion coefficient $D_S$ and the concentration gradient in radial direction $r$ [146].
\[
\frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_s r^2 \frac{\partial c_s}{\partial r} \right) \tag{2.10}
\]

although one has to keep in mind that many other materials like graphite and LiFePO_4 have a very anisotropic diffusion of lithium ions in their structure compared to the isotropic radial diffusion of an assumed sphere which is modeled in eq. (2.10) [63, 131, 151]. Additionally, some of the stage transitions in graphite are phase separating, which requires more sophisticated models [65, 131]. The assumption of isotropic radial diffusion might give misleading results for phase separation materials as discussed in literature [61, 62, 65].

Additionally, the potential drop in the porous electrode matrix \(\nabla \Phi_s\) can be described by Ohm’s law which is adapted for tortuosity by an exponent of 1.5 for the porosity \(\varepsilon_s = 1 - \varepsilon_e\) and conductivity in the solid \(\sigma\) as [146]:

\[
\nabla \phi_s = \frac{i_e - I}{\sigma} = \frac{i_e - I}{\sigma_\infty (1 - \varepsilon_e)^{1.5}} \tag{2.11}
\]

Furthermore, charge conservation is given by [146]:

\[
\nabla \cdot i_e = A i_n \tag{2.12}
\]

where \(A\) is the surface area on the particles and \(i_n\) the current density normal to the surface. This equation system will be used and simplified in section 3.1.2 for thin-layer electrodes.
3. Kinetics of graphite electrodes

This chapter describes the identification of the rate limiting factors of graphite particles. Furthermore, solutions to improve the performance are given by proposing chemical modifications of graphite. Section 3.1 and 3.2 are partially adapted from Heß and Novak [149].

3.1 Graphite in thin-layer electrodes

As discussed in section 2.4, graphite is one of the most important negative electrode materials used in lithium-ion batteries due to its very negative open-circuit potential, improved safety compared to metallic lithium and moderate cost. But it has some major drawbacks, such as its moderate specific charge of 372 mAh/g and its rather low practical rate capability, which is limited to ~2C for lithiation (charge with respect to a complete battery) and 20C for delithiation (discharge) in standard electrodes [152]. However, recent ab initio calculation based on density functional theory (DFT) and Monte Carlo simulations [136] yielded a diffusion coefficient larger than $D = 2 \cdot 10^{-8}$ cm$^2$/s for the diffusion of lithium in dense stage 1 and 2 in the presence of many vacancies. But the diffusion coefficient decreases to $5 \cdot 10^{-9}$ cm$^2$/s for the fully lithiated stages 1 and 2 due to a low number of vacancies for Li hopping [136]. Similar results have been found experimentally by Levi et al. [153], who determined the diffusion coefficient by applying the potentiometric intermittent titration technique at 60 °C using the Cottrell equation. These experiments revealed highly fluctuating diffusion coefficients of approximately $5 \cdot 10^{-9}$ cm$^2$/s for the transitions involving dense stage 1 and 2 that drop sharply to $10^{-10}$ cm$^2$/s at the end of each phase transition. For the liquid-like phases, i.e., stage 2L, 3L, 4L, and 1L, the diffusion coefficient was determined to be approximately $1-5 \cdot 10^{-8}$ cm$^2$/s, dropping to a minimum of $10^{-9}$ cm$^2$/s at the end of each phase transition [153]. This suggests a difference in the lithium diffusion coefficients of a factor of 10 for the liquid-like stages compared to the dense stages with LiC$_6$ in-plane density. In any case, from both the ab initio calculation [136] and the experiment [153], one would expect the rate capability of graphite to be higher than ~2C for charge and 20C for discharge [152] for particles in the micrometer range.

It is known that the performance of graphite electrodes depends significantly on the electrode preparation, due to its influence on the porosity, the tortuosity, and the overall electronic conductivity of the graphite network [152, 154]. To characterize the properties of graphite particles themselves, however, it is necessary to avoid parasitic effects, such as electrolyte diffusion limitation within the porous electrode, electronic conductivity limitations, and the influence of the counter electrode. It has been shown for electrochemical impedance spectroscopy and cyclic voltammetry that thin layers of graphite can be used to separate the different electrochemical in-
fluences in a graphite electrode [155]. Here, we have therefore prepared thin-layer electrodes of graphite flakes and thus aimed at avoiding porosity effects and reducing the active mass and consequently the specific currents applied to the electrolyte and the lithium counter electrode. These thin layers consist of 2-3 flat graphite flakes stacked above one another (approximately 1 µm thickness) and directly reflect the particles’ properties.

To understand the kinetics of graphite lithiation and delithiation, we separated the results into the different stage transitions. Starting from pure graphite, 4-7 % of lithium with respect to LiC₆ [state-of-charge (SOC) of 100 %] can be intercalated into stage 1L, solid-solution graphite [88], where every layer is filled with lithium ions in a liquid-like manner, i.e., without any in-plane order. Then, a phase separation occurs to form stage 4L from stage 1L, with every forth interslab filled in a liquid-like manner. The next transitions between stages 4L, 3L, and 2L are still under debate (see section 2.5). In stage 3L every third interslab is filled disordered while in stage 2L every other interslab is filled liquid-like. The transitions proceed via movements of the Daumas-Herold domains [131]. The next stage transition occurs from stage 2L, with every second interslab filled without any in-plane order, to the ordered dense stage 2, with LiC₆ in-plane ordering in every other interslab [114]. Finally, a phase separation from stage 2 to stage 1 occurs, forming a LiC₆ structure in every interslab. In the dense stages 1 and 2, the lithium ions align in straight columns, unlike all other alkali and earth alkali metals [100]. The intercalation kinetics of graphite can be understood in terms of these stage transitions. From more details on the stage transitions the reader is referred to section 2.5.

In the first section, the kinetics of a porous electrode will be discussed based on the work of Doyle et al. [146]. Their equation system will be used to identify the main influences governing the thin-layer half-cell electrode. In the second section, the thin-layer model electrode will be used to investigate rate capability of graphite considering the side reactions occurring in these electrodes.

### 3.1.1 Experimental preparation of thin-layer electrodes

Graphite SFG6 from TIMCAL was used for all experiments. This sample has a specific surface area of approximately 17.1 m²/g (from BET) and 50 % and 90 % of the graphite particles are smaller than 3.3 and 6 µm along the a and b-axis, respectively [156]. The dimension of the flakes along the c-axis of the SFG6 graphite sample is approximately 0.4 µm, as estimated from the scanning electron microscopy image shown in Figure 10a. This kind of graphite consists of highly crystalline graphite flakes with a primary crystallite size along the a- and b-axis of ~30 nm (Lₐ) and ~60 nm along the c-axis (Lₖ), as determined from XRD [156]. Slurries of graphite (90 wt%) and PVDF binder (Kynar Flex, 10 wt%) in N-methyl-pyrrolidone (NMP) were used to
cast the electrodes. For thin-layer electrodes, 3 wt% SuperP conductive filler (TIMCAL) were added to give a mass ratio of 87:10:3 to account for the lower in-plane electronic conductivity due to reduction in the number of conduction pathways compared to standard electrodes. The test electrodes were cast onto a copper foil current collector by two different methods. For standard electrodes with thicknesses of more than 30 µm, the doctor blade technique was used. For thin-layer electrodes of less than 20 µm, a spray nozzle technique was employed. The coated copper foil was dried in vacuum at 80 °C in order to remove the NMP. The heating time was minimized to reduce the risk of oxidation of the copper current collector. Subsequently, electrodes were punched out and dried under vacuum at 120 °C for 12 h in order to remove remaining water and NMP. The electrochemical test cells made from titanium were assembled in an argon-filled glove box, under continuous removal of N₂, O₂, H₂O, and organic volatiles. The SuperP electrodes used as a reference were prepared with PVDF (Kynar Flex) in a mass ratio of 80:20 and coated from a NMP slurry. An increased amount of PVDF was chosen due to the small particle size of SuperP carbon. For comparison, blank copper current collectors were coated with pure NMP and dried in a similar manner. 500 µl of 1M LiPF₆ in EC:DMC 1:1 (wt%, Novolyte) and a lithium counter electrode with a diameter of 13 mm were used in all experiments. Five nominally similar thin-layer electrodes of graphite have been cycled and used to extract trends.

Electrochemical cycling was performed using a device from Astrol Electronic AG for standard electrodes, and VMP3 (Biologic) for thin-layer electrodes. The VMP3 was essential because of its fast current response time of 40 µs, which is necessary at a rate of 1000C (3.6 s per half-cycle). All electrochemical tests were performed in an environmental chamber at 25 ±0.1 °C.

3.1.2 Theoretical background for thin-layer electrodes

Starting from the equation system described by Newman et al. [146, 147] which was described in section 2.7 for a porous electrode, the equation system can be simplified considering the implications of the thin-layer electrode.

Applying the conditions of a thin layer (monolayer-bilayer) of graphite versus a lithium counter electrode simplifies the equation system of Doyle et al. [146] in section 2.7. By using a lithium counter electrode, one does not need to consider solid-state diffusion and ohmic potential drop in the lithium disk counter electrode. Additionally, a very thin layer of graphite can be considered equipotential (if well connected electronically) neglecting thus the potential distribution in the graphite matrix (eq.(2.11)). Furthermore, the applied geometrical current density \( I \) at the current collector is transferred to the thin layer in the matrix as \( i_s \) and passes to the electrolyte \( i_e \) via surface reactions. The thin-layer electrode is assumed to suppress any inhomogeneous current distribution in the direction perpendicular to the graphite layer.
To estimate the influence of diffusion of lithium in the active intercalation material and the electrolyte, Doyle et al. [146] defined two dimensionless numbers. They allow the identification of diffusion limitations both in the solid and the electrolyte. The influence of the solid-state lithium diffusion is given as [146]:

\[
S_s = \frac{r^2 i}{D_s F (1 - \varepsilon_S) c_{s,\text{max}} h_s}
\]  

(3.1)

The dimensionless number of the solid \(S_s\) depends on the ratio of lithium diffusion to the total charge stored where \(c_{s,\text{max}}\) is the maximum concentration of lithium in the solid active material, \(h_s\) is the thickness of the porous electrode, \(\varepsilon_S\) is the electrolyte porosity of the electrode with the solid material, \(r\) is the particle radius and \(D_s\) the diffusion coefficient in the solid. The equivalent dimensionless number to estimate the influence of the diffusion of lithium-ions in the electrolyte \(S_e\) was also given by Doyle et al. [146] as:

\[
S_e = \left( h_e + h_s \right)^2 \frac{i}{D_e F (1 - \varepsilon_S) c_{s,\text{max}} h_s}
\]  

(3.2)

which correlates the diffusion perpendicular to the graphite layer in the porous electrode \(h_s\) and in the separator \(h_e\) to the total charge stored.

For an electrode containing 0.2 mg of graphite per 1.33 cm² geometrical area, the current density of 20 A/m² corresponds to a charging rate of 36C. Based on the values listed in Table 4, the dimensionless numbers \(S_s\) and \(S_e\) are 0.28 and 0.29, respectively. The similar magnitude of both dimensionless numbers indicates that the diffusion of lithium within the graphite particles plays a significant role in the thin-layer electrodes. The estimate by Doyle et al. [146] for standard polymer batteries approximated the diffusion of lithium in the electrolyte to be three orders of magnitude larger than the solid-state diffusion of lithium ions with \(S_e/S_s = 1500\). However, the calculation for our case underestimates the influence of solid-state diffusion of lithium in graphite because a spherical diffusion is assumed despite the fact that graphite is a layered two-dimensional intercalation host.

Additionally, graphite is known to undergo several phase separations during lithiation, where the concentration gradient of lithium-ions is mainly confined at the interface between two different phases, as in the case of LiFePO₄ [65]. In short, this comparison, which includes the additional crystallographic information, suggests that the diffusion of lithium in the solid contributes significantly to the overall kinetics of the lithiation of the graphite thin-layer electrode and must therefore be considered in both the calculations and the experiments.
To estimate the concentration gradient in the electrolyte of the half-cell, Fick’s first law was approximated by a linearization at steady state conditions:

\[ J = -D_e \frac{dc}{dx} \rightarrow -D_e \frac{\Delta c}{\Delta x} = \frac{i}{z F e_e} \] (3.3)

For the selected current density of 20 A/m² the linear approximated concentration difference would be 0.074 M across the separator with porosity \( e_e \). This value is considered negligible for a solution of 1M salt in an organic electrolyte.

The electrolyte resistivity can also be estimated using the ionic conductivity of EC:DMC 1:1 with 1M LiPF₆ at room temperature of 1.1 S/m [14]. For our geometry, this gives an electrolyte resistance of 3.4 Ω. Thus, the potential drop of the concentration-independent term in eq. (2.6) is 9 mV when applying the linear approximation in steady state (eq. (3.4)). This potential drop in the electrolyte can easily be subtracted from the total potential drop of the half-cell polarization to account for this resistive effect. \( I \) corresponds to the total applied external current density.

\[ \frac{-i_e}{\kappa_e} = \frac{I}{\kappa e_e} = \nabla \phi \approx \frac{\Delta \phi}{\Delta x} \] (3.4)

Furthermore, we can estimate the mass-transfer-limiting current density \( i_{lim} = -z F D_e e_e(x)/h_e \) [13] to be 68 mA/cm². Considering the porosity of the separator and neglecting tortuosity, this leads to a limiting current of 36 mA, corresponding to 480C for a 0.2 mg graphite electrode. Thus, at currents higher than 36 mA, the lithium depletion in the Nernst diffusion layer will govern the response of the system in our configuration.

In summary, we come to the conclusion that the limitations in the electrolyte play a minor role in the rate performance of the thin-layer electrode up to C-rates of around 36C or even higher. First, this is a result of the experimental minimization of the effects of porosity and tortuosity of a thin-layer graphite electrode. Second, the low active mass translates into a low current density in the electrolyte, causing small concentration gradients and small ohmic potential drops in the electrolyte. In addition to the negligible influence of the parameters in eqs. (2.6) and (2.7), we

Table 4: Parameter set to describe the thin-layer graphite half-cells used for the experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Ref.</th>
<th>Parameter</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_s )</td>
<td>1.65 µm</td>
<td>[156]</td>
<td>( e_s = e_e )</td>
<td>0.4</td>
<td>est.</td>
</tr>
<tr>
<td>( D_s )</td>
<td>( 1 \times 10^{-9} ) cm² s⁻¹</td>
<td>[153]</td>
<td>( h_s )</td>
<td>1 µm</td>
<td>meas.</td>
</tr>
<tr>
<td>( D_e )</td>
<td>( 1.4 \times 10^{-5} ) cm² s⁻¹</td>
<td>[12]</td>
<td>( h_e )</td>
<td>200 µm</td>
<td>meas.</td>
</tr>
<tr>
<td>( c_{s,max} )</td>
<td>34175 mol m⁻³</td>
<td>calc.</td>
<td>( i )</td>
<td>20 A m⁻²</td>
<td></td>
</tr>
</tbody>
</table>
have used a lithium-metal counter electrode, in which diffusion of lithium within the lithium metal (eq. (2.10)) and the ohmic potential drop in eq. (2.11) can be neglected except for the solid-electrolyte-interphase layer (SEI) on the lithium-metal surface. Therefore, the equation system can be simplified. The main possible remaining influences limiting the thin-layer electrode performance are the kinetics of the surface reactions described by the Butler-Volmer equation both on the graphite working and the lithium counter electrode, the diffusion of lithium within the graphite particles, and the ohmic potential drops due to the contact resistance $R_0$ and SEI resistance. Of course, the laws of conservation of mass in eq. (2.7), (2.10) and charge in eq. (2.12) apply. Therefore, our experiments with thin-layer electrodes have mainly two side effects that influence the response of the system: the lithium counter electrode surface reactions and the contact and SEI resistances of both, the lithium and the graphite electrode. Apart from this, the system response is mainly determined by the solid-state diffusion and surface reactions of the graphite particles in the thin-layer electrode.

### 3.2 Rate capability of thin-layer electrodes of graphite

#### 3.2.1 Electrochemistry of thin-layer graphite electrodes

Thin-layer porous graphite SFG6 electrodes were prepared by homogeneous coating of graphite slurry onto a copper current collector by the spray technique. The electrode is depicted in Figure 10a. The current collector shines through the porous electrode in the electron backscattering detector image in Figure 10b. From the SEM images we estimated that the porous electrode consists of 2-3 flat graphite particles stacked on top of one another. Monolayers of graphite particles can also be prepared as shown in Figure 11 but were not used for electrochemical characterization in this work because the very low active mass caused problems in the evaluation. The reasons for this, i.e., the side reaction of Cu$_x$O layer on the copper current collector and the in-plane current distribution, will be discussed below.

To compare the thin-layer electrodes with standard graphite electrodes, we first tested the rate capability of standard SFG6 electrodes ($m = 4.1 \pm 0.05 \text{ mg}$, $h = 55 \pm 2 \text{ µm}$). The galvanostatic response of the standard electrodes at different rates is shown in Figure 12. The results confirm that standard graphite electrodes are limited to ~2C lithiation rate and 20C delithiation rate. This is in agreement with our previously published results [152]. In Figure 12 one can see that the overpotential rises significantly with increasing rate for standard electrodes. The overpotentials decrease for graphite electrodes with intermediate thickness ($m = 0.7 \pm 0.1 \text{ mg}$, $h = 10 \pm 2 \text{ µm}$) as shown in Figure 13. The total overpotential decreases even more significantly when using the thin-layer graphite electrode ($m = 0.168 \pm 0.002 \text{ mg}$, $h = 1 \pm 1 \text{ µm}$) as depicted in Figure 14. To compare the different kinds of electrodes, the overpotentials at 35% SOC, i.e., during the transi-
tion from stage 2L to stage 2, were evaluated. For a lithiation rate of 2C, the overpotential of the thin-layer electrode drops from 50 mV to 11 mV and for a delithiation rate of ~20C from 640 mV to approximately 90 mV, thus constituting less than 22 % of the overpotential of the standard graphite electrode. The trend for the three different electrode thicknesses is compared in Figure 15. Again, a clear trend towards smaller overpotentials for thinner electrodes is observed.

Note that this difference in overpotentials is obviously not caused by limitations in the graphite particles but due to the diffusion limitations in the porous electrode, as discussed in the previous section 3.1.2. The experiments on thin electrodes revealed that graphite particles of a median particle size of 3.3 µm along the a and b-axis [156] and ~0.4 µm along the c-axis (estimated from SEM) can be lithiated at rates up to 6C (10 min charge) with ≥82% of specific charge in the galvanostatic mode. By contrast, the delithiation can be performed at rates of up to 680C with ≥82% of specific charge delivered galvanostatically. The discharge rate capability is more than two orders of magnitude higher than the charging rate capability. This is mainly due to the fact that the applied overpotential for lithiation is limited to ~90 mV. Without this limitation, lithium plating

Figure 10: SEM images of thin-layer electrodes of SFG6 graphite with a) secondary electron detector, b) electron backscattering detector (graphite appears black and copper appears gray).

Figure 11: Quasi monolayers of graphite particles with a) secondary electron detector, b) electron backscattering detector (graphite = black, Cu current collector = light gray).
would occur. In addition to this, there exist diffusion limitations within the stage 2L to 2 and stage 2 to 1 phase transitions, which decreases the respective practical specific charge associated with these transitions. These results compare well with single-particle experiments performed on MCMB (heat-treated at 2800 °C, spherical particles of 30 µm), where a discharge rate of 1000C delivered ~85 % of the specific charge in a potential window of 0- 2.5 V [157]. We can reach a similar rate in the thin-layer experiment, which confirms that our configuration is capable of investigating the properties of the active material. But one has to be careful comparing the results for MCMB with highly crystalline flakes of graphite because MCMB is composed of very small

Figure 12: Electrochemical lithiation and delithiation of a typical standard graphite electrode (h = 55 ±2 µm) at various rates.

Figure 13: Electrochemical lithiation and delithiation of a typical graphite electrode of intermediate thickness (h = 10±2 µm) at various rates.
graphitic domains mixed in between disordered carbon domains. MCMB therefore usually exhibits a higher diffusion coefficient, as shown by Takami et al. [110]. The experiment with a single MCMB particle shows the characteristic plateaus of the graphite stage-transition even at a rate of 1500°C, while no transition plateaus can be detected in the case of SFG6 graphite at rates higher than 170°C. It seems that the crystallite size, and thus the diffusion length, is important for particle rate performance.

Figure 14: Electrochemical lithiation and delithiation of a typical thin-layer graphite electrode (h = 1 ± 1 µm) at various rates.

Figure 15: Overpotential vs. electrode thickness for 2C charge and 20C discharge at 50% stage 2L-2 transition corresponding to 35% of the total SOC.
3.2.2 Characterization of side effects in thin-layer electrodes

A major challenge of the experiments with thin-layer electrodes is the influence of “parasitic reactions”. The first one is concomitant lithium insertion into the 3 wt% of SuperP conductive filler, which is needed to achieve good electronic conductivity of the electrode necessitated by the reduced number of available current pathways. Furthermore, and even more importantly, the conversion reaction of lithium with the naturally partially oxidized copper current collector needs to be considered. Figure 16 illustrates the cycling and rate performance of SuperP electrodes, yielding 250 mAh/g of specific charge at a low rate. This translates into a parasitic charge of 8.6 mAh/g in the composite electrode. Additionally, the tested blank copper current collector is depicted in Figure 17, for which the specific charge is normalized to a virtual graphite mass of 0.2 mg. The current collector is always slightly oxidized on the surface, exhibiting a layer of CuO on the outer surface and Cu$_2$O between the Cu bulk and the CuO surface layer. The additional specific charge for the reduction of copper oxides was estimated to be 32 mAh/g (normalized to 0.2 mg virtual graphite mass).

Based on Faraday’s law and assuming Cu$_2$O only, the calculated thickness of the Cu$_2$O surface layer is 21 nm, which is reasonable (CuO would be 11 nm thick, calculations in [149]). All other cell components (binder, titanium container, etc.) showed no measurable specific charge. The electrochemical double-layer capacity can also be neglected. A calculation with a specific surface area of 17 m$^2$/g for SFG6, 62 m$^2$/g for SuperP, and 1.33 cm$^2$ for copper current collector (times ~10x roughness) assuming 5 µF/cm$^2$ of specific capacity gives a double-layer charge contribution of only 0.6 mAh per 0.2 mg of active material [149]. In total, we estimated that the parasitic reactions contribute more than an extra 10% of specific charge. Especially for stage 1L

![Figure 16: Electrochemical cycling of a typical SuperP electrode at different rates.](image-url)
and the potentiostatic step at the end of each rate cycle, the experiment would show a much higher charge than the process under consideration itself, due to the influence of the oxidic layer at the current collector.

In fact, there are three major challenges associated with extremely thin electrodes. They are the parasitic side reactions, determination of the correct mass of the active material and aging of the electrode during cycling. The influence of all three effects on the course of the electrochemical curves can be estimated when one superimposes the results obtained for the three different active materials (graphite, SuperP, Cu₅O). This means that, if the potential of the composite electrode passes through the potential window of e.g. 1.5-0.3 V in a certain period of time, one can superimpose the contribution of the three different active materials, assuming a parallel circuit that shares the total current. This assumption is only valid if no phase transitions, manifested as plateaus on the galvanostatic curves, occur within the relevant potential window, because a phase transition reaction can be considered as a “constant potential step” for the other materials.

Since electrochemical cycling was conducted at a high charging (or discharging) rate followed by a discharging (or charging) rate of C/3, one can precisely calculate the mass of the active material in the electrode from the course of the respective low rate half-cycle (electrochemical mass estimate). This approach is valid if the specific charge ratio of all graphite stage transitions stays constant relative to one another, allowing the identification of the loss of electronic contact of some graphite particles in the electrode. From this calculated mass we can determine the extent of particle “loss” of graphite as well as the contributions of Cu₅O and SuperP for low and medium rates. At high rates, the simple linear superposition is not valid anymore due to shading ef-

![Figure 17: Electrochemical cycling of Cu current collector with a very thin layer of CuO and Cu₂O on the surface.](image)
Effects of the graphite particles on the current collector, which increases the diffusion length within the Cu\textsubscript{x}O layer. The equation applied to estimate these effects is given by:

\[
Q_{\text{TL}} = Q_{\text{LiC}_6} + 0.03 \cdot Q_{\text{SuperP}} + OF \cdot Q_{\text{Cu}_x\text{O}}
\]

\[
Q_{\text{TL},\text{LiC}_6,\text{SuperP},\text{Cu}_x\text{O}} = f(\Delta t, \Delta E)
\]  

(3.5)

with the specific charges Q of thin-layer electrode (TL), graphite (LiC\textsubscript{6}), SuperP, and Cu\textsubscript{x}O. The influence of SuperP has been adjusted for its mass fraction in the composite electrode and the thickness of the Cu\textsubscript{x}O layer can vary depending on the degree of oxidation, which is fitted by an oxidation factor OF. The fitting parameters are presented in Table 5. With this superposition approach, the active mass, aging effects, and parasitic influences can be determined with high precision. The systematic error due to these three effects can be reduced from approximately 30-36 % of the specific charge for the raw experimental data to about 6-8 %, i.e., by a factor of almost five. To account for stochastic errors, five nominally identical experiments have been evaluated in order to extract trends.

It is also very important to look into the current density distribution in the thin-layer electrode. Inhomogeneous current distribution is known to occur perpendicular to the coating in standard electrodes, where the diffusion limitations of the electrolyte in the porous electrode govern the response of the system at high rates. If the thickness is very low, this inhomogeneity can be neglected. But inhomogeneous reactions along the lateral direction of the electrode become important. Figure 18 illustrates a monolayer and a bilayer of active particles with a corresponding equivalent circuit across the copper oxide layer and between the active particles. Assuming the previously estimated Cu\textsubscript{2}O thickness at the current collector of 21 nm and a specific resistance of 5000 \(\Omega\)cm for semiconducting Cu\textsubscript{2}O [158], we can calculate the contact resistance of one particle in a monolayer (without interparticle contact). Assuming a full basal surface contact between SFG6 and Cu\textsubscript{2}O, the contact resistance is calculated to be 133 k\(\Omega\) which is particle size dependent [149]. Although there are smaller currents for smaller particles, this would not change the

Table 5: Parameter estimation from superposition (SuperP and Cu\textsubscript{x}O based on 3\textsuperscript{rd} cycle specific charge at C/3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>graphite mass [mg]</th>
<th>total estimated charge</th>
<th>Remaining error after correction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SuperP</td>
<td>Cu\textsubscript{x}O</td>
</tr>
<tr>
<td>1</td>
<td>0.168</td>
<td>8.6</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>0.165</td>
<td>8.6</td>
<td>33.7</td>
</tr>
<tr>
<td>3</td>
<td>0.206</td>
<td>8.6</td>
<td>19.7</td>
</tr>
<tr>
<td>4</td>
<td>0.209</td>
<td>8.6</td>
<td>59.4</td>
</tr>
<tr>
<td>5</td>
<td>0.217</td>
<td>8.6</td>
<td>16.5</td>
</tr>
</tbody>
</table>
electric potential of the particles relative to one another, if the thickness of all graphite particles was the same (same Q/I ratio). But this is obviously not fulfilled for real electrodes with a given particle size distribution, as seen in Figure 11 and Figure 18 for monolayers (R3 > R1 > R2), so that for monolayer electrodes no equipotential situation can be assumed.

However, bilayers of graphite particles also possess inter-particle contacts. The good electronic conductivity of graphite and the addition of a small amount of conductive filler lead to very small resistances between the active particles (limit: \( R4 \approx 0 \, \Omega \)). Therefore, all single-particle resistances are in parallel to one another and an electrode with 1.33 cm\(^2\) gives a calculated resistance of \( 14 \cdot 10^{-3} \, \Omega \) due to the nine-million particles in parallel to each other. This would be the ideal ohmic resistance assuming perfect contact between basal planes and the current collector, i.e., neglecting roughness. The real contact resistance will be in the order of a few ohms [153]. The sketch in Figure 18 shows the importance of a good inter-particle network. Therefore, the 3 wt% SuperP and a bilayer of graphite particles were chosen for the experiments.

### 3.2.3 Stage-dependent rate capability

The discussed galvanostatic cycling of the thin-layer electrode (as shown in Figure 14) provides more insights into the stage-dependent electrochemical performance of graphite particles. For lithiation, one can see that the 1L-4L-3L-2L stage transitions are associated with almost the same practical specific charge for the 18C as for the C/3 rate. By contrast, the stage 2L-2 and 2-1 transitions contribute less than half of their theoretical specific charges at the high rate of 18C. Plotting this kind of results for the different test cells clearly demonstrates this trend (Figure 19). The formation of the graphite solid-solution (called stage 1L) consumes almost the same specific charge for a lithiation rate of 20C as for a rate of C/3. By contrast, the practical specific charge of the stage 2L-2 and 2-1 transitions decrease drastically at this high rate. If one calculates the relative stage-specific charge fractions with respect to the low-rate charge from Figure 19, one can

![Sketch of lateral inhomogeneous current distribution](image)

**Figure 18**: Sketch of lateral inhomogeneous current distribution with particles in monolayer and bilayer configuration; the copper current collector (orange) is covered with an oxide layer (red).
visualize the stage-dependent charge fraction as displayed in Figure 20, which shows the trends for the experiments more clearly.

At high rates, the transitions between the liquid-like stages consume more than 80% of their theoretical specific charges, while the formation of graphite solid-solution (stage 1L) even consumes approximately 90% of its theoretical specific charge for a lithiation rate of 20C. By contrast, the transitions to the dense stages 2 and 1 consume only 40% and 45% of their maximum specific charges, respectively. This decrease is very significant because the transitions from stage 2L-2 and stage 2-1 contribute approximately 77% of the total specific charge of graphite. These differences in behavior are not due to charge-transfer overpotentials at the electrode/electrolyte interface, because the driving forces for the transitions are comparable with a potential difference of 90 mV for the 1L-4L-3L-2L stage transition and 76 mV for the dense stage 2-1 transition.

However, the differences in the stage-dependent practical specific charge at high rates can be explained by thermodynamic differences. Both stages 2 and 1 possess LiC₆ in-plane density [114]. By contrast, graphite stages 1L, 4L, 3L, and 2L have no in-plane order and lower in-plane densities [88, 89]. The liquid-like stages only possess ordering along the c-axis, which defines the respective stages. It seems that the solid-state diffusion coefficient of lithium in graphite is smaller for the dense stages than the liquid-like stages. This is consistent with the trends already described by Levi et al. [153] and Umeda et al. [159]. Both groups showed a difference in the lithium diffusion coefficients of one order of magnitude between the liquid-like stages compared to the dense stages. But, interestingly, the absolute values of the diffusion coefficients in references [153] and [159] also differ by a factor of 10 to 20.

The relative contributions of the different stage transitions to the charge released by the delithiation of graphite have also been analyzed (Figure 21). Here, the same trend as for lithiation can be observed. The contributions of both stage 1 solid-solution (stage 1ss) and the transition from stage 1 to 2 decrease sharply with increasing rate. But, surprisingly, the contribution of the stage 2-2L-3L-4L transitions compensate for the initial specific charge limitation during the dense stage transitions. This can be seen more clearly in Figure 22, where each stage transition fraction is normalized with respect to its initial low rate specific charge, thus visualizing the relative changes. Clearly, the stage transitions towards the dense stages (stage 1ss and stage 1-2) exhibit the same trend for discharge (Figure 21) as shown before for charging. Both transitions deliver only ~40-45% at charging and discharging rates of 20C with respect to their low-rate specific charges.

This shows that both processes, lithiation and delithiation, are symmetric with regard to the corresponding diffusion coefficient. Also, the same phase boundary movement must occur be-
tween the transitions for both charge and discharge. Here, the discussed compensation from the stage 2-2L-3L-4L transitions can be observed, delivering more practical specific charge between the rates of 1C-32C compared to the specific charge at a low rate of C/3. Of course, these stage transitions cannot deliver more than their thermodynamically defined specific charges. But it seems that the previous processes, i.e., stage 1ss and 2-1 transitions, are still ongoing when the

![Figure 19](image1.png)

Figure 19: Charge fraction vs. lithiation rate of the different stage transitions in percent of the total specific charge (colors: green for graphite solid-solution, blue for the transition of stage 1L to 4L, red for transition of stage 2L to 2, black for the transition of stage 2 to 1).

![Figure 20](image2.png)

Figure 20: Relative charge fraction vs. lithiation rate for the different stage transitions, normalized to a lithiation rate of C/3.
next stage 2-2L-3L-4L transitions start. This means that the phase boundaries of the previous stage transitions still progress further into the center of the particle while a new phase boundary develops at the edge surface of the graphite particles. Unfortunately, one cannot distinguish the plateaus of the stage 2-2L-3L-4L transitions to separate the diffusion associated with the dense stage 2 from the subsequent liquid-like phases (no detectable plateau). The relative contributions

Figure 21: Charge fraction vs. delithiation rate of the different stage transitions in percent of the absolute total specific charge (colors: magenta for stage 1 solid solution, stage transition: black for stage 1 to 2, red for stage 2 to 4L, blue for stage 4L to 1L, green for graphite solid-solution).

Figure 22: Relative charge fraction vs. delithiation rate for the stage transitions, normalized to the C/3 delithiation rate.
of the following transitions from stage 4L-1L and within the stage 1L (graphite solid-solution) increase sharply compared to their very low contribution to the total charge of graphite.

In summary, we found the following for the lithiation of graphite: In addition to the low applicable overpotential, the stage transition order is also important for the comparatively low lithiation rate capability of graphite. For delithiation, however, the fast liquid-like stage transitions compensate for the slow dense stage transitions, allowing them longer diffusion times, which are needed to propagate their phase boundaries further into the bulk of the particle. This can explain the long-known asymmetry in the rate capability for the charge and discharge of graphite [152]. These results will be used to explain the lithiation/ delithiation from a mechanistic point of view in section 6.1.

### 3.3 Overpotentials at thin-layer graphite electrodes

As discussed in the theoretical section 3.1.2 for thin-layer electrodes, not only the solid-state diffusion equation (2.10) has a strong influence but also the surface-reaction equations (2.8) for both the thin-layer electrode of graphite and the lithium-counter electrode. This includes the ohmic resistance which is implemented in the kinetic model of Newman et al. [146, 147] to be a linear resistive contribution to the total measured overpotential (eq. (2.9)).

In this section, the kinetic-driven overpotentials will be investigated with respect to their influence on the rate capability of graphite. It was shown by Shim and Striebel [154] that the diffusion limitations through the electrolyte in the porous electrode in standard graphite electrodes are one of the main limitations. The natural graphite they used with a medium density of 0.9 g/cm$^3$ and 5 mg/cm$^2$ loading delivered only ~85% of the total specific charge at C/2 charging rate in a standard electrode. The discharge of these electrodes also showed strong diffusion limitations with a smearing out of the stage transition potential plateaus at rates of >1C and high overpotentials (~400 mV at 5C discharge). In contrast, the rate capability of a single MCMB particle (30 µm, 2800°C heat treated) delivers a discharge rate of ~250C at 400 mV overpotential during galvanostatic discharge [157]. But which contributions increase the overpotential so drastically that a single particle and a standard electrode differ by a factor of ~50 times? What are the effects that determine the overpotentials in these graphite electrodes and what are the actual contributions from the graphite particles itself?

To investigate these effects the thin-layer electrode technique is used which avoids the diffusion limitations in the electrolyte in the porous electrode and is able to deliver similar results as the single-particle technique but is easier to handle as shown in the previous section 3.2.
To deconvolute the measured overpotential into the different contributions from the graphite thin-layer electrode, the lithium-counter electrode, and the electrolyte, the equations system has to be discussed shortly. First, the surface reactions can be described by the Butler-Volmer equation (2.8) where the overpotential is defined in eq. (2.9). Additionally, the potential drop in the porous electrode matrix \( \nabla \Phi \) can be described by Ohm’s law in eq. (2.11) but it will be a minor effect due to the very thin electrode with good electronic contact guaranteed by the 3 wt% conductive filler. The potential drop in the electrolyte can be described by eq. (2.6) and can be simplified to the first term (linear part) for thin-layer electrodes until rates of \(<40 \text{C}\) as discussed in section 3.1.2. Diffusion in the electrolyte will limit the system response for currents higher than 36 mA (27 mA/cm\(^2\)) for the used cell configuration (see section 3.1.2).

### 3.3.1 Cycling and side influences

The cycling of the thin-layer porous electrode of graphite SFG6 is presented in Figure 23 which is a modification of Figure 14. For both lithiation and delithiation the overpotentials increase with increasing rate as one expects. Only the first high rate delithiation cycle at a current density of 28 mA/cm\(^2\) (665C) shows more positive potential than the second high rate cycle at the same current but slightly higher normalized rate (681C) due to aging (particle loss). The third high rate cycle is performed at 42 mA/cm\(^2\) (1055C) and cannot be compared due to the different rate. There is also an apparent overshooting of the overpotential at the beginning of the first high rate delithiation. This effect can come from either the graphite or the lithium counter electrode since no reference electrode was used, and will be discussed later. For delithiation, the overpotentials do not limit the rate capability of graphite. For lithiation, the overpotentials also rise continuously but, in contrast to the delithiation, lead to a prematurity hitting of the galvanostatic cut-off potential. This difference was found to be due to the diffusion of lithium in graphite in dense stage 2 and 1 which leads to additional diffusion-limited overpotentials to the standard processes of surface reactions and ohmic drops as discussed in section 3.2.3.

To separate the influences from the thin-layer electrode of graphite and the lithium counter-electrode, the same high current densities have been applied to symmetrical Li-Li cells as depicted in Figure 24. Both lithiation/delithiation and currents are referenced with respect to the standard half-cell configuration with a virtual graphite mass of 0.2 mg. One can see clearly that the overpotentials from the Li-Li cell are significant compared to the 0.2 mg of graphite thin-layer electrode. At a current density of 42 mA/cm\(^2\) the graphite-Li cell shows overpotentials of circa 1.1 V while the symmetric Li-Li cell shows \(~0.83\) V. That means that even at very low amounts of loading of active material, the lithium-counter electrode contributes significantly to the overall
overpotentials in the half-cell configuration in EC/DMC 1M LiPF₆ electrolyte. This contribution can come from both surface reactions and the resistivity of the solid electrolyte interphase (SEI).

Another important feature can be observed in the first high current density cycles shown in the inset of Figure 24. An apparent overshooting of the overpotentials in the first high rate cycle is detected for the Li-Li cell which starts at ~0.96 V and decreases monotonically to 0.73 V within the 7.2 s of measurement. This overshooting seems to be of the same origin like the one observed for the thin-layer half-cell of graphite. The following cycles also show a small overshooting of the overpotential in the Li-Li cell but seem to be equilibrated at very short time. We did not find a particular order of the time constant for this “equilibration” process as they seem to differ with the rate for high current density delithiation. We will call this initial overshooting of the overpo-

![Figure 23: Cycling of thin-layer electrodes of graphite SFG6 at various rates vs. Li⁺/Li.](image1)

![Figure 24: Symmetrical Li-Li high rate cycling with same current densities as for Li-graphite configuration in Figure 23.](image2)
tential in the first cycles “high rate formation cycle” based upon the name of SEI formation. These high rate cycles are performed after three low rate SEI formation cycles.

To get an insight into the origin of this overshooting of the half-cell overpotential, a linear superposition is shown in Figure 25. If one subtracts half of the Li-Li overpotential of the first and second high rate formation cycle from the respective Li-graphite high-rate formation cycle, one can see that the remaining overpotential is almost identical (Figure 25a). This indicates that the observed initial overshooting originates mainly from the Li-counter electrode. These linear corrections can be done for all delithiation rates from Figure 23 and show the significant influence of the Li-counter electrode on the overpotentials in half-cell measurements (Figure 25b).

Figure 25: Superposition of the Li-graphite and Li-Li cell to extract a) influence of overshooting in first two high rate formation cycles, b) at various rates derived from Figure 23 and Figure 24.

Figure 26: Symmetrical Li-Li high rate cycling with scratched Li-metal electrodes.
A small overshooting of the overpotential for the graphite electrodes might also be observed for the first two high rate formation cycles because the slope of these delithiation rates differs from the following delithiation rates slightly (Figure 25b). One has to keep in mind that overpotentials of the lithium-counter electrode depend mainly on the current density and are independent on the loading of the working electrode. However, the history of the lithium electrode also influences the electrochemical response as shown in the inset in Figure 24. Therefore, experiments with standard electrodes should also have a strong contribution from the lithium counter electrode to the total overpotential of a half-cell (e.g. ~125 mV at 7 mA/cm²).

For comparison, we also measured the electrochemical response of symmetrical Li-Li cells where both lithium-metal electrodes have been scratched with a scalpel before assembling (Figure 26). The overshooting differs with respect to the time constant for the decrease of the overpotential. One possibility could be a difference in SEI composition with Li₂CO₃ and LiF [13] but will not be the subject of this study.

3.3.2 Stage-dependent overpotentials

The measurement of the high rates lithiation and delithiation shown in Figure 23 provides even more insight into the behavior of graphite, when one plots the overpotentials at certain state-of-charges (SOC). The overpotentials at the beginning of a new stage transition reflect the processes of the new phase in environment of almost only the previous phase (nucleation). This means that diffusion-limited overpotentials are very unlikely to contribute at these SOCs. The overpotentials at the beginning of a stage transition will stem mainly from ohmic drops, surface reactions, adsorption, and possible nucleation overpotentials. One can extract the overpotentials at a certain SOC within a stage transition, e.g. at 50% progress of a particular stage transition. At these SOCs, diffusion-limited overpotentials of graphite may contribute to the overall overpotentials.

These overpotentials can only be extracted for stage transitions with a plateau in the open-circuit potentials because the change in the derivative with respect to SOC is used to determine these points as in the previous section 3.2. The overpotentials of a progressing stage-transition are determined from the SOC at the beginning of a new transition plus half of the specific charge of the low rate cycle (C/3). This allows the independent extraction of overpotentials without the influences of the different diffusion coefficients between the dense and liquid-like stages which reduces the extracted specific charge of each transition differently as shown before[149].

Figure 27 shows the total overpotentials from the half-cell measurements for lithiation. The transitions from stage 1L-4L-3L-2L, stage 2L-2, and stage 2-1 could be evaluated because they show a significant change in the electrochemical response (plateau in OCP). The changes within
the transitions between the different liquid-like stages 1L, 4L, 3L, and 2L were not possible to identify especially at increasing rates due to very featureless characteristics in the galvanostatic response. Additionally, the ohmic drop has been included which was extracted from electrochemical impedance spectroscopy giving ~4\( \Omega \), and will be discussed later.

Furthermore, the contribution from the lithium-counter electrode was evaluated from the symmetrical Li-Li cells and plotted as additional overpotentials to the ohmic drop in the electrolyte (difference between green and yellow overpotentials in Figure 27). The remaining overpotential can be attributed to the different transitions which show differences between the beginning and the progression (20% or 50%) of the respective stage transitions due to diffusion limitation. A progression of 50% of stage 2L to 2 and stage 2 to 1 are in the center of the potential plateau of these transitions. In contrast, 20% of the transition of stage 1L-2L is located exactly at the end of the stage 1L to 4L plateau and therefore reflects almost pure stage 4L. Thus the diffusion-limited overpotential contributes much more at 20% stage 1L-2L compared to the 50% progressed two-phase transitions between stage 2L-2 and 2-1.

In general, it can be seen that the “parasitic effects”, namely the ohmic potential drop in the electrolyte and the influence of the lithium counter electrode, contribute ~60% to the overall overpotentials at 20C lithiation rate in a graphite half-cell. This visualizes clearly the important influence of the lithium-counter electrode even when the active mass and respective current density is very low (0.2 mg graphite with 0.7 mA/cm\(^2\) \(\approx\) 20C). These side effects can be subtracted from the original galvanostatic response of the Li-graphite half-cell which leads to the overpotential response on the graphite thin-layer electrode alone as shown in Figure 28. This assumption of linear superposition holds for operation at low current densities because the nonlinear effects in eq. (2.6) can be neglected, as shown in section 3.1.2. Additionally, the assumption to take only half of the overpotentials of the symmetrical Li-Li cell for the subtraction of the counter-electrode influences assumes the transfer coefficient \( \alpha \) of the Butler-Volmer equation (2.8) to be \( \alpha_a = \alpha_c = 0.5 \) (one step symmetric charge transfer).

The corrected overpotentials in Figure 28 indicate a Butler-Volmer type of process with a saturation of the overpotentials at less than 10 mV to the respective C/20 curve for the beginning of the stage-transitions. But the standard Bulter-Volmer equation for a one-electron charge-transfer needs more than 30 mV to be in the Tafel-regime [150]. Obviously, this process occurs at very low specific current of less than 0.5 A/g and is saturated at around 10 mV. This process cannot be due to an preceding adsorption process of lithium on the graphite composite electrode because the characteristic overpotential – current density diagram would indicate another profile being point-symmetric to our result [150].
So far this process could not be identified but it seems to be also seen by other researchers for LiFePO$_4$, although they interpreted their results with linear relationships for exponentially decaying overpotential vs. current density diagrams [68]. They interpreted their results as a hysteresis between charge and discharge due to the effects of the difference of miscibility gap and spinodal gap on the potential profile in the case of a large amount of phase separating particles [68]. In our case, a hysteresis might also exist (shown later) but the exponential behavior of the current vs. overpotential occurs at much higher current densities compared to [68].

Figure 27: Total lithiation overpotential for different stage transitions at beginning and 50% stage progression (vs. C/18) of thin-layer electrodes of graphite.

Figure 28: Lithiation overpotentials corrected for electrolyte and lithium-counter electrode influences derived from Figure 27.
A systematic measurement error can be excluded due to the fact that no such behavior is seen for the symmetrical Li-Li cell (green curve in Figure 27 and Figure 29). This phenomenon would result in a conflict for electrochemical impedance spectroscopy experiments (EIS) described in section 2.6.1d). This technique assumes for a standard evaluation approach with linear RC elements a linearity in the measured potential regime (e.g. when imposing 10 mV AC amplitude vs. OCP) which would be implicitly violated based on our findings. The experimental result would still hold but the interpretation with linear elements in Randles circuits [142] would not be valid anymore for graphite electrodes. However, to understand this phenomenon clearly and give a correct advice for EIS experiments, further experiments are needed.

The same procedure can be applied to extract the stage-dependent overpotentials for the delithiation of the thin-layer electrode of graphite versus Li-metal. Figure 29 presents these overpotentials for the phase transitions of stage 1 to 2, 2 to 4L, 4L to 1L, and finally st1L to pure graphite. The transition between stage 2-4L which would include the intermediate phases of stage 2L and 3L cannot be further separated due to the featureless potential rise in the SOC regime especially at rates of more than 5C. As a reference, the ohmic potential drop in the electrolyte across the separator has been added to show its contribution (electrochemical impedance spectroscopy determined \(\sim 4\Omega\)). Furthermore, half of the overpotentials of the symmetrical Li-Li cell have been added on top of the ohmic potential drop in the electrolyte.

For delithiation, the influence of the overpotentials of the lithium-counter electrode also contributes approximately 53% of the half-cell overpotential at 20C delithiation rate for the stage transition of stage 4L-1L and is less for the other transitions. At delithiation rates of 40C, the lithium counter electrode contributes even \(\sim 73\%\) to the half-cell overpotential for the stage 4L-1L transition. If one subtracts the parasitic contributions (ohmic drop in electrolyte and overpotentials of lithium counter electrode) from the respective stage-dependent galvanostatic response in Figure 29, the overpotentials of the pure graphite thin-layer electrode can be determined as depicted in Figure 30 (same procedure as for lithiation overpotentials). The beginning of a transition includes mainly the surface reactions and ohmic drops in the SEI and graphite particles while the transitions at a certain degree of progress, e.g. 50%, include additional diffusion-limitation of the new phase.

In general, one can observe a similar trend as for the lithiation of graphite. The phase transition from stage 4L-1L and 1L-graphite show very low overpotentials of less than 17 mV until rates of 40C. In contrast, the transitions of the dense stages 1-2 and 2-4L show a stronger increase of the respective overpotentials with respect to the specific current. The 50% progress of a particular stage transition is also evaluated and shows high additional diffusion-limited overpotentials for
the transition to dense stage 2 (stage 1-2). For the transition of stage 2-4L smaller additional diffusion-limited overpotentials can be observed. For the 50% progressed liquid-like stage transitions 4L-1L only very small diffusion limited overpotentials can be detected. These classifications are consistent with the previously discussed results in 3.2.3 which was shown to be due to a difference in the diffusion coefficient of the dense and liquid-like stages. Furthermore, the same phenomenon at low current densities is seen on the graphite electrodes for delithiation (Figure 30). The origin could not be detected yet, as also discussed for lithiation.

Figure 29: Total delithiation overpotential of thin-layer electrodes of graphite for the different stage transitions at beginning and 50% progression, normalized vs. C/18.

Figure 30: Delithiation overpotentials corrected for electrolyte and lithium counter electrode influences, derived from Figure 29.
For delithiation, rates up to 1000C could be achieved for graphite with the help of the thin-layer technique (Figure 23). However, the plateaus of the different stage transitions could only be separated clearly until rates of up to 40C. Above this rate an extrapolation of the trends for the beginning of transitions of dense stage 1 and 2 (as shown in Figure 22) was done to extract the overpotentials for rates up to 1350C. The results of this investigation are summarized in Figure 31 for the different samples and SOCs.

![Figure 31: Delithiation overpotentials at rates up to 1350C with the contributions of the lithium counter electrode from Figure 24 and linear part of ohmic drop in electrolyte.](image)

![Figure 32: Delithiation overpotentials at rates up to 1350C corrected for the contributions of the lithium counter electrode and linear part of ohmic drop in electrolyte, as seen in Figure 31.](image)
The contributions of the lithium-counter electrode from Figure 24 and linear part of ohmic drop in electrolyte have been added to show their influences on the half-cell behavior. One has to keep in mind that the limiting current density was calculated to be 27 mA/cm² for this cell configuration which corresponds to a rate of ~660°C (see section 3.1.2 with adapted rate for lower active mass due to aging). The influence of the limiting current density can be seen for the overpotentials of the symmetrical Li-Li cell which have been plotted in green in Figure 31. A deviation to more positive potentials can be observed at rates of more than 700-800°C which agrees with the previous calculations. Interestingly, no blocking effect due to depletion of the electrolyte can be detected. The effect of depletion would mean a steep increase of overpotential without an increase of the current density being confined to the limiting current density as shown in literature [150]. For the thin-layer electrode with the given aspect ratio of electrode mass to electrolyte salt concentration in Table 4 (page 29) the depletion of the electrolyte could fill the graphite particles even at rates above 660°C due to the excess of electrolyte. Therefore, only a small deviation of the measured Li-Li overpotential from the expected profile is observed.

The overpotential shows a characteristic profile for both the lithium-counter and graphite electrode. The relative contribution of the lithium counter electrode to the total overpotential decreases for very high rates (Figure 31). However, the linear part of the ohmic contribution of the electrolyte in eq. (2.6) contributes stronger for very high rates above 1000°C compared to rates below 200°C. Again the overpotentials from graphite contribute only about 40% to the total overpotential at 1350°C for the beginning of stage 1. For the estimated beginning of stage 2 the overpotentials show additional contributions compared to the beginning of stage 1 in Figure 32. However, this cannot be attributed directly to some effect of stage 2 alone since phase mixing is very likely to occur (see shrinking annuli model in section 6.1).

The overpotentials of graphite corrected for the contributions of both the electrolyte and the lithium counter electrode can be further separated. The overpotential on the thin-layer electrode of graphite can be further split in ohmic resistance from the solid-electrolyte-interphase and the surface reactions, as discussed in section 3.3. The additional phenomenon which occurs at very low current density can contribute to the overpotential at high current density where saturation is expected. The fit of the experimentally measured overpotential of graphite (Figure 32) for the beginning of stage 1 is presented in Figure 33. The relative contributions are indicated. The superposition of these effects (black) fits the experimentally determined overpotential profile (blue) for stage 1 well. The extracted parameters from the fit give 17 Ω/mg for the SEI resistance. The exchange current density was fitted best with \( i_0 = 0.7 \text{ A/m}^2 \) (normalized per BET) and a transfer coefficient of \( \alpha_s = \alpha_c = 0.5 \) for the surface reactions modeled by Butler-Volmer (eq. (2.8)).
The saturation overpotential was estimated to be 8 mV for the low current-density phenomenon as discussed earlier. The ohmic resistance of the solid-electrolyte-interphase gives a total resistance of 2.86 Ω for the 0.168 mg of active material on the electrode in Figure 33 of one out of five samples which is decreased due to the particle loss during cycling (section 3.2.2). The resistivity can be described by:

\[
R_{SEI} = \frac{\rho l}{A} = \frac{\rho l}{xA_0} = \frac{R_{0,SEI}}{x}
\]  

(3.6)

where the resistance of the solid-electrolyte-interphase \(R_{SEI}\) is a function of the specific resistance \(\rho\), the thickness \(l\), and the area \(A\) of the SEI. Assuming that the specific resistivity and the thickness of the SEI stay constant after the two low rate SEI formation cycles and the first two high rate formation cycles, one can include the particle loss \(x\) as an reduced cross-section of the initial area \(A_0\) of SEI. This leads to an increase of the relative SEI resistance with cycling due to particle loss. The SEI resistance is summarized in Table 6 for the continuous cycling (aging).

One can see that the SEI resistance of the cell is increasing with increasing particle loss due to the assumed dependence on the available SEI cross-section. However, the total resistance has to be normalized to the available active surface area (ASA) which means in the case of graphite the prismatic surfaces. The basal surface area is known to be inactive for lithium-ion intercalation except of local defects [160]. Since no experimental ASA determination is available, we estimate the ASA by a calculation for the dimensions from a SEM image as discussed in section 3.1.1.

Figure 33: Fitting of experimental overpotential of thin-layer electrode of graphite, contributions from surface reactions (red), ohmic SEI resistance (green), low current-density phenomenon (cyan), superposed overpotential fit (black) compared to experimental one (blue) from Figure 32.
The median particle diameter is determined to be 3.3 μm [156] and the stacking in c-axis ~0.4 μm (SEM estimate). This gives a ratio of 20% prismatic to 80% basal planes for an assumed cylinder with a specific ASA of circa 3.34 m²/g based on a BET of 17.1 m²/g. The ASA surface reaction and equation (3.6) give a specific resistance of ρ·l = R_{SEI}·A_{ASA} = 16 Ωcm². In general, the measured SEI resistance of 2.9-3.6 Ω (Table 6) is very small compared to the resistances which are usually found in EIS experiments. The EIS resistance of the SEI is usually around 46 Ω according to Levi et al. [155] for thin-layer electrodes and needs to be modeled with four R||C elements. So there is a strong discrepancy between our SEI resistance and usual EIS extracted values. However, an SEI resistance of 46 Ω would be more a heat-source than a battery system.

Also the Butler-Volmer surface reaction has to be adapted for the aging of the electrode as shown in Table 6. But here the total exchange current is I = i_0·A_{BET}·x which is used for the fitting. However, to get the exchange current density normalized to the active surface area alone, we have to apply the same calculation as for the SEI resistance. This results in an exchange current density of i_{0,ASA} = 3.58 A/m² (0.36 mA/cm²). Using this exchange current density to calculate the linear resistance of the Butler-Volmer-equation at very low current density and below

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>Discharge Rate [C]</th>
<th>Particles x [%]</th>
<th>Ohmic SEI resistance [Ω]</th>
<th>exchange current i_0·A [mA]</th>
<th>Surface reaction resistance R_{BV,lin} [Ω]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.064</td>
<td>1</td>
<td>2.86</td>
<td>2.01</td>
<td>12.8</td>
</tr>
<tr>
<td>2</td>
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<td>1</td>
<td>2.86</td>
<td>2.01</td>
<td>12.8</td>
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<tr>
<td>3</td>
<td>665</td>
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<td>2.88</td>
<td>2.00</td>
<td>12.8</td>
</tr>
<tr>
<td>4</td>
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<td>3.01</td>
<td>1.91</td>
<td>13.4</td>
</tr>
<tr>
<td>5</td>
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<td>1.85</td>
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</tr>
<tr>
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<td>3.14</td>
<td>1.83</td>
<td>14.0</td>
</tr>
<tr>
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<td>3.20</td>
<td>1.80</td>
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</tr>
<tr>
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<td>3.25</td>
<td>1.77</td>
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</tr>
<tr>
<td>9</td>
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<td>3.25</td>
<td>1.77</td>
<td>14.5</td>
</tr>
<tr>
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<td>3.29</td>
<td>1.75</td>
<td>14.7</td>
</tr>
<tr>
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<td>0.858</td>
<td>3.33</td>
<td>1.73</td>
<td>14.9</td>
</tr>
<tr>
<td>12</td>
<td>9.1</td>
<td>0.854</td>
<td>3.35</td>
<td>1.72</td>
<td>15.0</td>
</tr>
<tr>
<td>13</td>
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<td>1.69</td>
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</tr>
<tr>
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<td>1.68</td>
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<tr>
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<td>1.65</td>
<td>15.6</td>
</tr>
<tr>
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<td>0.812</td>
<td>3.52</td>
<td>1.63</td>
<td>15.7</td>
</tr>
<tr>
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<td>0.805</td>
<td>3.55</td>
<td>1.62</td>
<td>15.9</td>
</tr>
<tr>
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<td>0.795</td>
<td>3.60</td>
<td>1.60</td>
<td>16.1</td>
</tr>
<tr>
<td>20</td>
<td>0.40</td>
<td>0.791</td>
<td>3.62</td>
<td>1.59</td>
<td>16.1</td>
</tr>
</tbody>
</table>
overpotentials of ~20 mV (eq. (3.7)) gives a resistance of 71.5 Ω cm² which is very similar to the results of Dokko et al. [157] for a single MCMB particle although they did not correct their overpotentials for SEI resistance. The linear resistance which should be measured by EIS experiments is also given in Table 6 and shows a resistivity of 13-16 Ω for very low overpotentials. These results will be compared to EIS experiments of thin-layer graphite electrodes further below.

\[ R_{BV,lin} = \frac{RT}{F \nu_{ASd}} \]  

(3.7)

Another aspect which needs to be addressed is a possible hysteresis of the overpotential for charge and discharge in graphite. For another phase separating material, e.g. LiFePO₄, a hysteresis of 20 mV has been detected [68]. They claim that such a hysteresis occurs for all phase separating materials due to the open-circuit potential overshooting in the SOC regime between miscibility and spinodal gap, as shown for the open-circuit-potential profile by Bai et al. [56]. Therefore, the measured potential profile with increasing rate was plotted in Figure 34 which is not corrected for any side influence. One can clearly see the additional phenomenon at very low current density which was discussed above.

Furthermore, the overpotentials at 50% progress of a stage transition are also shown which increase rapidly for the stage 1 to 2 transition and intersect with the beginning of the stage 2-4L transition already at ~15C. This means that the new stage transition is already nucleating while the previous one is still progressing into the particle (see section 6.1 for description). To get an insight into a possible hysteresis, Figure 34 was zoomed to rates below 1C for both lithiation and

![Figure 34: Overpotential evolution for increasing rate, non-normalized, legend for lithiation.](image-url)
delithiation which is shown in Figure 35. The beginning of the stage transitions (stage 1-2, 2-2L, 4L-1L) show a distinct hysteresis. The estimated potential difference of the hysteresis is 6.6 mV ($\sigma = 0.64$ for six samples) for the transition of stage 1-2, 13.25 mV ($\sigma = 0.69$) for the transition of stage 2-2L, and 12.1 mV ($\sigma = 0.85$) for the transition of stage 4L-1L.

But there is also another interesting feature which can be observed in Figure 35. The overpotentials for both transitions from stage 1-2 and 2-2L have a different slope for lithiation and delithiation while the transition from stage 4L-1L has the same slope. When one plots the slope of the stage 4L-1L transition as a reference in between the curves for stage 2-2L transition, the deviation can be seen more clearly. It seems that there is some effect which lets both the lithiation and delithiation deviate from the normal slope. This low current density slope is determined by the linear part of the Butler-Volmer equation, the SEI resistance, and the linear regime of phenomenon x. The measured hysteresis might come from a similar effect as discussed by Dreyer et al. [68] based on the spinodal decomposition of phase separating materials but might also come from surface wetting effects as shown by a new modeling approach by Cogswell and Bazant [161]. This determination is beyond the scope of this study but would be important for the evaluation of EIS experiments because a hysteresis would add a non-linear feature to the equivalent-circuit-model.

Another feature which was suggested by J. Christensen, Bosch RTC during private communications concerns a shift of the open-circuit-potential of graphite to more negative potentials with aging. Figure 36 depicts the overpotential profile at low rate C/3 lithiation and delithiation of graphite with cycling number. Especially the beginning of a stage transition is of interest.

![Image of graph showing hysteresis of graphite stage transitions at low current densities, zoom of Figure 34.](image-url)
Usually, one would expect either a constant overpotential for the same rate with cycling or a slight increase which would be due to a continuous growth of the SEI even after the two SEI and high rate formation cycles. This increase can be seen when one compares the first cycles (cycles 1-3) with the subsequent ones (>5 cycles). After these initial five cycles (SEI + high rate formation cycles) a decrease of the overpotential at the beginning of stage transition 1-2 and 2-2L can be observed. For delithiation the C/3 rate overpotential insects the initial C/20 reference potential at about 30 cycles. For lithiation, the beginning of stage 2 shifts drastically to more negative potentials which might be due to a suppression of the formation of stage 2L. Stage 2L has been shown to be kinetically very slow compared to C/3 cycling [96].

In contrast, the overpotentials at the beginning of stage 4L-1L transition at C/3 rate stay constant during cycling for both lithiation and delithiation. Only the progression of this stage transition indicates a shifting to more negative potentials with lithiation cycling. It has to be stressed that 20% progression of stage 1L-2L corresponds to expected pure stage 4L. This might indicate a small aging of stage transition 1L-4L. This was shown to be possible if the degree of turbostratic disorder increases; however evaluated for MCMB [111].

Different features have been found during the investigation of the overpotentials for thin-layer electrodes of graphite. Some of these might have a strong influence on other electrochemical measurement techniques, e.g. EIS. Therefore, these influences need to be addressed.

![Figure 36: Shift of graphite overpotentials during cycling at C/3 rate, legend based on lithiation.](image-url)
3.3.3 Electrochemical impedance spectroscopy of thin-layer electrodes of graphite

To get a better insight into the electrochemical response of a lithium-graphite half-cell, electrochemical impedance spectroscopy can be applied which uses alternating voltage excitation to determine the impedance for a broad variety of frequencies (see section 2.6.1). Usually, the influence of the lithium-counter electrode vanishes if one uses a reference electrode [142]. However, changes in the electrode configuration need to be avoided to compare the results for the thin-layer electrode technique directly with the EIS results. Therefore, full-cell EIS has been performed.

To compare the EIS of a lithium-graphite half-cell with our previous findings, first, the influence of the lithium-counter electrode has to be determined. Therefore a symmetrical Li-Li cell is built with the same dimensions and configuration as the thin-layer electrode of Li-graphite. In general, all effects like diffusion, surface reactions, and ohmic losses should be similar for the Li-Li cell since the thin-layer electrode of graphite adds almost no additional tortuosity to the standard diffusion through the separator. Also, an equipotential is expected for the bilayer of graphite with 3 wt% SuperP as discussed in section 3.1.2. The Nyquist plots of the EIS of symmetrical Li-Li cells are shown in Figure 37 for the first SEI formation cycle and the “lithation” in the second cycle. Lithiation/delithiation and rates are normalized to a virtual active mass of 0.2 mg of graphite.

One can clearly see the increase of the resistances of both semicircles during the SEI formation cycles. The first “lithiation” shows the strongest increase which is consistent with the know growth of SEI in the first cycle [13]. The biggest increase can be seen during the first hour of cycling (blue) while further growth seems to decrease continuously similar to a reaction of first order in time. An additional increase in resistance in the second lithiation is marginal.

After this formation cycle, high current densities have been applied as shown in Figure 38. The current densities have been varied in the same order and with the same density as for the thin-layer electrodes. After each “lithiation” and “delithiation” an EIS has been measured. One can clearly see a very strong decrease of the resistances of the symmetrical Li-Li cell after the first high current density “discharge” (blue). It seems that an additional semicircle develops at low frequencies. Further cycling at high current density “discharge” shows a continuous improvement of the cell to smaller resistivity. It has to be mentioned that during the subsequent low rate “charge” of the symmetrical Li-Li cell the resistances increase again slightly. It seems that the resistance tries to go increase back to its state before the high-current density “discharge”. This shows that there exist a strong difference between the SEI formation cycles and the high rate formation cycles as discussed above.
The activation which was seen for the overpotentials of the Li-Li cell especially during the first two high current density discharges can be confirmed by the EIS results. The overpotentials during galvanostatic high-rate discharge of the Li-Li cell in Figure 26 decrease with continuous galvanostatic cycling. However, this continuous phenomenon cannot be captured in Figure 38 due to the interruption of galvanostatic cycling to perform EIS measurements. EIS was only performed at the end of “charge” and “discharge” of the Li-Li cell. The combination of both results (galvanostatic and EIS) suggests that an decrease of resistivity of the lithium electrode occurs which can be either due to an improvement of the SEI on lithium, an increase of the surface area due to possible dendrite formation or other effects.

![Nyquist plot of symmetrical Li-Li cell during formation cycles.](image1)

![Nyquist plot of impedance spectroscopy of a symmetrical Li-Li cell after each high rate discharge conducted with the same current densities as the thin-layer graphite experiments.](image2)
To extract parameters of the processes in the Li-Li cell, a fitting with equivalent circuits can be performed. Mostly, electrical circuits with resistivity $R$, capacitance $C$, and inductive $L$ elements can be combined in Randles circuits. Additionally, Warburg impedance is used to model diffusion of lithium in the solid. For electrochemical energy storage systems mainly parallel circuits of $R\|C$ are used which are then attributed to different “physical” effects while the correct process is often still under debate. One of the problems to fit the Nyquist plot with equivalent circuits is the problem to determine the number of $R\|C$ circuits to fit the experimental data. Many researchers take several $R\|C$ elements (five in [155]) and account four of them to the SEI. These four different processes are attributed to four different SEI components (= four inorganic and organic layers). However, the more circuits one uses the better the fit (although maybe non-physical).

To avoid this problem, a method was developed by Franklin and Debruin [140] which uses the imaginary part of the impedance and transforms it into Fourier space. The imaginary impedance is sufficient because the real and imaginary parts of the impedance are correlated by the Kramers-Kroenig relation [140]. Afterwards, a filter is applied to delete higher order oscillations after which a back-transformation in the frequency space is performed. The resulting spectra are called distributed-relaxation-time (DRT) since they reflect the information about the time-constants $\tau = RC$ of the parallel $R\|C$ circuits.

The DRT method was successfully applied to LiFePO$_4$ based batteries by Schmidt et al. [162]. The filter after the Fourier transform was chosen to be a Hanning filter as in [162] for which the cut-off was determined to be after eight harmonics by visual inspection. But the Hanning filter itself allows an influence of higher Fourier coefficients due to its characteristic damping function. The resulting spectra of the DRT method are presented in Figure 39 and Figure 40 for the SEI formation cycle and the high rates cycles, respectively.

To interpret these graphs, information about the position, height, and full-width at half maximum FWHM has to be extracted. If the position of the reflex changes its frequency, the respective time constant $\tau = RC$ changes. The FWHM reflects the degree of distributed times in eq. (3.8) in a constant phase element $Q$ which is often used instead of a real capacitor due to a broad variety of double-layer capacities for different pores or grain boundaries in an electrochemical cell. If the FWHM of a reflex is very broad in the DRT plot, the exponent of the distributed phase element is rather small (~0.7). In contrast, if the reflex is a single line the exponent would be 1 which means that the constant phase element is a pure capacitor. But since a filter is applied which cuts-off the high frequency harmonics, a peak broadening would occur also for the pure capacitor element where the FWHM depends on the number of harmonics considered for the
back-transformation. Additionally, cut-off oscillations can be introduced at the upper and lower frequency of the investigated frequency domain due to the filter.

If we interpret the results of the DRT method for the low rate SEI formation cycles in Figure 39 we can observe several changes during progressing cycling. The pristine Li-Li electrode shows three weakly defined time-constants at 0.5 Hz, 2000 Hz, and ~35000 Hz and a long “plateau” regime between those frequencies. This “plateau” in the spectra indicates either several different time-constants or a non-linear effect which is not captured by pure R||Q elements. With

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**Figure 39:** Distributed relaxation times of Li-Li during SEI formation cycles based on Figure 37.

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**Figure 40:** Distributed relaxation times of Li-Li after high rate activation based on Figure 38.
cycling at very low rates to form the SEI, four distinct spectral time-constants are observed. Two of them (at ~0.5 Hz and ~4 Hz) remain at their frequency during the course of cycling compared to the pristine electrode EIS. In contrast, the other two time-constants at higher frequency of 30 Hz and 2000 Hz change their peak position to 20 Hz and 500 Hz, respectively. This indicates that these two effects might change either their capacitance or resistance.

Additionally, the low frequency time-constant shows a very small FWHM compared to the other three time-constants which indicates that the exponent of the constant-phase element is closer to a value of of $p \approx -1$ and might even be a capacitor due to the artificial broadening of the applied Hanning filter. Additionally, the height of all spectral DRTs grows with time indicating that the resistances are increasing which is known to occur for lithium-metal electrodes in organic electrolytes for both calendric and cyclic aging [13]. Minor effects might be presented but are convoluted in the spectra in Figure 39.

Such a transformation of the EIS Nyquist plot can also be done for the high current-densities cycles which were presented in Figure 38. The resulting distributed-relaxation-times are plotted in Figure 40 where both the pristine and DRT after the SEI formation cycles have been included for reference. The first high-current density formation cycle shows a drastic decrease of the height of the peak intensities for the DRTs except for the one at very low frequency which increases and changes its peak position to slightly lower frequency. In the subsequent high-current-density cycles a decrease of all DRT heights can be observed.

Another feature is the stability of the position of the DRTs during the course of the high-current-density cycles. Only the high frequency DRT at 500 Hz after formation is shifting slightly back to higher frequencies (~600 Hz) but never reaches the original peak position in the pristine electrode. Saturation can be observed for all peak heights, positions and FWHMs which indicates a stabilization of the conditions in the Li-Li cell. Only a slightly change can be observed after the third high-current density cycle compared to the 10th and 20th cycle. This stabilization of the parameters was also observed for the overpotentials of the thin-layer electrode of graphite after the first high-rate formation cycles in Figure 24 (section 3.3.1).

The DRTs during the SEI formation and high-rate formation cycles are performed with continuous cycling at various rates based on the standard cycling protocol as shown e.g. in Figure 23. We can determine mainly four different R||Q circuits where one out of the four might be even a R||C parallel circuit. Additionally, a linear resistance is needed to account for the electrolyte resistance in the cell. No Warburg impedance is needed for the symmetrical Li-Li cells because no solid-state diffusion occurs and diffusion in the electrolyte is very fast compared to the frequency range measured here (see discussion in section 3.1.2).
Unfortunately, the fitting with four independent $R||Q$ circuits was not distinct for the fitting of the Nyquist plots in Figure 37 and Figure 38. Therefore, the circuits have been reduced to three independent $R||Q$’s. The extracted parameters are displayed in Figure 41. One can see that the electrolyte resistance is very slowly increasing with increasing cycle number which is incremented for each charge and discharge continuously. The electrolyte resistance is starts at $\sim 3.9 \ \Omega$ in the first cycle and growth to $\sim 4.2 \ \Omega$ in the twentieth. Only at the starts of new measurement protocols (indicated as *), the EIS has been measured at the end of previous and start of new protocol to measure relaxation influence during non-operation of the cell. There the EIS parameters have been plotted for the same cycle number since no cycling was performed between these EIS measurements.

The capacitance $C$ can be derived from the constant-phase element $Q$ by the formula [163]:

$$C = \frac{(Q * R)^{1/p}}{R}$$  \hspace{1cm} (3.8)

$$C = Q (\omega_{\text{max}})^{p-1}$$  \hspace{1cm} (3.9)

$$RQ = \tau^p$$  \hspace{1cm} (3.10)

where the resistance $R$ of the parallel $R||Q$ circuit is needed to detect the maximum angular frequency $\omega_{\text{max}}$ of the semicircle as shown in eq. (3.9). The exponent $p$ determines the distribution of time-constants $\tau$ which show different activation energies of the underlying processes [163]. Either the capacitance or the resistance can be distributed depressing thus the impedance semi-

Figure 41: Parameter fitting to EIS data of symmetrical Li-Li cell with three independent $R||Q$ circuits and one linear electrolyte resistance (fits to Figure 37 and Figure 38). Dashed line is end of formation cycles, star indicates start of new measurement protocol and capacitance of $R3||Q3$ cycled was divided by 500 to be displayed in same plot.
circle in the Nyquist plot. The extracted capacitance can be further used to get an estimate of the used surface area for the process. A double-layer capacity of ~5 μF/cm² is often seen for organic electrolytes [164]. This area specific capacitance will be used hereinafter.

Additionally, the extracted capacitances and resistances from the EIS fits are for the full Li-Li cell which means that resistances are added up while capacitances are summed by the inverse. Assuming that both Li electrodes behave symmetric due to the very low amount of exchanged lithium per cycle (19 μg per 1.33 cm² adding 0.27 μm on the lithium electrode) the resistance can be divided by a factor of two while the capacitance has to be double with respect to a single lithium-metal electrode:

\[
R_{\text{tot}} = R_{Li,1} + R_{Li,2}
\]  
(3.11)

\[
\frac{1}{C_{\text{tot}}} = \frac{1}{C_{Li,1}} + \frac{1}{C_{Li,2}}
\]  
(3.12)

with \( R_{Li,1} = R_{Li,2} \) and \( C_{Li,1} = C_{Li,2} \) result in \( R_{Li} = R_{\text{tot}} / 2 \) and \( C_{Li} = 2C_{\text{tot}} \), respectively.

The electrolyte resistance increases strongly in the first “charge” from 3.6 Ω for the pristine to 4.1 Ω for the symmetrical Li-Li cell which is most probably a consequence of the further growth of the SEI on Li-metal. However, the conductivity of the electrolyte should stay almost constant. During the following “discharge” the resistance increases to 4.2 Ω and stays almost constant for the subsequent 40 cycles (4.3 Ω after 41 charge and discharges). Therefore, the electrolyte resistance \( R_{\text{elyte}} \) in Figure 41 seems to be influenced mainly during the SEI formation cycle and can be assumed to be almost constant afterwards (~4.2 Ω for experiments in section 3.3.2).

The three independent \( R||Q \) circuits evolve differently. The first one can only be separated clearly at the end of the formation cycle because the features are weak in comparison to the other two processes as discussed above (Figure 39). During the “plateau” regions in the DRT, this \( R||Q \) circuit diverged during the fitting procedure where the resistance was very close to zero and the capacitance fluctuated strongly as shown in Figure 41.

Of more interest are the other two \( R||Q \) circuits. The resistances of the two main processes \( R_2 \) and \( R_3 \) increase continuously with cycling at low rate during the first cycles (SEI formation cycles). These resistances decrease drastically during the first high-current-density “discharge”. The subsequent low-current “charge” shows a strong relaxation of the resistance of the third process \( R_3 \) to almost the state before the high-current-density “discharge” while the resistance of the fourth process \( R_4 \) relaxes only slightly. The second high-current-density formation cycle indicates a further improvement of both resistivities, \( R_3 \) and \( R_4 \). The trends shows exponentially de-
creasing resistances which try to relax (or heal) back to their state before the high-current density “discharge”. The strongest improvements in resistivities are seen during the first three high-current density formation cycles which seem to approach an asymptote. During the subsequent much lower current densities, no “healing” back to the initial resistance is observed anymore (current densities same in Figure 24 for galvanostatic cycling). This shows clearly, that the processes can be stabilized after at least three subsequent high-current-density cycles.

The capacitances which are derived from the constant-phase-elements by eq. (3.8) show a more diverse picture of the different processes. The capacitance of the first R||Q circuit (C2) is very difficult to fit except at the end of the formation cycles and diverges as the resistance approaches zero (as discussed above). But the capacitance of process #3 starts at around 200 μF and increases very strongly during the first high-current-density “discharge” formation cycles and subsequent low rate “charge” to about 30 mF (factor 150) as presented in Figure 41. In contrast, the capacitance of process #4 increases very slowly and saturates at about 20 cycles at ~17 μF which is three orders of magnitude smaller than the capacitance of process #3.

If we estimate the surface area from the area specific double-layer capacity (~5 μF/cm² for organic electrolytes) and account for eq. (3.12) we get circa 0.6 cm², 836 cm² and 1.2 cm² for the surface areas of process #2, #3 and #4 in the first cycle, respectively. The maximum estimated surface area is 1.52 cm² (cycle 5, end of formation), 11900 cm² (cycle 7, after C/3 “charge”) and 7 cm² (cycle 40, saturation) for process #2, #3 and #4, respectively. The geometric surface area of the lithium electrode is 1.33 cm². Therefore, process #3 cannot be in direct contact to the electrolyte because its estimated area is more than three orders of magnitude deviating from the geometric surface area. But process #2 and #4 could correspond to the double-layer capacities between the electrode and the electrolyte based on the judgment of the approximated surfaces.

Because the resistivities of process #3 and #4 show a similar evolution during the SEI formation cycles and subsequent high-current-density formation cycles, no assignment can be done to the processes of surface reactions or ionic conductivity in the SEI. But the evolution of the capacitance with the respective surface area is evolving very differently for those two processes. Figure 42 shows the relative changes of the resistivities and capacities of process #3 and #4. The resistivities have a similar profile but the relative changes are stronger for process #3. In contrast, the capacitance #3 is decreases when the resistance is increasing during the SEI formation cycles (indirect proportional) while both R3 and C3 seem to behave directly proportional during the high-current-density formation cycles. For process #4 the direct opposite is observed. During the SEI formation cycles R4 and C4 are directly proportional while they are indirect proportional during the high-current-density formation cycles.
The correct assignment of the observed parameters changes of resistances and capacities to physical processes in the battery is very difficult. Dendritic growth is known to occur on the lithium-metal electrode which shows accelerated growth during high-current-densities due to the more inhomogeneous current distribution and decrease of surface diffusion time [72]. During dendrite growth, a surface area increase is expected which will decrease the resistivity of the surface-reactions as eq. (3.7) shows where the exchange current is a function of area times exchange current density. But the SEI resistance also decreases with increasing surface area as eq. (3.6) shows. Also, the most significant surface area increase is seen after the high-current-density “discharge” while an area decrease is seen during low current density “charge”. Therefore, process #4 can be related to the surface area increase due to the dendritic growth where the area increases from initially 1.2 cm$^2$ to 7 cm$^2$ during the 40 cycles. The dendritic growth (process #4) influences the resistance and capacitance mainly by the increased surface area which enhances the surface reactions governed by the Butler-Volmer reaction due to an increasing surface area. However, the changes are not very small from cycle to cycle as shown in Figure 41.

In contrast, process #3 shows a direct proportionality between the resistance and capacitance for the high-current-density cycles. It was also discussed above that this process seems to be unrelated to a double-layer capacitance with the liquid organic electrolyte because of the very high surface area. Therefore, it could be related to the grain boundaries of the composite SEI. To get an approximation, if the grain size is reasonable, a rough estimation can be done. Assuming an SEI thickness of 50 nm on the 1.33 cm$^2$ lithium electrode with an area specific capacity of 6 μF/cm$^2$ (like ionic-liquid without any solvent shell [165]) as rough estimates, the grain size of

![Figure 42: Relative changes of resistances and capacities during cycling, changes with respect to the preceding cycle derived from data of Figure 41, second graph is a zoom of first one to show relative changes during SEI and high-current-density formation cycles.](image)
the primary cubes can be calculated from the volume \( V = n \cdot a^3 \) and \( C = C_{\text{spec}} \cdot A = C_{\text{spec}} \cdot n \cdot 6a^2 \) where \( a \) is the length of the cube. For those values and the capacity at the end of the SEI formation cycle, the grain size would be \( a = 4.03 \) nm which might be reasonable with circa \( 1 \cdot 10^{20} \) grains in the SEI. A smaller grain size might lead to more tortuosity which increases resistance. Under those circumstances, both the resistance and capacitance would be directly proportional which is consistent with the observations for process #3 for high-current densities in Figure 42.

The relative comparison of the changes of process #3 shows that during the first high-current-density “discharge” at 28 mA/cm\(^2\) (500C for Li-graphite cell) the capacitance is increasing by a factor of 45 which could not be plotted in Figure 42 due to the scale. The subsequent low rate “charge” (C/3 for Li-graphite) shows only an increase of a factor of 3. This means that the primary grain size would decreases from the fifth cycle (after SEI formation) from circa 580 nm to \( \sim 12 \) nm after the high-current-density cycles (cycle 6) and finally 4 nm for the low-current-density “charge” (cycle 7). This seems to be a bit unrealistic. Therefore, the physical origin of process #3 cannot be confirmed accurately. However, it can be stated that this process cannot originate from a process that is in contact with the organic electrolyte (double-layer).

Process #2 cannot be assigned so far. However, the decrease in resistivity and capacity of process #3 and #4 during high-current-density operation seem to show an improvement of the SEI ionic conductivity during these cycles while the low-current-density “charges” might lead to a “healing” of the SEI. This “healing” effect is very strong after the first high-current-density “discharge” and is much more suppressed during the following high-current-density cycles (Figure 41. Experiments with a reference electrode would be necessary to extract differences between the two lithium-metal electrodes to confirm the results of this study.

But what are the changes on the thin-layer electrode of graphite during SEI formation cycles and the high-current-density formation cycles? To get an insight, electrochemical impedance spectroscopy has also been performed on Li-graphite cells. The mass of the thin-layer electrode of graphite has been increased slightly to 0.33 mg to decrease self-discharge during the EIS measurement. In contrast to the Li-Li EIS, the Li-graphite EIS is performed at two different DC cell voltages being 10 mV and 1.5 V which corresponds to stage 1 and almost pure graphite versus lithium-metal. An EIS has been measured for the pristine cell and after each charge and discharge, respectively.

The results are plotted as Nyquist plots and presented in Figure 43 for both the delithiated graphite electrode (Figure 43 left) and stage 1 (LiC\(_6\)) electrode (Figure 43 right). The EIS of the pristine Li-graphite cell has been plotted together with the EIS of discharge graphite samples (~1.5 V) but was performed at 3 V vs. Li\(^+\)/Li. The pristine electrode shows blocking electrode
characteristics as the diffusion impedance increases steeply which shows that diffusion in the solid graphite particles is hindered strongly. This is consistent with previous findings that Li intercalates in graphite solid-solution (stage 1L) at potentials below 0.8 V vs. Li⁰/Li [88].

For delithiated graphite a resistance growth can be seen during the SEI formation cycles in Figure 43a) which is consistent with the observations for the symmetrical Li-Li cell in Figure 37. After the first high-current-density formation cycle, a very drastic decrease of the resistance of the first semi-circle (blue) can be observed which continues to decrease even after the second high-current-density formation cycle (red). The following high-current-density cycles do not alter the EIS response anymore and almost only the diffusion resistance can be observed. This change is very drastic and was never observed for standard electrodes to the best of our knowledge.

For LiC₆, a similar evolution of the EIS with cycling can be observed as shown in Figure 43b). The EIS is always plotted before the delithiation cycle of graphite so that the states before the high-current-density alteration can be compared. After the SEI formation cycles, a very high resistance is detected which changes very slightly from the first lithiation (black curve) to the second lithiation cycle (blue). However, the same significant decrease in resistivity can be observed after the first high-current-density formation cycle (red). The second high-current-density formation cycles decreases the first semi-circle further but of smaller extend. The next seventeen cycles influence the semi-circle slightly and a saturation of the EIS response can be observed.

To compare the results of the EIS of Li-graphite with the ones of the symmetrical Li-Li cell, parameter fitting of the Nyquist plots has been performed. Here, the fitting was separated for the

![Figure 43: Nyquist plot of impedance spectroscopy of a Li-graphite cell at a) 1.5V (left) and b) 10 mV (right) after and before each high rate discharge conducted with the same current densities as the thin-layer graphite experiments in Figure 23.](image)
lithiated and delithiated graphite-Li cells because the response is very different between these two state-of-charges. First, the lithiated stage 1 vs. Li was evaluated with one resistance for electrolyte conductivity and two parallel R||Q circuits in series to the electrolyte resistance. A Warburg impedance and a capacitor have been added for the diffusion EIS response.

The evaluated electrolyte resistance $R_{\text{elyte}}$ and the two resistances of parallel R||Q circuits are plotted in Figure 44 for the EIS at 10 mV. One can see the almost constant resistance of the electrolyte (4.1 Ω after the first lithiation) increases slightly to 4.25 Ω over the course of the 42 charge and discharge cycles.

The other two resistances of the R||Q parallel circuits are much more changing during the cycling. The resistance of process #2 and #3 are increasing during the SEI formation cycles and seem to saturate which is consistent with the SEI growth observed in literature [13]. However, a drastic decrease of the resistivities is seen after the high-current-density formation cycles by a factor of 6.4 for process #2 and 2.8 for process #3. During the second high-current-density formation cycles (HCDFC) a further decrease is seen by a factor of 1.4 and 1.5 for process #2 and #3, respectively. Process #3 has reached its equilibrium as it stays almost constant after the second HCDFC throughout the subsequent cycling (7.9-8.2 Ω). In contrast, process #2 is decreasing continuously during the cycling from 3.6 to 2.3 Ω (third HCDFC to end of 42 cycles).

Also the capacities show a different evolution for process #2 and #3 which have been derived from the constant-phase-elements by eq. (3.8). Process #2 shows a continuous increase of the capacitance with cycling. However, a strong growth is observed for process #2 after the high-current-density discharges which was also observed for process #4 of the Li-Li system as shown.

![Figure 44: Parameter fitting to EIS data of Li-graphite cell at 10 mV with two independent R||Q circuits, a linear electrolyte resistance and Warburg diffusion impedance (fits to Figure 43b). Dashed line is end of SEI formation cycles, star indicates start of new measurement protocol.](image-url)
above in Figure 41. Also a saturation of the capacitance is seen but at 10 times higher values than the Li-Li system. The capacitance of process #3 is much more volatile for the Li-graphite cell. The initial high capacitance of ~300 μF during the SEI formation cycles decreases after the high-current-density formation cycles. Saturation can be seen at around 150 μF if one excludes the points in the third protocol. The relative changes of the parameters of process #2 and #3 can also be plotted as presented in Figure 46b) for the case of the 10 mV Li-graphite system. Process #2 shows an indirect proportional behavior of its resistance and capacitance which was also seen for process #4 of the Li-Li system. In contrast, no correlation can be found for the resistance and capacitance of process #3 of the Li-graphite system since the stable resistance R3 is parallel to a very fluctuating capacitance C3. Therefore, process #2 might be assigned to dendrite formation based on the similarities to process #4 of the Li-Li cell. Process #3 cannot be assigned but shows similar characteristics as process #3 of the Li-Li cell. However, a clear separation between the influences of the lithium and graphite electrode cannot be made.

A fitting of the EIS response of the Li-Graphite system at 1.5 V can also be investigated by Randles circuits. Figure 45 depicts the evolution of the system which was fitted by a linear electrolyte resistance R_{elyte}, two parallel R||Q circuits, a capacitance and a Warburg diffusion impedance as R_{elyte}+Q2/R2+Q3/R3+C4+Wd4. The fitting could be done for the SEI formation cycles and first two HCDFC. Subsequent HCD cycles show almost no semi-circle before the Warburg impedance and are almost featureless. Therefore, the extracted parameters for higher cycle numbers are very fluctuating and should be treated with care. The electrolyte resistance shows the same trend as the one evaluated at 10 mV for the Li-graphite system in Figure 44 which is only

![Figure 45: Parameter fitting to EIS data of Li-graphite cell at 1.5 V with two independent R||Q circuits, an electrolyte resistance and Warburg diffusion impedance (fits to Figure 43a)). Dashed line is end of SEI formation cycles, star indicates start of new measurement protocol, R3 and C3 are divided by a factor of 50 and 5, respectively, to be plotted in same figure.](image-url)
3.9 Ω for the pristine electrode and increases to 4.2 Ω after the SEI formation cycles staying constant for the subsequent cycles. In contrast, the resistance of process #2 is increasing during the SEI formation cycle and drastically decreasing during the HCD FC reaching a value of ~1.5 Ω after the first HCD cycle. The resistance of process #3 increases after the HCD cycles, however, shows high scattering which is related to a difficult fitting of this process after the HCD cycles due to the dominant influence of the Warburg impedance as shown in Figure 43.

The capacities of process #2 and #3 are plotted in Figure 45b). Process #2 shows a similar increase of capacitance C2 as for the EIS evaluation at 10 mV and for the Li-Li system which saturates after ~20 charge and discharge cycles. Process #3 undergoes a drastic increase in the related capacitance after the first HCD formation cycle followed by smaller increases during the next two HCD FC and stays nearly constant during the subsequent cycles. Additionally, the relative changes of the processes for the Li-graphite system at 1.5 V (Figure 46a) show similar characteristics as the one at 10 mV. But the indirect proportionality of process #2 is only seen for the SEI formation cycles and first HCD FC. Afterwards, some minor deviations from this trend can be seen which are most probably due to the very featureless Nyquist plot for 1.5 V as discussed above. The resistance and capacitance of process #3 are direct proportional for the first few cycles and become fluctuating for the subsequent cycles.

The two processes from the Li-graphite system cannot be easily attributed to processes on the graphite thin-layer electrode due to the influence of the Li-counter electrode. But process #2 shows the same characteristics as process #4 of the Li-Li system which was attributed the surface area increase due to dendrite formation on the lithium-metal electrode. This increases the surface

![Diagram](image-url)

Figure 46: Relative changes of fitted parameters of EIS experiments for a) 1.5 V of Li-graphite from Figure 45 and b) at 10 mV from Figure 44, changes with respect to preceding parameter value, dashed line to separate SEI formation cycles.
area for surface-reactions, thus decreasing the resistance of this process as shown in eq. (3.7). If one estimates the related surface area from the capacitance and an area specific double-layer capacity of 5 μF/cm² as also done for the Li-Li system, one can see that the initial surface area of 1-2 cm² increases to 40-50 cm² during the cycling for process #2. The geometric surface area of the lithium-counter electrode is 1.33 cm² and the estimated graphite surface area is \( A_{\text{tot}} = A_{\text{BET}} \cdot m \) which gives \( A_{\text{tot}} = 17.1 \text{ m}^2 / g \cdot 0.33 \text{ mg} = 56 \text{ cm}^2 \). The resistance of process #2 shows initially 80 Ω and decreases to ~3 Ω during the HCD cycles. The symmetric Li-Li system showed a resistance of 60 Ω after the formation cycles which decreases to ~18 Ω after the HCDFC.

If we use the equations for the full cell where the parallel R||Q circuits of graphite and lithium are in series, we can extract the parameters for graphite. With eq. (3.12) and assuming that the Li-Li cell has symmetric R||Q circuits, we get a capacity of 11 μF (~2.1 cm²) after the SEI formation cycles and -28 μF (~ -5.7 cm²) after the first three HCDFC. This shows clearly that the processes of the Li-graphite system cannot be separated here and seem to be a convolution of different processes. A reference electrode is needed to separate the effects from the graphite thin-layer electrode and the lithium-counter electrode.

However, a general conclusion can be made for both the Li-Li and Li-graphite cell. During SEI formation the resistances within the cell increase which is consistent with previous findings [13]. But during the high-current-density cycles, the resistances decrease drastically for both the Li-Li and Li-graphite cell which is a new finding. Usually, all resistances are continuously increasing with further cycling or time (cycling and calendric aging). But here a significant improvement of the performance of the cell can be shown after application of very high current densities. These decreases in resistance are partially healing after the first three HCD formation cycles but are staying almost constant for the subsequent cycles even when the current density is much lower (C/3). This shows that at least three high-current-density formation cycles are necessary to reach the steady-state on each electrode. This is consistent with the previous findings for the overpotential evolution during cycling in section 3.3.1 for the lithium-electrode and section 3.3.2 for the graphite electrode.

This finding should guide future investigations of the rate-capability of active materials vs. a lithium-metal counter-electrode since results might substantially differ if one increases the current-density each time instead of starting with a very high-current-density. Additionally, the strong contributions of the lithium-counter electrode to the overpotentials of a half-cell need to be taken into account if one wants to evaluate the rate-capability of a materials since both the overpotential evaluation in section 3.3.2 and the EIS experiments show high resistivities on the lithium-counter electrode.
3.4 Comparison of different graphite morphologies

With the help of the thin-layer technique, the stage-dependent rate capability and the kinetic limitations have been tested for graphite SFG6 (Timcal) which possesses flaky morphology and high crystallinity. But how do other morphologies like spherical or exfoliated graphite particles influence the rate capability of the material itself and, thereinafter, the response in a standard electrode for commercial lithium-ion batteries?

To compare the graphites to each other both the standard electrode with thicknesses of >50 μm and the thin-layer electrode can be used. Figure 47 depicts the two complementary electrode preparation techniques with the doctor-blade technique which can be used for electrode thicknesses of ~20 to ~200 μm (dried thickness after solvent removal). Thinner electrodes are usually not possible to be prepared due to scratching effects of small agglomerates during blading. Thicker electrodes are often not favored due to sedimentation effects of conductive additives and the binder in the liquid slurry. Additionally, small cracks can often occur due to electrode contraction during the solvent removal. For thicker electrodes, the doctor blade technique can be applied several times in a row but problem with electronic conductivity at the interphase of the two layers can occur.

In contrast, for thinner electrodes than 20 μm, another technique was developed as discussed in section 3.1.1. This technique can produce very thin-layers of a quasi-single-particle layer up to several micrometers and closes the gap between single-particles experiments [157] and standard electrodes [152]. These two techniques will be used in this section to compare different graphites with respect to their rate capability. The thin-layer technique is used to investigate for the rate capability of the graphite material itself (without porosity effects) while the standard electrode is used to investigate the influences of various graphites for commercial applications.

Figure 47: Preparation of electrodes with a) doctor-blade technique for standard electrodes [courtesy of P. Novak and PSI] and b) spray-nozzle technique for thin-layer electrodes.
3.4.1 Particle size effects

The particles size is expected to influence the rate capability of graphite directly due to the longer diffusion path for lithium ions in the solid as shown in section 3.2.3 and the smaller available surface area per mass of graphite which is needed for the surface-reactions and SEI resistance as shown in section 3.3.2. To prove these effects, different graphites have been used in the thin-layer electrode which minimizes effects of the electrolyte and lithium-counter electrode as discussed in section 3.1.2. Figure 48 presents the SEM images of some of the prepared thin-layer

![Figure 48: SEM images of thin-layer electrodes of SFG6 (1st line), SFG44 (2nd line) and MCMB (PSI11, 3rd line), left) secondary electron and right) electron back-scattering detector.](image-url)
electrodes of graphites with SFG6 (Timcal) in the first row, SFG44 (Timcal) in the second row, and a spherical mesocarbon microbead (MCMB, Osaka Gas) in the third row. Two images have been taken for each thin-layer electrode of graphite with the secondary electron detector for an overview of the morphology and the electron-back-scattering detector to show the copper current-collector shining through the electrode (light-grey).

SFG6 is characterized by a median particle size of 3.3 μm and 90% of the particles are less than 6 μm [156]. SFG44 has a median particle diameter of 23.9 μm and a D90 value of 44 μm [156]. They show similar high crystallinity with LA = 62 nm and LC = 30 nm for SFG6 and LA = 57 and LC = 40 nm for SFG44 and show a difference in the surface area measured by BET of 17.1 m²/g for SFG6 and 4.6 m²/g for SFG44 [156]. Additionally, very different carbons like MCMBs can also be tested in comparison to high-crystalline graphites. They usually have smaller graphitic domains and some amorphous carbon between these domains. Other standard graphites have also been used to prepare thin-layer electrodes (SLP30, KS6, KS75, exfoliated graphite, etc. (Timcal)) but are not shown in Figure 48 because they form similar thin-layer electrodes. One can clearly see the differences between the flaky graphite SFG particle and the spherical MCMB. This particle shape might play a role in standard electrodes since they form a different pores size distribution and pore connections [154]. For thin-layer electrodes the differences were unknown up to date.

Therefore, these thin-layer electrodes have been cycled galvanostatically at various rates with a similar electrode loading. Figure 49 shows an electrode of SFG6 graphite with a mass of 0.64 mg with 10% PVDF binder. The mass has been increased to the thin-layer experiments in section 3.2

Figure 49: Galvanostatic cycling of graphite SFG6 with D90 = 6 μm, a graphite mass of m=0.64±0.05 mg and an electrode thickness of h=10±1 μm.
to avoid problems with the oxide-layer on the copper current collector and that no conductive
additive is needed. This avoids the parasitic effects which have been investigated and corrected
in section 3.2.2. Only low and medium current densities have been measured to avoid all non-
linear effects discussed in the previous sections. Figure 49 indicates that SFG6 shows very low
overpotentials at 2C charge (lithiation) compared to the low rate charge C/7. Additionally, only
low overpotentials are detected for medium rate delithiation at 25C discharge rate while the full
specific charge can be extracted.

To compare this cycling behavior with the same graphite type (flake, high crystalline), also
SFG44 has been tested under the same conditions as depicted in Figure 50. The rates have been
adapted to the mass which could be more precisely measured after the cycling due to the vari-
ation of the mass of the copper current collector after electrode punching. Therefore, the rates of
the different electrodes can vary slightly due to the mass adaptation after cycling has been per-
formed. In contrast to the cycling performance of SFG6, the bigger graphite particles of SFG44
show much higher overpotentials for 1.5C charge rate compared to the 2C charge of SFG6. Ad-
ditionally, the extracted specific charge of SFG44 during charging is lower than that of the
smaller counterpart. This is consistent with the investigation in section 3.2.3 which shows that
the diffusion limitations in the dense stage 1 and 2 are one of the main limitations during charg-
ing if the applicable overpotentials is not limiting.

During discharge, the same trend can be observed. The overpotentials for 28C discharge of
SFG44 are higher than the respective ones of SFG6. Also a small decrease in the extracted spe-
cific charge can be observed for SFG44 which is also consistent with the previous findings on

![Figure 50: Galvanostatic cycling of graphite SFG44 with D_{90} = 44 \mu m, a graphite mass of
m=0.59\pm0.05 mg and an electrode thickness of h=14\pm1 \mu m.](image)
the stage-dependent rate capability in section 3.2.3. The longer diffusion path hinders the progression of the dense stages into the particle and, thus, decreases the galvanostatically delivered specific charge. The difference in the overpotentials between the medium rate discharge (>20C) of SFG6 and SFG44 can only depend on the influence of the graphite material itself since diffusion limitations in the electrolyte are avoided by the thin-layer technique. Moreover, the influence of the lithium-counter electrode is exactly the same for the SFG6 and SFG44 electrode due to the same current-densities applied for those cells with slightly different mass giving, thus, a slightly different rate.

However, the BET of SFG6 is circa four times higher and since the particle shape is of similar morphology, the specific prismatic surface area should also be higher for SFG6 compared to SFG44. This means that the overpotential of the surface reactions have to be higher to account for a lower prismatic surface area of SFG44. Additionally, the available surface area for the SEI is reduced which increases the resistance as eq. (3.6) indicates. These two factors increase the total measured overpotential has to be higher for bigger particles with the same morphology (SFG44: SFG6) due to the lower specific prismatic surface.

As discussed above, also other standard graphites can be tested with respect to their influence of particle size and should follow the same trend. Figure 51 shows the galvanostatic cycling of a KS6 graphite electrode. In comparison, Figure 52 presents the galvanostatic cycling of a KS75 graphite electrode. KS graphites also consist of flake-like particles which have a slightly different aspect ratio than SFG graphite. The prismatic area seems a bit smaller from SEM images but

![Graph showing galvanostatic cycling of graphite KS6](image)

**Figure 51:** Galvanostatic cycling of graphite KS6 with $D_{90} = 6 \, \mu m$, a graphite mass loading of $m=0.58\pm0.05$ mg and an electrode thickness of $h=6\pm1 \, \mu m$. 
there are many small graphite domains attached on the basal plane on a main particle. Although there is a difference observed in the irreversible specific charge in the first cycle which is higher for KS graphites in both EC/DMC and EC/PC compared to the SFG counterpart [156], very little difference might be seen for the rate capability for small and medium rates.

The BET surface area of KS6 graphite is 13.8 m²/g where 90% of the particles are smaller than 6 μm (D₉₀) and 50% are less than 5.6 μm and the crystallite domains is Lₐ = 48 nm and Lₜ = 28 nm which is only very slightly smaller than SFG6 [156]. In comparison, KS75 graphite flakes have a BET of 3 m²/g with a D₉₀ value of 75 μm and D₅₀ of 24 μm with a primary crystallite domain size of Lₐ = 54 nm and Lₜ = 34 nm. So, KS graphites are also very high crystalline graphites with a slightly smaller BET than the respective SFG graphite counterparts. The prismatic surface ratio of KS graphites cannot be determined so that direct comparison of the surface reactions and ohmic resistance is not possible.

During charging of a thin-layer electrode of KS6 in Figure 51 only low overpotentials are observed for 2C charge compared to the low rate C/7 one. In contrast, the charging of KS75 at 2C rate in Figure 52 shows slightly increased overpotentials at the beginning of a stage-transition, e.g. stage 2-1, while strong diffusion-limited overpotentials arise during progression of the particular stage-transition. These diffusion limitations are even a bit higher for KS75 than in the smaller SFG44 which show a similar extracted specific charge at 3C compared to the 2C of KS75. This is consistent with the findings of the diffusion-limitations in dense stage 1 and 2 as discussed in section 3.2.3.

![Figure 52: Galvanostatic cycling of graphite KS75 with D₉₀ = 75 μm, a graphite mass loading of m=0.67±0.05 mg and an electrode thickness of h=22±2 μm.](image-url)
The discharge of KS6 shows low overpotentials for medium discharge rates of 17C while the KS75 graphite electrode shows almost overpotentials of a factor of 2x at medium rates compared to KS6. This is consistent with the estimations done for SFG graphite because the BET surface area of KS75 is a factor of 4.5x smaller than that of KS6 graphite giving similar changes of the contributions of the surface reactions and SEI resistance as discussed for SFG graphite. KS75 graphite shows similar overpotentials at 21C discharge rate with regard to the 28C discharge rate of SFG44, thus indicating higher overpotentials at the same rate for KS75 which is also consistent with the BET ratio of SFG44: KS75 of a factor of 1.5.

In general, this comparison of highly crystalline graphites shows that smaller particles show a better charging performance for both overpotentials and extracted specific charge. In contrast, for discharge only the overpotentials increase for bigger particles while almost the full specific charge can be extracted for all measured highly crystalline graphite particles until a particle size distribution of $D_{v0} < 75 \, \mu m$. Only small specific charge losses are seen for the bigger graphite particles which are less than 20% at medium high rates of ~20C which are sufficient for most applications. The extracted specific charge dependence on the order of the stage transitions because the dense stages possess a smaller diffusion coefficient as discussed in section 3.2.3 while during discharge the liquid-like stage transitions can compensate for this limitation of the dense stages. The overpotentials clearly depend on the available surface for reactions (prismatic area, although often only the BET is known) as shown in this section. This is consistent with theoretical predictions from the kinetic equations governing the system response.

Including the finding of Buqa et al. [156] for the irreversible charge loss in the first cycle in EC/DMC, we propose the use of a smaller particle size of highly-crystalline graphite particles for high power applications where an initial irreversible charge loss needs to be accepted (e.g., hybrid electrical vehicles with a small battery pack). In contrast, bigger graphite particles should be used for high-energy applications where specific charge losses need to be avoided and recharging can be done slowly (e.g., laptops, cell phones).

A combination of smaller particles closer to the separator while the bigger particles are closer to the current collector might be a good intermediate electrode because it can account for high current pulses and could allow equilibration of the electrode during relaxation. Therefore, particle size engineered electrode might be beneficial for pulses application (e.g., start-stop of power tools, electrical vehicles). Similar mixing of electrodes is done in the positive electrode by using fast manganese spinel and high energy materials like NCA or NMC [4]. The evaluation of these mixed graphite electrodes are beyond the scope of this work and are just proposed as a possible solution for applications.
3.4.2 Effects of particle shape on electrode performance

It was shown above that the particle size of graphite determines the galvanostatic response in thin-layer electrodes. But what determines the response in a standard electrode of graphite where diffusion limitations and tortuosity in the porous electrode contribute significantly to the electrochemical response? Shim et al. [154], Buqa et al. [152] and many others showed that the response of a standard electrode depends mainly on the diffusion in the electrolyte in the porous electrode. But what determines the porosity of an electrode?

In an uncompressed electrode, the particles are loosely connected and are mainly held together by the binder (fibers and matrices of PVDF, PTFE, CMC, etc.). The pores are often very large and the fraction of porosity of the total electrode volume can be ~35-40%. The pore shape should mainly be defined by the particle shape and the pore size should depend mainly on the particle size of the active material. Conductive additives and the binder influence the porosity according to their volume fraction. The influence of the particle size on the thickness of an uncompressed electrode can be clearly seen from the thin-layer electrodes in the previous section where a similar mass ratio of the different flaky graphite particles SFG6: SFG44: KS6: KS75 with a mass of 0.64: 0.59: 0.58: 0.67 mg shows a strong increase of the electrode thickness with particle size with 10: 14: 6: 22 μm (Figure 49-Figure 52). This shows clearly that bigger particles form bigger pores between them, thus increasing the electrode thickness. In contrast, highly compressed electrodes are often pressed to the closest packing structure which is obviously different for spheres than for flakes or quadratic particles. In a compressed electrode, the pores might be very small and the connections between these pores might vary strongly with the particle shape.

To compare different graphites in a standard electrode, a colleague in the group, Dr. Wolfgang Märkle, studied different graphites with different particle size, BET, morphology, particle shape, and crystallinity with respect to their performance in a compressed electrode. The defined standard electrode consists of 91 wt% active material (carbons, Timcal) with 8 wt% of PVDF binder (Kynar Flex) and 1 wt% SuperP conductive additive (Timcal) were the electrode is compressed by calandering to an electrode density of 1.3 g/cm³ at an electrode thickness of 30 μm.

The discharge response of these defined standard electrodes where tested at different C-rates where the response of the 15C discharge rate is shown in Figure 53 for three different samples of an MCMB (PSI11), a special treated graphite, and an expanded graphite (PSI52). A clear difference can be observed for the specific charge which can be extracted galvanostatically for these three different carbons in the standard electrodes. However, it has to be stressed that the MCMB has a smaller total specific charge (~300 mAh/g) compared to the expanded graphite (~400 mAh/g). When one plots the ratio of galvanostatic specific charge to the total specific
charge of the electrode, one can compare the 15C-discharge performance for different carbons. Figure 54 shows this comparison for 63 different graphites and graphite-like carbons. The MCMB (PSI11) delivers ~90% of the total specific charge galvanostatically at a discharge rate of 15C. In contrast, the expanded graphite can deliver less than 30% of its charge galvanostatically. These results come from an investigation by Dr. Wolfgang Märkle and are just shown for reference in the standard electrodes.

Figure 53: 15C discharge rate performance of different carbons in a standard electrode configuration with a ratio of active material: PVDF: SuperP = 91:8:1, a density of $\rho = 1.3$ g/cm$^3$ and an electrode height of $h=30$ μm [courtesy of Dr. Wolfgang Märkle, PSI].

Figure 54: Galvanostatic part of 15C discharge experiment in standard electrode configuration for different carbons [courtesy of Dr. Wolfgang Märkle, PSI].
To compare the carbons, the best and worst samples in Figure 54 have been chosen to be tested in the thin-layer electrode configuration. Figure 55 presents the galvanostatic response of a thin-layer electrode of an MCMB which showed the best performance at 15C discharge while Figure 56 shows the cycling of expanded graphite which was the worst sample during the galvanostatic discharge at 15C in the compressed standard electrode. The MCMB consists of spherical particles with a D$_{90}$ value of 15 μm and a D$_{10} = 7$ μm with a BET of only 1.8 m$^2$/g [Dr. W. Märkle]. This small BET is due to the spherical shape of the MCMB particles which minimizes the surface to bulk ratio compared to other particle shapes. In contrast, the expanded graphite consists of graphite particles which have been exfoliated partially on the prismatic surfaces with a D$_{90}$ value of 40 μm and D$_{10} = 5$ μm where the BET is measured to be 22.5 m$^2$/g [Dr. W. Märkle]. This BET surface area is five times higher compared to SFG44 with a similar D$_{90}$ value mainly due to the exfoliated prismatic surfaces.

The charging of the MCMB (lithiation) in the thin-layer electrode in Figure 55 shows that the overpotentials increase significantly for 1C and 2C compared to the low rate C/5. Additionally, the specific charge extracted galvanostatically decreases very strongly delivering less than 40% at a 2C rate. Furthermore, the stage transition between graphite solid-solution (stage 1L) and stage 4L is very badly defined even at low rates of C/5 which is consistent with findings of Takami et al. [110] who showed that increasing disorientations of the graphitic domains decrease the existence of stage 1L to 4L transition.

![Figure 55: Galvanostatic cycling of a mesocarbon microbead MCMB (PSI11) with a loading of active material of m=0.9±0.1 mg and an electrode thickness of h=16±2 μm.](image)
In contrast, the expanded graphite shows very good performance during galvanostatic charging at 1C and 2C rate in Figure 56. The overpotentials of the expanded graphite are smaller than the once of the MCMB at the beginning of a stage transition for the same rate. Additionally, much smaller diffusion-limited overpotentials are observed during the progression of a stage transition. More than 70% of the total specific charge can be extracted during 2C galvanostatic charge as compared to ~40% of specific charge for the MCMB.

For discharge a similar trend can be observed. The MCMB particles show very high overpotentials during 29C discharge while the expanded graphite shows roughly half of the overpotentials at 32C discharge rate (~0.48 V: ~0.26 V at 50% SOC). Additionally, the MCMB cannot deliver its specific charge at 43C discharge while still more than 80% of the specific charge can be extracted galvanostatically from the expanded graphite at 68C. This shows clearly that the best sample of the compressed standard electrode (MCMB) which was three times better than the expanded graphite electrode completely changes its behavior in the thin-layer technique when particle properties dominate. Additionally, the particle size (D₉₀ value) is more than 2.5 times higher for the expanded graphite compared to the MCMB so that the trends are even more surprising.

The explanation for these contrary results can be explained by the morphology of the two different carbons. The MCMB consists of spherical particles as shown in Figure 48 (third row) which form a very good porosity network in a compressed electrode with good connection between these major pores. The expanded graphite, however, staples in the electrode where the ends of the basal surfaces (at the edge to the prismatic surfaces) are expanded due to the exfolia-

Figure 56: Galvanostatic cycling of graphite expanded graphite (PSI52) with a loading of active material of m=0.7±0.05 mg and an electrode thickness of h=13±2 μm.
tion. During calandering of the electrode, these flakes staple where the exfoliated ends of the basal plane block the connection between pores very efficiently. Therefore, the diffusion through the porous electrode is hindered much more than for spherical particles which increases electrolyte-diffusion-limited overpotentials and leads to a prematured hitting of the cut-off potentials although the particles itself would be able to respond much faster.

The main conclusions of this investigation shows that the particle properties (size, crystallinity) with their respective influence on the solid-state diffusion, surface reactions and SEI resistance define the response in a thin-layer electrode while they seem to play a minor role in compressed electrodes. There the particle shape defined the pores (size, shape) and especially the connection between these pores, thus dominating the galvanostatic cycling during medium and high rates.

3.5 Galvanostatic-intermittent titration of graphite

There exist some influences which are very difficult to access and measure experimentally. Some of these effects are e.g. the influence of the solvation energy of the lithium-ions when they pass from the electrolyte where they are fully solvated by the organic solvents to the non-solvated lithium-ion in the bulk of graphite. When lithium ions intercalate in graphite while staying partially solvated, exfoliation can occur [1, 13]. A properly built SEI protects the graphite from a possible co-intercalation of the solvation shell. Some electrolytes are known to passivate the prismatic surface not properly like in the case of propylene carbonate or acetonitrile which can lead to an exfoliation of the graphite [13].

Another effect which is often discussed for modeling of the stage transitions in graphite concerns the elastic energy during lithium insertion and extraction in graphite (see section 2.5). During insertion, the interlayer distance of the graphene sheet increases from 3.35 Å [107] to 3.706 Å [80] by 10.6% while only a slight increase of ~1% is observed within the graphene layer (1.42 Å to 1.435 Å [80, 107]). Also, modeling approaches on the bending energy for staggered and matching domain walls found that there exist some contribution favoring either staggered or matching domain walls depending on the ion size [130, 138].

To get an insight if either elastic energies or solvation energies can play a role for the overpotentials on graphite, the standard kinetic equation system has to be considered (section 2.7). Usually, all processes like diffusion, surface reactions and ohmic potentials drops are very dominant in graphite electrodes. The thin-layer electrode approach already suppresses some of these influences as discussed in section 3.1.2. But diffusion limitations in graphite (section 3.2.3), surface reactions and ohmic potential drops (Figure 33) are still significant during charge and discharges.
One technique, namely the galvanostatic-intermittent-titration technique (GIT, section 2.6.1c) might be able to access influences which contribute independently from rate to the overpotential. This technique is usually used to determine the pseudo-open-circuit potential of a material. The charge/ discharge is performed at a low rate and intermitted after a certain time or a certain cut-off potential after with the relaxation of the overpotential is monitored. This relaxation can last from, e.g., 1-10h or until a certain slope of the relaxing voltage is reached.

Figure 57 presents the GITT of a thin-layer electrode of graphite SFG6 with 0.84 mg of active material in a ratio of 90:10 of SFG6: PVDF where the electrode thickness was determined to be 11-12 μm. The mass of the electrode was increase compared to the bilayer electrode experiments in section 3.1.1 to reduce the parasitic effects of the copper current collector and avoid the use of SuperP conductive additives. Additionally, the increased mass leads to a smaller normalized discharge-current since parasitic reactions are normalized with respect to a higher active material mass as previously done for the EIS experiments in section 3.3.3. Figure 57a presents the GITT with a cycling rate of C/37 and relaxation times of 10 hours. In this graph, the potentials are plotted versus the specific charge where the relaxation of the potentials is shown as “spikes” because the state-of-charge does not change during the relaxation (zero current).

The characteristic stage transitions of graphite are clearly visible. Additionally, a hysteresis between charge and discharge for each stage transition can be observed as also discussed for the thin-layer experiments in Figure 35. A zoom in the GITT reveals more insight into the hysteresis and very low rate overpotentials as shown in Figure 57b. The relaxation overpotentials during charge are higher compared to the ones for discharge. This is consistent for all stage transitions, however, less for the transition of stage 2-1. Moreover, the hysteresis of the transitions of stage

![Figure 57: Galvanostatic intermittent titration technique of graphite SFG6 thin-layer electrodes at a cycling rate of C/37 with 10 hour relaxation at predefined potentials and charging times, a) full GITT with stage transitions indicated and b) zoom to allow comparison of overpotentials.](image-url)
1L-4L and 3-2L-2 is still present even after 10h of relaxation while the transition from stage 2-1 shows a strong decrease of its hysteresis. The hysteresis of stage 2-1 is even smaller during GITT operation in comparison to the hysteresis during galvanostatic cycling as shown in Figure 35.

If one compares the overpotentials of each stage transition (Figure 58), a trend can be observed. All overpotentials of the C/37 rate to the 10h relaxed state show higher overpotentials for charging than for discharging. To allow comparison, the evolution of the discharge overpotential has been mirror at 50% progression of the respective stage transition. The so called relaxation overpotentials seem to differ mainly for the stage transition from stage 4L to 2L where they seem to decrease with progressing stage transition. This sloppy voltage regime where the exact transition of the different phases is still under debate (sec. 2.5) is the only transition in graphite showing this decreasing evolution of the relaxation overpotential. Stage 2-1 shows the smallest difference in the relaxation overpotentials between charge and discharge.

But what can be the origin of these different relaxation overpotentials? The GITT of the thin-layer electrode of SFG6 gives more insight into the relaxation phenomenon. If one plots the potential of the graphite electrode (measured vs. Li$^+$/Li) with respect to time, one can observe different relaxation features of the overpotential for charge and discharge. Figure 59 presents a representative GITT vs. time plot where the cycling at C/44 was interrupted periodically and a relaxation of the overpotential was allowed for a period of 10 hours. The general known open-circuit-potential is almost impossible to imagine in this plot since the total time for a full charge needs ~44 hours while the accumulated time of all relaxations consumes in total 240 hours.

![Figure 58: Overpotentials of low rate galvanostatic cycling at C/37 compared to relaxation after two hours (dotted lines = discharge, solid lines = charge), different stage transitions marked with various colors, vertical line indicate pure phases, discharge SOC is mirrored for each phase transition to allow comparison of increasing overpotentials with progression of phase transition.](image-url)
The progress of the potential of graphite is better depicted in Figure 57. If one zooms in special regions of the charge and discharge profile of the GITT, one can show the different relaxation phenomena during charge and discharge. Figure 60 presents the zooms into the region of transitions between the stages 1L-4L-3L-2L and 2L-2-1. During the stage transitions from stage 1L-4L a diffusion relaxation can be observed. In contrast, the 10h relaxation between the stages 4L-3L-2L shows no apparent saturation phenomenon. An ohmic potential drop is followed by an almost linear potential increase with time. This is very unusual for intercalation materials. During the stage transitions from stage 2L-2 a diffusion related part can be observed followed by the linear potential increase with proceeding relaxation. In contrast, the transition from dense stage 2-1 shows a pure diffusion related relaxation which saturates after ~2h. Pure stage 1 shows the standard diffusion related relaxation in its solid-solution regime.

Also the discharge of the thin-layer electrode shows uncommon relaxation phenomena as presented in Figure 61. During the transition from stage 1-2-2L and 2L-3L-4L-1L a small self-dis
charge current can be observed. The overpotentials decrease at the beginning of the relaxation by an initial ohmic potential drop after which it increases slightly. This can be observed where the open-circuit-potential changes its value by a variation of the state-of-charge. Thus, this effect of self-discharge cannot be observed during potential-plateau regions. During the relaxation of stage 1 in its solid-solution, an ohmic potential drop and a linear potential rise can be observed. During the transition from stage 1-2 a diffusion relaxation can be detected on top of the ohmic potential drop after which the relaxed potential saturates. During stage 2 and the transition from stage 2-2L a potential rise after on ohmic potential drop can be detected. In contrast, the transitions from stage 2L-3L-4L show an ohmic potential drop after which the potential stays constant. This is the opposite of the relaxation during charge where even after 2 hours of relaxation no sever deviation from a linear rising potential can be observed. The subsequent stage transition from stage 4L-1L shows a diffusion related relaxation to an initial ohmic potential drop. The relaxations in the Figure 61b last only two hours because a previous GITT of the same cell had to be taken because of a current shut-off.

In summary, we see that an ohmic potential drop is present at the beginning of each potential relaxation after current interruption. During the stage transitions a diffusion-related potential profile can be observed following a profile in time of approximately $e^{-t}$ which is expected for diffusion. During pure stages and the transitions of stage 2L-3L-4L (and reverse), no significant diffusion relaxation is observed. But during these transitions very contradicting profiles appear for charge and discharge. During charge no saturation can be seen even after 10 hours of relaxation while the potential is almost instantaneously relaxed after a few minutes during discharge and stays constant throughout the 10 hours of open-circuit.

To test the influence of side reactions on the GITT in Figure 57 - Figure 61, two different investigations have been carried out. Figure 62a shows the irreversible specific charge during oper-
ation of the thin-layer electrode of graphite SFG6 for the GITT investigation. A relative small irreversible specific charge was observed during galvanostatic cycling at C/8 and C/5 rate with ~20 mAh/g irreversible charge loss. During the GITT experiments at C/44 with either 2h or 10h relaxation times, the irreversible specific charge seems to be independent of the relaxation time. Both GITT experiments with 2h and 10h show an average irreversible charge of 96 mAh/g. This results is counter-intuitive since one would expect a higher irreversible charge during extended operation in the instability regime of the electrolyte (~ < 0.8 V vs. Li+/Li).

To test the self-discharge of the electrode, the cell voltage has been monitor under open-circuit conditions in Figure 62b). Starting from pure stage 2 which corresponds to 50% SOC, the self-discharge is measured and the potential reaches 1.5 V after 1427 hours under open-circuit idling. Stage 2 was chosen since the stage 1-2 transitions shows very little features. A small interruption is seen at ~ 700 h of monitoring due to a system crash. The time of non-operation of 64.75 h was added to the timeline. Above 1.5 V a significant deviation from the standard graphite OCP is observed. The voltage should rise quickly to 3 V since almost no lithium-ions are stored anymore in the bulk of graphite. Only surface groups are known to be cycled at these voltages [13]. Therefore, two different possibilities can be considered. Either the SEI can decompose which is known for many other compounds like on CuO in the voltage range from 0-3 V [78] or very little side-reactions occur above 1.5 V, thus the OCP is stabilizing.

It is very important to stress that almost no deviation from the standard OCP of graphite is observed below 1.5 V which was used for the previous experiments in sections 3.2 - 3.4. From the self-discharge experiment we can estimate the change of the open-circuit potential of graphite during the 10 h of relaxation. Figure 63 presents a zoom in the self-discharge experiments of

![Figure 62: a) Irreversible specific charge during galvanostatic and GITT operation, b) self-discharge experiment of same thin-layer electrode of graphite SFG6 as used for the GITT experiments in Figure 57 - Figure 61.](image-url)
Figure 62a) and indicates the different potential changes at different graphite open-circuit potentials. The interruption of the experiment is seen at ~700 h of the experiment but shows no significant deviation from the standard profile indicating that the leakage current through the measurement device is negligible.

At the steepest potential rise of the graphite OCP, 3.7 mV/10h are measured while 12.3 mV/10h are measured at the relaxation potential different in Figure 60a) at the same potential and subtraction of the ohmic potential drop. During the 2 h of relaxation of the discharge GITT in Figure 61b) a potential rise of ~0.1 mV is seen although this value is within the noise of the measurement equipment. The self-discharge corrected average potential change during relaxation of graphite is +0.86 mV/h for charge and -0.32 mV/h for discharge showing a much stronger relaxation during charge of the graphite SFG6. However, it is difficult to judge if the self-discharge is leading to the potential plateau during the relaxation in the discharge GITT in Figure 61b) and the constantly increasing potential during the relaxation of the charge GITT in Figure 60a). But since the self-discharge can contribute up to 30% of the relaxation voltage (maximum, measured in the steepest OCP region), results have to be treated carefully.

In general, significant differences in the relaxation profile can be observed for the different stage transitions and also for charge vs. discharge. Dense stage 1 and 2 seem to follow the standard diffusion profile during relaxation after an initial small ohmic potential drop followed by a small self-discharge potential rise. In contrast, the liquid-like stage 4L, 3L and 2L show a very uncommon continuous potential rise during the relaxation after low-rate charge while staying constant during the relaxation after low-rate discharge. The initial ohmic potential drop is also detected for all liquid-like relaxations as expected. However, more experiments would be needed to prove these indicators of different overpotentials for charge and discharge of graphite at very low rate where kinetic influences like surface-reactions and diffusion are negligible.

Figure 63: Zoom in self-discharge experiment with potential changes during a 10 h idling period.
3.6 Summary of kinetics on graphite

With the help of the newly developed thin-layer technique, several different properties of graphite could be investigated. It could be proven that highly-crystalline graphite

1) is one of the fastest lithium-ion intercalation materials known up to now. Delithiation can be done until rates of 680C above which electrolyte diffusion limitation hinder further investigation. However, lithiation can be done only up to 6C based on a galvanostatically extracted specific charge of 82% of the total specific charge (see section 3.2).

2) Besides the limited overpotential for the lithiation of graphite of ~80 mV the order of the stage transitions is important. Due to the reduced diffusion coefficient in the dense stages of graphite [136] compared to the liquid-like stages [153, 159], lithiation can deliver less specific charge during galvanostatic cycling. The dense stage transitions come at the end of the lithiation process thus allowing less time for the propagation of the dense stages into the bulk of graphite. In contrast during delithiation, the liquid-like stage transitions come at the end of the discharge process. Since they possess a higher diffusion coefficient, almost the full specific charge can be extracted in the same overpotential regime of 80 mV.

The transition towards the dense stages, namely stage 1 and 2, deliver ~40% of their specific charge at rates of 20C while the transitions towards the liquid-like stages, namely 2L,3L, 4L, and 1L deliver more than 80% of their respective specific charge during lithiation. During delithiation these liquid-like stage transitions can even compensate for the initial specific charge loss of the dense stage transitions thus allowing rates of at least 680C when high overpotentials are allowed (section 3.2.3). Usually, such high rates are only seen if the intercalation material is nanosized which reduces the diffusion length drastically. But the investigated graphite has a median diameter of 3.3 μm which is two-orders of magnitude higher than comparably fast intercalation hosts thus four orders of magnitude different if standard Fickian diffusion is considered (eq. (2.10)). A model will be presented in section 6.1 which can explain this behavior. This finding can explain the long-know charge-discharge asymmetry in graphite.

3) The kinetic bottlenecks of graphite can be determined for different specific currents. For very low currents of <0.5 A/g, an unknown phenomenon dominates the overpotentials of graphite which saturates at ~ 8 mV for both lithiation and delithiation. For specific currents ranging from 4 to ~50 A/g, surface-reactions dominate the overpotential contribution while at higher currents of more than 160 A/g both ohmic potential drops in the SEI and surface reactions contribute almost equally to the total overpotentials (Figure 33 in section 3.3). The extracted exchange current density has a value of $i_0 = 0.7 \text{ A/m}^2$ per BET (~3.6 $\text{ A/m}^2$ per estimate ASA) with an as-
sumed transfer coefficient of $\alpha_a = \alpha_c = 0.5$ ($\alpha$ cannot be guaranteed because no high overpotentials could be measured for lithiation due to possible lithium plating). The ohmic resistance was measured to be $\sim 2.9 \, \Omega$ for the electrode which corresponds to $16 \, \Omega \cdot \text{cm}^2$ if one normalizes over a prismatic surface area of $3.3 \, \text{m}^2/\text{g}$ (estimated from dimensions of the graphite SFG6 particles).

4) An activation process of the Li-graphite and Li-Li electrode can be observed during the first two to three high-current-density discharges (section 3.3). Both high-rate experiments and electrochemical impedance spectroscopy found that the resistance decreases on the lithium-metal electrode. The reduction of the resistance of the solid-electrolyte-interphase seems to be the dominating process to improve the cell performance. It seems that the amount of grain boundaries increase significantly during the high-rate-formation cycles which leads to a strong reduction in resistance since diffusion through the SEI is suggested to occur mainly on these grain boundaries [13]. However, direct evidence of an increase of the amount of grain boundaries could not be found; only a high surface area increase could be detected which seems to be not in contact with the electrolyte. A dendritic growth can also be seen but contributes much less to the improvements of the galvanostatic response as estimated from EIS. A significant effect on the graphite electrode could not be investigated because deconvolution of the EIS of the Li-graphite thin-layer electrode was impossible.

5) Nonlinear effects are detected for the charge-discharge behavior around the open-circuit potential ($\pm 10 \, \text{mV}$) as shown in section 3.3.2. A hysteresis of $6.6 \, \text{mV}$ for the transition of stage 1-2 and $12-13 \, \text{mV}$ for the transitions of stage 2-2L and 4L-1L where detected. Furthermore, an unexplainable phenomenon at very low current density has been observed which saturates at $\sim 8 \, \text{mV}$. These two effects lead to very strong nonlinearity for the electrochemical impedance spectroscopy in this voltage regime which could be an explanation for the failed deconvolution of the Li-graphite EIS although the symmetrical Li-Li cell could be deconvoluted easily.

6) The particle properties of different carbons dominate the electrochemical response of a thin-layer electrode since electrolyte diffusion limitations are suppressed. But in standard electrodes of graphites, these properties contribute minor to the overall response since electrolyte diffusion limitations become dominating. Therefore, the particle shape seems to become the dominant property of carbon since it defines the pore structure and connection between different pores. This is shown clearly when one compares the best carbon (MCMB, spherical particles) with the worst carbon (expanded graphite, flakes) of a compressed 30 $\mu \text{m}$ thick electrode in the thin-layer electrode configuration. There the exact opposite rate performance can be observed. The MCMB delivers less specific charge and possesses higher overpotentials at the same rate than the expanded graphite as shown in section 3.4.
7) Difference in the polarization at very low rates can be detected by the galvanostatic-intermittent-titration-technique. Higher overpotentials are observed for lithiation compared to delithiation. Additionally, very uncommon relaxation phenomena can be observed on top of the initial ohmic potential drop and diffusional relaxation as discussed in section 3.5.

Besides these different findings for graphite, also many parasitic effects had to be investigated to allow proper analytical evaluation of the respective data. The conversion reaction of the copper-oxide layer on the surface of the copper current collector and insertion of lithium in the conductive additive SuperP deliver additional specific charge to the graphite electrode. Additionally, a proper determination of the active mass had to be found due to the variation of the mass of the copper current collector by 25±0.1 mg while the active mass is ~0.2 mg (discussed in sec. 3.2.2).

Overpotentials of the lithium-metal counter electrode have to be considered when one wants to evaluate the overpotentials of the active material which is usually neglected leading to incorrect estimations of kinetic parameters (see sec. 3.3.1). Also, changes of the electrode during cycling have to be taken into account like particle loss of graphite during cycling (aging), changes of ohmic resistances during SEI formation, and high-current-density formation cycles (sec. 3.2.2). Self-discharge of the Li-graphite cell need to be consider during operation at very low current density and GITT measurements as discussed in section 3.5. Without the evaluation of these influences, the correct influences of the graphite electrode cannot be analyzed precisely.

The discussed findings lead to implications for the application of graphite as a negative electrode in lithium-ion batteries:

1) Ideally engineered electrodes of graphite with particles >3.3 μm will probably never exceed 6C rates for the recharging of a battery while high discharge rates of >20C are feasible (3.2.3).

2) Mainly the particle shape of the carbon defines the electrochemical response of a standard compressed and thick electrode due to the better pore structure of, e.g., spherical particles (3.4).

3) The influence of the SEI resistance should be very low in a standard electrode since the active surface area reduces the low ionic resistance of $R_{\text{SEI}} = 16 \, \Omega \cdot \text{cm}^2/ \text{AASA}$ giving only 2.86 Ω for the thin-layer electrode with an ASA of ~5 cm². Thus standard electrodes under homogeneous reaction should have small SEI potential drops which is in strong contrast to EIS experiments [155]. Also, surface reactions should have minor contribution in standard electrodes due to the large active surface area (only under homogeneous electrode reaction). This shows clearly, that the diffusion in the electrolyte should be the dominating effect governing the galvanostatic response of standard graphite electrode in a lithium-ion battery which is shown by several authors [152, 154, 166] (section 3.3.2).
4. Chemical modifications of graphite

The previous section discussed several different kinetic limitations in graphite. Especially, the classification of the different diffusion coefficients of the dense stages compared to the liquid-like stages and the kinetic overpotentials until rates of up to 20C are of strong interest, when one wishes to improve the recharging rate capability of graphite. Only rates of up to 20C are of interest for applications since they correspond to a full recharge of the battery in 3 minutes which would be sufficient for a recharging of an electrical vehicle at a power station (if the power supply can be guaranteed from the electrical grid).

Therefore, this section will investigate possible chemical modifications of the graphite particles to overcome the limitations investigated in section 3 where the research will be focused especially on the lithiation of graphite which corresponds to the recharging of a full battery. The general concept will be focused on the increase of the interlayer distance of the graphene sheets to introduce either a surface stress or to pillar the whole structure. These modifications are intended to reduce elastic energies during lithium insertion and a possible modification of the surface reaction or diffusion coefficient of lithium in graphite. Figure 64 presents a simple sketch of the idea. The distance between the graphene sheets should be increased from 3.35 Å to more than 3.706 Å which would correspond to the stage 1 interlayer distance. Additionally, a fixation of the graphene layers in AA stacking would be ideally. The first section will evaluate the influence of a coating to “freeze” an expanded interlayer distance at the prismatic surfaces of graphite while the second part of this chapter will use a modification of graphite, namely graphite-oxide, to pillar the bulk of graphite chemically.

Figure 64: General concept of lattice expansion in graphite at either surface and/or bulk to enhance lithiation rate.
4.1 Titanate coating of the prismatic surfaces of graphite

To apply a surface stress on the prismatic surfaces of graphite particles, one needs a very well defined model material which has a clear separation between prismatic and basal planes. Timrex graphites like SFG6 (Timcal) are very good for this purpose. In contrast, MCMB particles with mixed small graphitic domains would be non-ideal for this investigation. The basal planes should still stay uncoated if possible to avoid extra electrochemically inactive mass in the electrode. The coating on the prismatic edge planes of graphite needs to fulfill several different conditions to allow good cycling of the graphite material after a chemical surface modification. The coating should:

- bond chemically to the surface groups of graphite (OH, COOH, CHO)
- be ionically conducting for lithium ions
- form a solid solution with lithium between 0-1.5 V vs. Li⁺/Li or should be a nano-sized phase separating material
- and be chemically stable at 0 V vs. Li⁺/Li.

Some unknown boundary condition which might be helpful for the performance of the graphite in an electrode can be either

- an electrical conducting coating to have low Ohmic losses in the electrode or
- an electrical insulating coating to replace the SEI partially reducing the irreversible specific charge in the first SEI formation cycles.

The chemical bond between the coating and the pristine graphite is necessary to guarantee long-term stability during the 10% volume expansion in c-axis direction during cycling and prevent the electrolyte to diffuse between the coating and graphite through capillary forces. The coating should be ionically conducting for Li-ions to reduce the ohmic potential drop across the coating thus minimizing the additional overpotential losses during cycling compared to standard graphite (see section 3.3). Furthermore, the material should preferably form a solid-solution during lithium intercalation in the potential regime of graphite to be able to offer most of the intercalated lithium at every side on the coating thus avoiding local phase-boundaries [65]. Additionally, nano-sized phase separating materials can be used since they become essentially non-phase separating due to high energetic costs of building up a phase boundary within the bulk [50]. Another aspect concerns the chemical stability of the coating versus lithium-metal. Most oxides undergo an ion exchange with lithium at very negative potentials like CuO [78], LiFePO₄ [51] or other materials.
One unknown condition concerns the electronic conductivity of the coating on graphite. An electronic insulator but ionic conductor would form an artificial solid-electrolyte interphase (SEI) which could reduce the irreversible specific charge in the first cycles since it would hinder the reduction of the organic electrolyte at very negative potentials. However, if the coating is synthesized on the active material before the casting of the electrode, conductive pathways through the thickness direction of the electrode could be blocked. Then conductive additives would have to be added guaranteeing a conductive pathway, thus, reducing the specific energy of the electrode.

Several different possible coatings fulfill these theoretical requirements. Titanium-oxide, TiO₂, is such a candidate which is also used as an active material in a lithium-ion battery itself. It can exist in several forms like anatase, brookite, rutile or TiO₂(B) [75], as discussed in section 2.4. But there exist a very fast intercalation host, namely titanium-spinel (Li₄Ti₅O₁₂) which allows 3D diffusion of lithium ions in the structure. Since it is a phase separating material with a potential plateau at $\sim 1.55$ V vs. Li⁺/Li [2], it would need to be nano-sized. The coating should bond chemically to the graphite during an expanded state meaning that an ion is intercalated in the bulk material to increase the c-axis interlayer distance. The chemical bonding of the titanate to the graphite should ideally form a C-O-Ti bond. The goal of the surface coating is the hindering of collapse of the graphite back to its normal interlayer distance of 3.35 Å as much as possible. This should introduce the desired surface stress in the first few nanometers of graphite. A shift of the graphene layers back to AB stacking might not be hindered due to the small forces of the coating compared to the bulk material.

The synthesis was performed by adding a complex of TiCl₄ x 2THF to potassiated graphite SFG6 in tetrahydrofuran (THF) as a solvent. Afterwards, a washing with deionized water was used to form titanate from the titanium-metal on the prismatic surfaces. After an addition of an excess (2x) of LiOH a calcination was done in a tubular furnace at 600°C under Argon atmosphere. The respective reaction equations are

$$4 \text{KC}_8 + \text{TiCl}_4 \times 2 \text{THF} \quad \xrightarrow{\text{THF}} \quad \text{Ti} @ \text{graphite} + 4 \text{KCl}$$

$$\text{Ti} @ \text{graphite} + \text{H}_2\text{O} \quad \xrightarrow{\text{THF}} \quad \text{TiO}_2 @ \text{graphite}$$

$$\text{TiO}_2 @ \text{graphite} + \text{LiOH} \quad \xrightarrow{600\text{°C}} \quad \text{Li}_4\text{Ti}_5\text{O}_{12} @ \text{graphite}$$

The amount of TiCl₄ was increased by a factor of 50x to be able to observe the titanate coating in SEM images and by other methods. This was done to prove the synthesis method before applying it to the desired 3-5 atomic layers of coating. Figure 65 presents the SEM images of the pristine SFG6 graphite particles (1st row) and the titanate coated SFG6 particles (2nd row). The
coating can be clearly seen on the prismatic edge planes which show even small cracks being probably due to the harsh reaction with the deionized water during the washing procedure. A coating of the basal planes cannot be judged from the SEM images. Small residues of unknown composition are also deposited between the graphite particles as shown in Figure 66.

To get an insight into the homogeneity of the coating on the prismatic planes and to detect if the basal planes might be coated, scanning-tunneling-microscopy images have been taken at 15 kV as shown in Figure 67. No clear difference between the coating and bulk could be observed.

Figure 65: Scanning-electron-microscopy-images of standard SFG6 graphite flakes (1st row) and titanate-coated SFG6 (2nd row).

Figure 66: Deposions between graphite particles after reaction.
which might come from the very thin-coating of a few nanometers and may be due to misalignments of the particles to the electron beam. However, a clear coating can be observed in the SEM images and is mainly present at the prismatic planes. This is consistent with the reaction pathway since the potassium ions can only react with TiCl₄ at the ends of the graphene layers which act as confined ion channels for the reaction. Additionally, no exfoliation of the graphene sheets is observed which is important for battery operation as shown in Figure 67.

To investigate the elemental distribution and composition of the coated graphite SFG6 particles, energy-dispersive x-ray spectroscopy (EDX) has been used which is equipped to the SEM.

![SEM, 15 kV](image1)
![STEM, 15 kV](image2)
![SEM, 15 kV](image3)
![STEM, 15 kV](image4)
![SEM, 5 kV](image5)
![SEM, 5 kV](image6)

Figure 67: SEM and scanning tunneling electron microscopy images of titanate coated graphite SFG6, inhomogeneous coating observed where exfoliated graphite surface are not coated.
Figure 68 presents the EDX results of the titanate-coated graphite SFG6 powder which shows an atomic distribution of 90.8% carbon, 6.2% oxygen and 1.3% titanium while minor amounts of potassium (0.6%) and chlorine (0.15%) are detected. Silicon comes as a trace signal from the detector and is often detected for this SEM machine although not present in the sample. This shows clearly that some titanates have been formed while some residues of KCl are still present in the sample powder after only a single washing step.

Figure 68: Energy-dispersive x-ray spectroscopy (EDX) of titanate-coated graphite SFG6 with corresponding SEM image and elemental distribution of carbon, oxygen, silicon, chlorine, potassium and titanium, powder with low amount of residues.

Figure 69: Energy-dispersive x-ray spectroscopy (EDX) of titanate-coated graphite SFG6 with corresponding SEM image and elemental distribution of carbon, oxygen, silicon, chlorine, potassium and titanium, many residues present in sample as seen in respective SEM image.
Figure 69 shows the EDX investigation of a spot with many residues present. The elemental distribution differs strongly to the one presented in Figure 68 detecting much more potassium (7.2 at%), chlorine (2.7 at%) and slightly increased oxygen content (9 at%) as compared to the previous EDX. This shows that the residues are probably mainly consisting of KCl and KOH because hydrogen cannot be detected with this method. A proper washing with several washing steps or warm water might dissolve the reaction products more effectively.

To detect what kind of titanate is formed on the surface of graphite, Raman spectroscopy has been carried out. Figure 70 presents the Raman spectra of pristine graphite SFG6 and SFG44 in the wavenumber range of 200-1700 cm$^{-1}$. The characteristic D and G band of graphite can be detected at 1340 and 1586 cm$^{-1}$ wavenumber, respectively [167]. Figure 71 shows the corresponding Raman spectra of titanate-coated graphite SFG6 and SFG44. No additionally Raman reflexes...
can be detected. But the broad reflexes at ~500 and ~930 cm\(^{-1}\) disappear when one measures the
Raman spectra without a glass disk covering the powder which can be seen in Figure 71 for the
SFG44 sample. The fitting of the D and G band of graphite by Lorentzian peak shapes are sum-
marized in Table 7. A Lorentzian distribution can be fitted by three fitting parameters in the for-
mula:

\[
y = \left( w^2 + \frac{w}{4(x - x_c)^2} \right) \cdot \frac{2A}{\pi}\]

(3.13)

where \(y\) is the intensity at a certain wavenumber \(x\) with respect to the center position \(x_c\) of a peak
with the width \(w\) and an area \(A\). Three main peaks could be detected where the D band is con-
ected to the so called disordered structure of graphite at ~1340 cm\(^{-1}\), the G band which corre-
sponds to the Raman signal of the crystalline graphite at ~1586 cm\(^{-1}\), and a side band next to the
G band at ~1623 cm\(^{-1}\). The D/G ratio is considered to reflect the crystallite length in a, b-
direction of the graphite single crystal domain, \(L_a\), indicating a higher disorder for SFG6 com-
pared to SFG44. This would indicate a smaller crystallite length in in-plane direction of graphite
consistent with the findings of Buqa et al. [156]. In general, no modification of graphite can be
detected and no titanate reflexes can be observed with Raman spectroscopy. Also no traces of
KCl or KOH can be found as compared to the EDX measurements above. The amount of titanate
might be too small to be detectable with Raman spectroscopy.

To evaluate the influence of the titanate coating on the electrochemical response on the graph-
itive electrode, thin-layer electrodes of graphite SFG6 have been prepared. The electrode is com-

| Table 7: Evaluation of Raman spectra of pristine and titanate-coated graphite SFG6 and SFG44
<table>
<thead>
<tr>
<th>from Figure 70 and Figure 71 with a Lorentzian peak shape.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine material</td>
</tr>
<tr>
<td>SFG6</td>
</tr>
<tr>
<td>1(^{st}) peak position (x_c)</td>
</tr>
<tr>
<td>1(^{st}) peak width (w)</td>
</tr>
<tr>
<td>1(^{st}) peak area (A)</td>
</tr>
<tr>
<td>2(^{nd}) peak position (x_c)</td>
</tr>
<tr>
<td>2(^{nd}) peak width (w)</td>
</tr>
<tr>
<td>2(^{nd}) peak area (A)</td>
</tr>
<tr>
<td>3(^{rd}) peak position (x_c)</td>
</tr>
<tr>
<td>3(^{rd}) peak width (w)</td>
</tr>
<tr>
<td>3(^{rd}) peak area (A)</td>
</tr>
<tr>
<td>D/G ratio</td>
</tr>
<tr>
<td>(L_a = 8.3/Rgd)</td>
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</table>
posed of 87:10:3 (wt%) of SFG6 to PVDF binder to SuperP conductive additive to allow comparison to the thin-layer experiments of pristine SFG6 in section 3.2 and 3.3. Figure 72 presents the first two SEI formation cycles with the aging over the first one-hundred cycles in the inset. Additionally, the rate performance is shown in the second part of Figure 72.

One can see an electrochemical reaction from 1.75 V to 1.6 V in the first lithiation which is in the same potential regime as the titanates (see section 2.4). An additional minor reaction can be observed at 0.8 V corresponding to the SEI formation in EC:DMC 1M LiPF$_6$ [13, 156]. A standard cycling profile of graphite SFG6 can be observed in the second cycle since the back-reaction of the titanate is avoided by keeping the potential negative to 1.5 V vs. Li$^+/Li$. During the subsequent medium and high-rate cycling a little increase of the overpotentials can be observed with regard to the cycling response for the pristine SFG6 thin-layer electrode in Figure 23. This increase was expected since an excess of a factor of 50 was used to form the titanate coating on the prismatic surface which adds an ionic diffusion resistance to the standard limitations of graphite. No improvement of the extracted specific charge can be observed for the thick coating.

However, the aging of the electrode (inset in Figure 72) indicates much less particle loss during cycling where 87% of the capacity can be still withdrawn after 100 cycles with reference to third cycle during discharge. The cycling of a pristine SFG6 thin-layer electrode delivers only ~70% after 50 cycles as shown in Figure 133 (page III in appendix). An electrochemical rate test of a very thin coating of titanate on the prismatic surface of SFG6 would clarify if an increase of the charge performance can be achieved by this method. But the improvement will be small since only the first few nanometer of graphite will be affected by the surface-coating thus the bulk will be almost unaffected.

Figure 72: Electrochemical cycling of titanate-coated SFG6 a) formation cycles, b) various rates of four different cells with a mass of m = 0.3-0.5 mg.
4.2 Pillaring of graphite

Another idea concerns the so called pillaring of graphite which means that some molecules are located in the interslabs of graphite thus increasing the c-axis distance between the respective graphene sheets in graphite. Several methods could be used to create these molecular pillars. For example concentrated sulfuric and nitric acid intercalate in graphite [100] and could be used to react with alkali-metals thus forming salts in the interslabs of graphite. However, a problem would be that the acid would react mainly at the prismatic surfaces of graphite in a similar manner as the alkali-metal used for the titanate coating in the previous section 4.1. Additionally, hydrogen gas release during the reaction might exfoliate the graphite particle if released in the bulk as seen for DMSO solvated potassium intercalates in graphite during heat-treatment [168] or other gas release reactions in graphite [100]. Therefore, one needs a chemically modified graphite which carries the anion for the salt formation or formation of a certain functional group already in the structure releasing no or very little gas during a subsequent chemical reaction. The preferred cation is lithium for the usage in a lithium-ion battery while other metals like K, Cs, Rb, Ca, Ba, Sr, Eu, Y [100] and metal-chlorides like FeCl₃, AlCl₃ [100] or solvated metal-chlorides like MnCl₂ and MgCl₂ [168] could be used for other applications. To evaluate the influence of a pillaring in graphite, a partially-disproportionated graphite-oxide is used which was developed by Dr. Tommy Kaspar (ETHZ) which contains mainly epoxide groups and also some hydroxide and carboxyl groups attached to the graphene layers in graphite.

4.2.1 Characteristics of partially-disproportionated graphite-oxide (GOpd)

Parts of this chapter (synthesis, some figures, and tables) are adapted from the work for the doctoral dissertation of Dr. T. Kaspar [169] already published [170] and are cited accordingly.

Graphite oxides can be synthesized by several different methods including but not limited to the work by Brodie [171] or Hummers [172]. For this work, an adaptation of the Brodie method has been chosen using 2 g of graphite SFG6 (Timcal) with 20 g of NaClO₃ (analytical grade, Fischer Scientific AG) and 20 ml of fuming nitric acid (HNO₃, 99%, VWR) [169]. Graphite and sodium chlorate have been mixed in a Schott flask. A cryostat has been used to constantly cool the mixture to -20°C. Fuming nitric acid was added in very small quantities over a period of 4 hours where the atmosphere was kept in the flask by a small plastic cap on top of the Schott flask. An open apparatuses was chosen to account for the risk of an explosion. Evolving gases are mainly Cl₂ and NOₓ gases [169]. The reaction product was kept overnight without cooling. Afterwards a heating at 60°C over a period of 12 hours was performed after which the product was washed with deionized water several times (centrifuge and decantation) until the pH value
was close to 7. The product was dried in an oven at 60°C overnight after which it was kept in an exsiccator. The product has an ivory-white color and consists of epoxide and hydroxide groups as shown in a sketch in Figure 73. The interlayer distance between the graphite-oxide sheets is ~5.7-5.8 Å [169].

The partially-disproportionated graphite-oxide was synthesized from graphite oxide by disproportionation under Argon atmosphere. The name of the resulting product is changed from partially-reduced graphite-oxide as used in [169, 170] to partially-disproportionated graphite-oxide in this work due to the inert atmosphere used during the heat-treatment. 500 mg of graphite oxide from the precursor SFG6 graphite where heated in a quartz tube to 190°C. A very slow heating rate of 0.1 K/min was chosen from 190°C to 250°C due to strong gas release around 192°C and ~210°C attributed to the hydroxide and epoxide decomposition, respectively, which form H₂O, CO, and CO₂ (Fig. 3.3 in [169]). This small heating rate is necessary to avoid pulverization of the graphite-oxide to soot during disproportionation. Heating above 250°C can be done at 10 K/h and further reduces the interlayer distance of the partially-disproportionated graphite-oxide forming an interlayer ranging from 4.5 Å for the GOpd heat-treated at 250°C to standard graphite distance of 3.35 Å when heated to >1000 °C [169]. The shift of the c-axis can be observed by x-ray diffraction because the macroscopic structure of the graphite SFG6 flakes is preserved. The interlayer distance varies with the respective final disproportionation temperature as shown in Figure 74 [169]. One can observe that the GOpd with interlayer distances of 4.4 Å shows the broadest FWHM which reflects the unordered stacking of the oxidized graphene layers in the GOpd44. With decreasing interlayer distance, the stacking order increases.

To get an insight into the chemical composition of the products after the partial disproportionation, an elemental analysis was carried-out as presented in Table 8 (adapted from [170]). The composition changes from the precursor, graphite-oxide, to less oxygen and hydrogen with heat-

Figure 73: Chemical structure of graphite oxide as a single graphene layer sketch [173].
treatment temperature. First, the hydroxide surface groups on the basal planes of the graphite-oxide sheets get reduced showing a drastic decrease by a factor of four between the graphite-oxide and GOpd44 which is the highest distance that can be reached by the thermal disproportionation [169]. With further increase of the temperature the amount of both surface groups decreases further. This attribution of the oxygen and hydrogen content from elemental analysis to hydroxide and epoxide groups is based on the assumption that carboxyl and carbonyl groups contribute negligibly to the overall composition in GOpd [170]. The evolution of these surface groups is depicted in Figure 75 and shows the interlayer distance gap between the graphite-oxide (5.7 Å) and highest GOpd44 (4.4 Å) directly.

For the electrochemical experiments, two different GOpd’s are used (GOpd43 and GOpd36) although many other intermediates exist between GOpd44 and GOpd33 [169, 170]. They have been chosen because of a relative high interlayer distance and a low amount of hydroxide groups since the lithium-exchange on the hydroxides at very negative potentials might release protons

![Graphite Oxide XRD](image)

Figure 74: XRD (00z) reflexes of graphite-oxide, partially-disproportionated graphite-oxides, and graphite (Cu K-α source, adapted by M. Hantel, PSI, of Fig. 3.4 in [169], investigation done by Dr. T. Kaspar).

Table 8: Elemental analysis of graphite-oxide and the partially disproportionated graphite-oxide adapted from [169, 170] (adapted from Table 1 in [170] in EA done by Dr. T. Kaspar).

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Elemental composition</th>
<th>c-axis distance from XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor: Timrex graphite SFG6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>C₆</td>
<td>3.35 Å [107]</td>
</tr>
<tr>
<td>Intermediate product: graphite oxide from SFG6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GOpd44</td>
<td>C₆O₁.₆₅(OH)₀₉₈</td>
<td>5.74 Å [170]</td>
</tr>
<tr>
<td>GOpd43</td>
<td>C₆O₀.₉₆(OH)₀₅</td>
<td>4.33 Å [170]</td>
</tr>
<tr>
<td>GOpd42</td>
<td>C₆O₀.₉₀(OH)₀₁₆</td>
<td>4.23 Å [170]</td>
</tr>
<tr>
<td>GOpd36</td>
<td>C₆O₀.₈₁(OH)₀₂</td>
<td>3.63 Å [170]</td>
</tr>
</tbody>
</table>
which could attach the anion of the salt in the electrolyte (LiPF₆) and form HF which could corrode the battery in a real application.

Figure 75: Evaluation of elemental analysis of GOpd of various interlayer distances attributed to hydroxide and epoxide per C₈ (Fig. 2c in [170], analysis done by Dr. T. Kaspar).

4.2.2 Electrochemical characterization of partially-disproportionated graphite-oxide and pristine graphite oxide

This section discusses the electrochemistry of GOpd for the use in lithium-ion batteries. Improvements and limitations with respect to pristine graphite will be discussed.

4.2.2.1 Experimental

GO and GOpd were used as received (from Dr. T. Kaspar). Electrodes for electrochemical testing were made using 80 wt% GOpd with 10 wt% PVDF binder (Kynar Flex) and 10 wt% SuperP conductive additive. The binder was dissolved in N-methyl-2-pyrroolidone NMP and mixed for 5 min with GOpd and SuperP using a stirrer. The highly viscous slurry was casted on copper foil with the doctor blade technique. The slurry was heated for 4h at 80°C in vacuum to remove the NMP. Electrodes of a diameter of 13 mm were punched with an active mass of 2.2-2.5 mg of GOpd giving an electrode thickness of 74 - 88 μm (copper current collector: m = 24.98±0.1 mg, h = 21 μm). The electrodes have been heated for 12h at 120°C in vacuum to remove remaining water and NMP. Half-cells have been built using lithium-metal as counter and reference electrode, a glass fiber separator and ethylene-carbonate: dimethyl-carbonate EC:DMC 1:1 (wt) with 1M LiPF₆ (Novolyte, battery grade) electrolyte in an argon filled glove box equipped with N₂,O₂,H₂O, and active carbon filter. Electrochemical testing was either done on Astrol Electronics or Biologic VMP3. For SEM images, the electrodes have been washed with DMC three times to remove LiPF₆ salt and dried at 120°C for 2h to remove remaining DMC washing solvent.
4.2.2.2 Requirements of GOpd for application in Li-ion batteries

From a theoretical point of view, lithium intercalation in highly ordered graphite seems to be driven by electrostatic effects which are elastically hindered. This leads to the well-known staking phenomena in graphite-intercalation compounds. The idea of this study is the removal of this elastic stress due to c-axis expansion from graphite compared to standard LiC₆ with the help of molecular pillars. Therefore, non-exfoliated partially-disproportionated graphite-oxide was used for this investigation. Some of the requirements will be discussed here to use GOpd for the application in lithium-ion batteries.

First, it is very important that the starting material is non-exfoliated and possesses a very low BET surface area because the irreversible specific charge consumed during the solid-electrolyte-interphase formation depends approximately linearly on the surface area between the conducting materials in the electrode and the organic electrolyte [13]. Many researchers exfoliate graphite or graphite-oxide into single graphene sheets which they let collapse during the solvent removal. They insert different interstitial molecules between these single-graphene sheets e.g. fullerenes and carbon-nanotubes (CNT) [174], SiO₂ and Co₃O₄ [175] or LiO₂ after Li-NH₃ reduction of GO [176]. However, the resulting structures form a very unordered stacking with turbostratic disordered and wrinkled domains as shown in the SEM and TEM images of these mentioned investigations (Fig. 1,4c in [174], Fig. 1,4 in [175], Fig. 3 in [176]). This can lead to long diffusion pathways for lithium ions in the structure unless defects are introduced into the graphene sheets. Additionally, an increased specific surface area between the composite (graphene Aₜₜₒₑᵣₑ ~2500 m²/g) and the electrolyte would lead to an increase of the irreversible specific charge in the first cycles. The low BET specific surface area is not a requirement for half-cell experiments where a lithium-reservoir is used as the counter-electrode and, thus, often not discussed in articles with nano-sized or very-high surface area active materials like silicon [77] or the mentioned stacked graphene sheets with interstitial molecules [174-176]. The lithium uptake will be mainly detrimental for full cells of lithium-ion batteries where the amount of lithium is limited and small amounts of lithium “consumption” in side-reactions lead to a direct decrease of the charge of the battery. A good example of the SEI formation on graphene is observed during Raman measurements [177].

Another requirement is the increase of the interlayer distance compared to graphite while keeping a reasonable ordered stacking structure of the GOpd sheets as discussed in the introduction to section 4.2. During the first charge, the lithium ions should bond to the epoxide and hydroxide groups leading to an in-situ chemical reduction of the GOpd. This could lead to the formation of lithium-alkoxides C₆-OLi, and Li₂O and LiOH molecules in the interslab between two adjacent
GO pd layers which might lead to the discussed improvement of the charge rate capability compared to pristine graphite. Additionally, it might be possible to store more lithium in the structure comparable to, e.g., disordered carbons [81] due to the reduced steric hindering. Up to seven layers of interstitial alkali and earth-alkali layers are known to be possible as in the case of Li$_3$Ca$_2$C$_6$ [178].

The third requirement concerns the solvent shell co-intercalation which would lead to a reduction of the electrolyte within the GO pd structure if the potential is decreased below the stability limit of the respective electrolyte (in this case of EC: DMC 1:1 1M LiPF$_6$ at circa 0.8-0.9 V). This could lead to the deposition of electrolyte reduction products in the interslab and possibly an exfoliation during the gas release as seen for e.g. propylene carbonate [113, 156, 179, 180].

Fourth, the structure of the formed GO pd with the molecular pillars should not be altered during cycling which might lead to an aging of the material. Fifth, the volumetric expansions during cycling should be small to avoid electronic contact losses in a “breathing” electrode when cycled in the instability regime of the electrolyte (circa < 0.8 V in EC: DMC, 1M LiPF$_6$). Last, the hydrogen content of the GO pd should be low to avoid HF formation as a decomposition product of LiPF$_6$ as discussed in the previous paragraph.

### 4.2.2.3 Electrochemical cycling of GO and GO pd

First, graphite-oxide was cycled in a standard electrode configuration described in paragraph 4.2.2.1. The active mass of the electrode is $m_{\text{eff}} = 4.43$ mg with an electrode thickness of $h = 64-65$ µm in a ratio of 80:10:10 of GO: PVDF: SuperP. Conductive additive in needed compared to standard graphite electrodes because GO and GO pd are electronically insulating. Figure 76 presents the electrochemical cycling in the potential range of 0.01-3 V vs. Li$^+$/Li. During the first formation cycle (inset in Figure 76a) a very high irreversible specific charge of 936 mAh/g was measured. During the subsequent cycles, a rapid fading can be observed which saturates at approximately ~70 cycles and stays almost constant at ~100 mAh/g (slightly increases during cycling >100 cycles). The ratio of the specific charge of delithiation charge over lithiation charge is called the cycling efficiency as depicted in the inset of Figure 76b). During the mentioned first fifty cycles a high irreversible specific charge can be detected being ~ 10% in the first cycles (2nd – 10th cycle) and decreases slowly to reach more than 98 % cycling efficiency after the 50th cycles. Therefore, pure graphite-oxide seems to be not suitable for the use as a negative electrode in lithium-ion batteries.

The cycling of partially-disproportionated graphite-oxide with an interlayer distance of 3.6 Å is shown in Figure 77. The mass of the active material is $m_{\text{eff}} = 3.40$ mg with an electrode thickness of $h = 102-104$ µm. The standard electrode was also mixed in a ratio of 80:10:10 of GO pd:
PVDF: SuperP and cycled in the same potential range as GO. During the first lithiation a very high specific charge of 1130 mAh/g can be inserted while only 580 mAh/g can be extracted in the subsequent delithiation thus leaving 550 mAh/g as irreversible specific charge during the first cycle. During the following cycles a specific charge of 530 mAh/g can be inserted from which ~97% can be extracted during the delithiation. However, an exponential decay of the specific charge can be observed during the first ~70 cycles after which the cycling efficiency increases to over 99%. The specific charge of the first 15 cycles is higher than the theoretical specific charge of graphite which is marked by a dashed line in Figure 77.

The first lithiation is very different to all subsequent ones while delithiation in the first cycle is similar to the following ones. Therefore, the first lithiation might be connected to an activation process of the GOpd36. This is expected since the oxygen groups in the bulk of GOpd36 are intended to react with lithium to form the desired chemical pillars in the interslabs. The profile of the charge/discharge curves is very different to graphite and shows rather a capacitor-like behavior than an intercalation process. For graphite, the main intercalation occurs at potentials negative to 0.25 V vs. Li⁺/Li as shown in section 2.5. For GOpd36 the main lithiation occurs at potentials negative to 1.5 V and delithiation mainly negative to 2 V although a certain specific charge is extracted during the potentiostatic step at 3 V during delithiation. Additionally, a hysteresis between low rate C/25 cycling of >1V can be observed which decreases with progressing aging.

The cycling of the GOpd43 with 4.33 Å interlayer distance between the graphene-oxide sheets is presented in Figure 78. The mass of the active material is $m_{\text{eff}} = 3.22$ mg with an electrode thickness of $h = 78-88$ μm. Here a similar trend can be observed as for the GOpd36 above. The

Figure 76: Electrochemical cycling of graphite-oxide GO vs. Li-metal in EC: DMC 1:1 (wt), 1M LiPF$_6$ a) selected cycles with formation cycle in inset, b) aging and charge-discharge efficiency of the electrode cycled between 0-3V vs. Li⁺/Li.
first lithiation shows a very different lithiation potential profile with regard to the subsequent lithiations. The specific charge of the lithiation in the first cycle delivers 1187 mAh/g while delithiation can extract only 700 mAh/g from the structure giving, thus, an irreversible specific charge of 487 mAh/g. The second and third lithiation deliver 677 and 674 mAh/g, respectively with a cycling efficiency of ~98.9 % in average. The respective cycling profiles of the second and third cycle are almost identical as shown in Figure 78a. During continuous cycling at a rate of 1C, a fading of the specific charge can be observed similar to the one of GOpd36. However, the fading is more sever for GOpd43 compared to GOpd36 because it delivers a higher specific charge in the first cycles and decreases to a lower specific charge (~259 mAh/g) in the hundredth cycle.

Figure 77: Electrochemical cycling of partially-disproportionated GOpd36 with 3.63 Å c-axis distance vs. Li-metal in EC: DMC 1:1 (wt), 1M LiPF₆ a) selected cycles, b) aging and charge-discharge efficiency of electrode cycled between 0-3V.

Figure 78: Electrochemical cycling of partially-disproportionated GOpd43 with 4.33 Å c-axis distance vs. Li-metal in EC: DMC 1:1 (wt), 1M LiPF₆ a) selected cycles, b) aging and charge-discharge efficiency of electrode cycled between 0-3V.
cycle, thus, decreasing the specific charge by 420 mAh/g or 62% compared to the second cycle. GOpd36 delivered still 273 mAh/g in the hundredth cycle, thus, undergoing a specific charge loss of 260 mAh/g or 49%. This shows clearly that the GOpd43 delivers higher reversible specific charge during the first cycles but suffers from a more severe aging. The potential hysteresis between lithiation and delithiation is more than 1V for GOpd43 and decreases with progressing aging similar to GOpd36. The cycling efficiency is very low with ~97-98 % in the first fifty cycles and increases to more than 99 % for the cycles above 70 cycles as shown in the inset in Figure 78b.

The cycling of graphite SFG6 with an interlayer distance of 3.35 Å is presented in Figure 79 and serves as a reference material. The mass of the active material is $m_{eff} = 3.02$ mg with an electrode thickness of $h = 48-54 \mu m$. The electrode was also prepared with the same composition as the previous electrodes with a ratio of 80:10:10 of SFG6: PVDF: SuperP and cycled in the same potential range (0.01-3V vs. Li⁺/Li) which differs to the standard graphite composition and potential window in the previous sections 3 and 4.1. A distinct difference of the potential profile of graphite SFG6 with respect to GO, GOpd36, and GOpd43 can be detected immediately. During the first lithiation, a specific charge of 482 mAh/g can be inserted while 390 mAh/g can be extracted during the first delithiation leaving thus only 92 mAh/g or 19 % irreversible specific charge during the SEI formation cycle.

The subsequent cycles show a very low irreversible specific charge due to a continuous SEI growth especially on the lithium-counter electrode due to small dendrite formation. But all cycles after the tenth one show a cycling efficiency of more than 99.8 %. The specific charge in-

![Figure 79: Electrochemical cycling of graphite SFG6 with 3.35 Å c-axis distance vs. Li-metal in EC: DMC 1:1 (wt), 1M LiPF$_6$ a) selected cycles, b) aging and charge-discharge efficiency of electrode cycled between 0.01-3 V.](image)
creases even slightly from 390 to 430 mAh/g from the 10th to 550th cycle which are both above the theoretical specific charge of graphite of 372 mAh/g. This extra specific charge comes mainly from the lithium insertion in SuperP as shown in Figure 16 which would give 70, 36, and 32 mAh/g in the first, second, and tenth cycle as an extra specific charge to the graphite electrode due to the ratio of 80:10 of SFG6: SuperP. The extra specific charge from CuO is negligible except for the first cycle giving 17, 0.35, and 0.22 mAh/g in the first, second, and tenth cycle as an extra specific charge to the graphite electrode due to the normalization with a higher active mass of 3.02 vs. 0.2 mg in section 3.2.2. Thus, the specific charge of graphite SFG6 alone with the subtraction of the SuperP and CuO layer on the current collector gives 395, 365, and 358 mAh/g which matches perfectly with the practical specific charge of graphite SFG6 of ~362 mAh/g. Thus, the SEI formation on graphite and lithium-metal in the first cycle consumes just 33 and 3 mAh/g during the first and second lithiation.

In contrast to GO and GOpd, almost no specific charge can be inserted or extracted from graphite positive to 1 V but the aging is almost negligible over the first 580 cycles with an efficiency at the detection limit of the Astrol machine above 99.8 %. The extra specific charge after 100 cycles might come from a reversible cycling of part of the SEI as observed for CuO [78].

Partially-disproportionated graphite-oxide can be also used for the positive electrode in an electrochemical capacitor. Therefore, GOpd43 has been cycled between 3-5 V against a lithium counter electrode, thus, depleting the electrolyte EC: DMC 1:1, 1M LiPF₆ by its salt. The galvanostatic cycling is depicted in Figure 80. During the first charge, an activation process starting at 4.5 V can be observed where a specific charge of 178 mAh/g can be inserted while 111 mAh/g

![Figure 80: Electrochemical cycling of GOpd43 with 4.33 Å c-axis distance as a positive electrode with PF₆⁻ insertion vs. Li-metal in EC: DMC 1:1 (wt), 1M LiPF₆ a) selected cycles, b) aging and charge-discharge efficiency of electrode cycled between 3-5 V.](image-url)
can be extracted, thus, leaving 67 mAh/g as irreversible specific charge. The PF$_6^-$ insertion is also known to occur for pristine graphite which intercalates at potentials positive to 4.5 V to form stage 2 with PF$_6$C$_8$ in-plane density as the final GIC giving up to 140 mAh/g where the c-axis expands to 4.5 Å for stage 2 [123, 179].

For GOpd43, a lower specific charge can be extracted since the insertion is stopped at 5 V although pristine graphite needs to be cycled up to 5.5 V to form stage 2 [123]. During the second and third cycle a very high irreversible specific charge is detected which is also seen for the PF$_6^-$ intercalation in pristine graphite (second charge in Fig. 2 of [123]). But here, EC: DMC has been used as the electrolyte which is thermodynamically unstable at potentials positive to circa 4.2 V vs. Li$^+$/Li [181]. Therefore, these high irreversible specific charges in the first five cycles might be mainly due to electrolyte decomposition forming a solid-permeable-interphase (SPI) on the positive electrode [13].

This SPI is different from the SEI on the negative electrode because electrolyte can still permeate through the mainly polymeric SPI, thus, allowing a continuous decomposition in the subsequent cycles as opposed to the SEI which decreases electrolyte decomposition to a very low amount after the first cycle [13]. The aging is very rapid as seen in Figure 80 and the cycling efficiency reaches only 90% after 25 cycles and exceeds never 96 % during the following 500 cycles. A specific discharge of 112 mAh/g can be extracted during the first three cycles in this potential range which might make GOpd43 a possible candidate for capacitor materials if a stable electrolyte can be found. Ethyl-methyl-sulfone EMS with 1M LiPF$_6$ might be more suitable because it seems to be oxidation-stable up to 5.63 V vs. Li$^+$/Li [123].

### 4.2.3 Investigation of the formed solid-electrolyte-interphase by SEM imaging

If one takes a closer look on the first lithiation, one needs to find out if GOpd might exfoliate due to a solvent-shell co-intercalation which needs to be avoided as discussed in the previous section 4.2.2.2. Figure 81 and Figure 82 show the SEM images of GOpd43 at several stages in the cycle life with the pristine material, after cycling to only 0.8 V and back to 3 V, after the first full activation and SEI formation cycle, and after 408 cycles. Exfoliation of GOpd could be avoided during the thermal disproportionation under Argon atmosphere which can be seen in Figure 81 (1$^{st}$ row). The particles are comparable to the precursor graphite SFG6 in shape and morphology which can be seen in Figure 83a) for comparison.

The SEM images of GOpd43 cycled to 0.8 V with a subsequent delithiation back to 3V are depicted in Figure 81 (2$^{nd}$ row). Also no exfoliation can be detected and no SEI formation on both the prismatic and basal planes can be observed by eye because the instability regime of the elec-
trolyte EC: DMC 1:1, 1M LiPF₆ is avoided (~0.8 V). The SEM images after the first full cycle between 0.01-3 V in Figure 82 (1st row) show also no signs of exfoliation. Especially, a closer look on the edge-planes reveal no exfoliation of the GOpd43 but the expected formation of a solid-electrolyte-interphase comparable to the SEI at standard graphite electrodes shown for comparison in Figure 83b). The SEI on GOpd43 after the first cycle seems to be thin.

In contrast, after 408 cycles a very thick and rough SEI can be observed on GOpd43 as shown in Figure 82 (2nd row). The fibers in the graph are left-overs from the glass-fiber separator and the small particles between the GOpd43 particles correspond to the 10 wt% of SuperP (see section 4.2.2.1). The SEI is especially very rough at the prismatic edges of the particles. The second picture after 500 cycles shows an exposed prismatic surface of GOpd43 which has been uncovered probably during the sample preparation for the SEM investigation. One can see that even after 408 cycles, no apparent exfoliation can be detected and the SEI seems to be rather thin at the basal surface which is consistent with SEI observations on cycled pristine graphite [13]. The SEI morphology of GOpd43 after 408 cycles appears to be very similar to the one for graphite SFG6 electrodes after several high-rate cycles as shown in Figure 83b).

![Figure 81](image)

Figure 81: Scanning-electron-microscope images of partially-disproportionated graphite-oxide, 1st row) pristine GOpd43, 2nd row) after one cycle between only 0.8-3 V in EC: DMC 1:1, 1M LiPF₆ showing the SEI formation and stability of the structure towards exfoliation.
The aspect that parts of the SEI broke-off the GOpd43 particle in Figure 82 (2\textsuperscript{nd} row b) show that the SEI might not be well-attached to the surface of the particle, e.g. there might be no covalent bonds. Additionally, the fact that the SEI on the prismatic surfaces broke-off together with parts of the SEI on the basal plane show a good mechanical adhesion within the SEI over a long

![Figure 82: Scanning-electron-microscope images of GOpd43, 1\textsuperscript{st} row) after one full cycle between 0.01-3 V, 2\textsuperscript{nd} row) after 408 full cycles in EC: DMC 1:1, 1M LiPF\textsubscript{6} showing the SEI formation and stability of the structure towards exfoliation.](image)

![Figure 83: Scanning-electron-microscope images of graphite SFG6 a) pristine and b) after several high rate cycle (a sample electrode of section 3.2.1) in EC: DMC 1:1, 1M LiPF\textsubscript{6} showing the SEI formation and stability of the structure towards exfoliation.](image)
range which is probably due to some polymers in the SEI from the electrolyte reduction as seen for the SEI on graphite [13]. Thus, the SEI on GOpd43 and graphite seems to be of similar composition and morphology.

A very interesting and seldom feature can be observed on the GOpd43 particles in Figure 84. One particle shows holes which are several hundred graphene-oxide layers deep and seem to be “burned” through the basal planes of the graphite-oxide precursor. This originates probably from the thermal disproportionation during the heat-treatment of graphite-oxide under Argon atmosphere where products like H₂O, CO, and CO₂ develop from the starting material C₆O₁.₆₅(OH)₀.₉₈ to form C₆O₀.₉₆(OH)₀.₀₅ as shown in Table 8 [169, 170].

To get an estimate of the carbon loss during the thermal treatment, an approximation can be done. Assuming that all hydrogen is bonded to hydroxide and carboxyl groups which leave as pure water vapor and that the epoxide and remaining oxygen from hydroxide reactions leave as pure carbon-monoxide, a carbon loss of 23 % compared to the starting graphite-oxide is expected as shown in reaction equation (3.14). A thermal disproportionation of the starting graphite oxide to H₂O and CO₂ would consume only 10.5% of the starting graphite oxide based on the reaction equation in eq. (3.15). The practical mass loss will be somewhere between these extremes since both CO and CO₂ develop [169]. These holes facilitate the diffusion of ions into the bulk material but might also increase the specific surface area which would lead to a higher irreversible charge during the SEI formation cycles. But it has to be stressed that only one particle is found containing these holes. However, many defects at the surface and in the bulk are expected due to the estimated mass loss between 10.5-23%.

\[
C₆O₁.₆₅(OH)₀.₉₈ \rightarrow 0.77 \cdot C₆O₀.₉₆(OH)₀.₀₅ + 1.38 \cdot CO + 0.47 \cdot H₂O
\]

(3.14)

\[
C₆O₁.₆₅(OH)₀.₉₈ \rightarrow 0.895 \cdot C₆O₀.₉₆(OH)₀.₀₅ + 0.63 \cdot CO₂ + 0.55 \cdot H₂O
\]

(3.15)

Figure 84: SEM images of pristine GOpd43 electrode showing holes in one out of over hundred investigated particles. The very small carbon network corresponds to 10 wt% SuperP.
To get an insight into the aging and SEI formation on the other investigated modifications of pristine graphite, SEM images have also been taken for graphite oxide after 422 (Figure 85), GOpd36 after 102 cycles (Figure 86) and during the cycling of GOpd43 at positive potentials between 3-5 V after 527 full cycles (Figure 87). All electrodes have been cycled in EC: DMC 1:1, 1M LiPF$_6$ in the standard electrode configuration described in paragraph 4.2.2.1. Only the GOpd43 electrodes for the cycling at very positive potentials of 3-5 V have been prepared on an aluminum current-collector since copper dissolves at potentials positive to ~3.4 V vs. Li$^+$/Li.

For graphite-oxide, the SEI appears to be very similar to the one on graphite SFG6. But on the prismatic edges, linear cracks can be observed which indicate that the underlaying GO sheets are partially exfoliated as shown in the zoom in Figure 85b. But this exfoliation is very small compared to an exfoliation of pristine graphite in, e.g., propylene-carbonate [13]. No total exfoliation can be observed which excludes the exfoliation process to be the main aging mechanism for GO. However, the observed slight exfoliation might contribute to a minor amount to the total loss of specific charge during the first few cycles as shown in Figure 76.

![Figure 85: SEM of graphite-oxide electrode after 422 full cycles in EC: DMC 1:1, 1M LiPF$_6$ as shown in Figure 76, SEI and slide exfoliation can be observed.](image)

![Figure 86: SEM of GOpd36 electrode after 102 full cycles in EC: DMC 1:1, 1M LiPF$_6$ as shown in Figure 77, SEI can be observed but exfoliation is absent.](image)
The SEI on GO\textsubscript{pd36} can be seen in the SEM images in Figure 86. A very homogeneous morphology of the SEI is detected which seems to be very similar to the one on pristine graphite in Figure 83 but much more homogeneous on the prismatic edges compared to the above discussed GO\textsubscript{pd43} in Figure 82. This might come from the fact that the GO\textsubscript{pd36} images have been taken after 102 cycles while the GO\textsubscript{pd43} electrode has seen 408 cycles being four times more. No visible signs of exfoliation can be observed for the GO\textsubscript{pd36} electrode either. Thus, the aging of the electrode in Figure 77 can also not be due to a major exfoliation process. Other aging mechanisms must dominate the specific charge loss during the first 70 cycles.

In contrast to the GO, GO\textsubscript{pd}, and graphite SFG6 electrodes which have been cycled between 0.01-3 V, the GO\textsubscript{pd43} electrode at positive potentials shows a significant difference in the surface film on the particles as shown in Figure 87. A polymeric film with many voids and cross-linked fibers is formed on the particles. This film is called a solid-permeable-interphase SPI and forms due to the oxidation of the electrolyte at very positive potentials [13]. As described in the introduction section in 2.3, the SPI is permeable for the electrolyte which leads to a continuous oxidation of the organic electrolyte in every cycle. This is very consistent with the observation in Figure 87 which shows many voids between the polymeric films. The disadvantage of this SPI is the continuous electrolyte decomposition in every cycle while the PF\textsubscript{6} diffusion through a dense film (like the SEI on the negative electrode) would probably be very limited or even almost impossible. Thus, an electrolyte which is more stable towards oxidation would be needed.

Work for GO\textsubscript{pd} for electrochemical capacitors shows that acetonitrile and propylene-carbonate can be used as solvents with the salt tetraethylammonium-tetrafluoroborate TEABF\textsubscript{4} and have a good cycling performance once activated to 4.8 V while cycled only between 3-4.5 V in the subsequent cycles [170]. But a full study for the application of GO\textsubscript{pd} in the positive electrode for lithium-ion batteries is beyond the scope of this work.

Figure 87: SEM of electrode of GO\textsubscript{pd43} on Al current collector after 527 full cycles in EC: DMC 1:1, 1M LiPF\textsubscript{6} between 3-5V as shown in Figure 80, solid-permeable-interphase observed.
4.2.4 Investigation of elemental distribution of GOpd43 by EDX

To get more insight into the composition of the solid-electrolyte-interphase and bulk of an electrode of GOpd43, energy-dispersive x-ray spectroscopy (EDX) has been applied to the electrodes at four different aging states. First, a pristine electrode with a ratio of 80:10:10 of GOpd43: PVDF: SuperP has been investigated (Figure 89) which corresponds to the SEM images in Figure 81 (1st row). Figure 89 was taken at 15 kV over a measurement time of one minute and includes a SEM image of the measured electrode spot and the detected elemental distribution.

The pristine electrode was also assembled in a standard half-cell configuration with electrolyte EC: DMC 1:1, 1M LiPF₆ to allow comparison with cycled samples because residues of the salt and glass-fiber separator might remain even after three times washing in DMC solvent. One can see that the atomic ratio of carbon to oxygen of the pristine GOpd43 electrode is circa 7.6: 1 although the elemental analysis indicates a composition of C₆O₀.₉₆(OH)₀.₀₅ (Table 8) which would be a ratio of C: O of 5.9: 1. But one has to keep in mind that SuperP also contributes to the signal of the EDX measurement due to its 10 wt% of the overall electrode composition. SuperP has a very high carbon to oxygen ratio compared to GOpd43, thus, perturbing the carbon: oxygen ratio to higher carbon content.

Furthermore, it can be observed that the washing procedure was very successful, removing almost all LiPF₆ salt since the phosphorus content is within the noise of the EDX measurement. But the fluoride content contributes in total 5.5 at% to the overall composition of the electrode. This can clearly not come from the LiPF₆ salt but from the PVDF binder which has a weight contribution of 10 wt% to the electrode. The theoretical estimated atomic contribution of C: O: F in an electrode with 80 wt% C₆O₀.₉₆(OH)₀.₀₅, 10 wt% SuperP (~100% C), and 10 wt% PVDF (C₂F₂H₂)n would be 100: 13.9: 4.75 while the detected ratio from EDX corresponds to 100: 13.1: 6.6. This deviation is within the error bars of the EDX or might originate from compositional variations in the electrode. The detected silicon content comes most probably from residues of the glass-fiber separator while the chloride and sodium content might come from residues of the graphite-oxide synthesis with NaClO₃ as described in section 4.2.2.1.

The EDX result of the GOpd43 electrode lithiated once to 0.8 V vs. Li⁺/Li and delithiated back to 3 V is shown in Figure 89 corresponding to the SEM images in Figure 81 (2nd row). Figure 90 shows the EDX of the GOpd43 electrode cycled 1x between 0.01-3 V while Figure 91 shows the GOpd43 electrode after 408 cycles 1x between 0.01-3 V corresponding to the SEM images in Figure 82 in the 1st and 2nd row, respectively. The carbon content decreases with progress of the cycling of the GOpd43 electrode which might be due to the formation of a surface film (SEI). In contrast, the oxygen, fluoride, phosphorus and chloride content increase with increasing cycle
number. Table 9 summarizes the elemental distribution from the EDX investigation where each cycled electrode has been measured at two different spots to detect possible variations in the electrode. Only the GOpd43 electrode after 408 cycles has been investigated three times where the third spot was chosen containing a large fiber (probably from the glass-fiber separator) in the center of the SEM image.

Figure 88: Energy-dispersive x-ray spectroscopy (EDX) of pristine GOpd43 electrode exposed to EC: DMC 1:1, 1M LiPF₆ with corresponding SEM image and elemental distribution at 15 kV.

Figure 89: EDX spectroscopy of GOpd43 electrode cycled once to 0.8 V in EC: DMC 1:1, 1M LiPF₆ with corresponding SEM image and elemental distribution taken at 15 kV.
The SEM images with the large fiber shows an increase of Si, Na, and oxygen while carbon, fluoride and phosphorus decrease in the atomic contribution compared to the two other measured spots on the GOpd43 electrode after 408 cycles. One can estimate the difference of the oxygen content based on the decrease of the carbon content of sample b) and c) at 408 cycles (25.6-23.3·58.5/62.3 = 3.7 in Table 9) while the Si and Na difference is 1.71 and 0.75, respectively.

Figure 90: EDX spectroscopy of GOpd43 electrode cycled once to 0.01 V in EC: DMC 1:1, 1M LiPF₆ with corresponding SEM image and elemental distribution taken at 15 kV.

Figure 91: EDX spectroscopy of GOpd43 electrode cycled 408x between 0.01-3 V in EC: DMC 1:1, 1M LiPF₆ with corresponding SEM image and elemental distribution taken at 15 kV.
A glass-fiber separator made of SiO$_2$ and Na$_2$O would need 3.8 at% increase in oxygen, thus, showing that observed fiber in the SEM images of sample c) is most probably originating from the separator which would have an estimated chemical composition of 80:20 (wt%) of SiO$_2$ to Na$_2$O. No reference of the real composition of the separator from a datasheet could be found. Thus, the contribution of Si, Na, and Cl in the elemental analysis by EDX can be explained.

To illustrate the evolution of the elemental composition from Table 9 for the different elements, Figure 92 has been created. All samples have been included although sample c) at 408x cycled GOpd43 electrode has been marked differently and is excluded to draw trends due to the influence of the glass-fiber separator as discussed above. Additionally, the samples of the EDX investigation after 408 cycles have been shifted on the arbitrary x-axis to match the linear extrapolation of the EDX results of the pristine, 0.8-3V and 0.01-3V electrodes. This should help to judge the evolution of the respective elements with respect to the bulk GOpd43.

In general, the SEI seems to grow during cycling since the carbon signal decreases with time. This is consistent with the observations from the SEM images discussed in the previous paragraph. The SEI growth over time/cycling is very non-linear which might be misleading by the arbitrary chosen x-axis in Figure 92. It is known to be mainly formed in the first lithiation below the stability limit of the organic electrolyte [13]. In general, the carbon content can be used to judge about the formation of the SEI on the GOpd43 and SuperP particles since the EDX possesses a certain penetration depth which is non-linear [182, 183]. While the carbon value decreases with progressing cycling, all other elements show an increase which indicates their contribution to the SEI composition. Oxygen, fluoride, and chloride increase almost proportionally to the decrease of carbon. Both oxygen and fluoride are both parts of the SEI on the basal and prismatic planes as Li$_2$CO$_3$ and LiF as shown by x-ray photoelectron spectroscopy (XPS) in EC:

Table 9: Atomic composition extracted from EDX measurements of GOpd43 at different cycling states for an electrode with 80: 10: 10 of GOpd43: PVDF: SuperP in EC: DMC 1:1, 1M LiPF$_6$ summarized from Figure 88 - Figure 91.
DMC 1:1, 1M LiPF$_6$ [13]. The increases in both contents are most probably due to SEI growth as the samples were transferred to the SEM by an air-tight transfer chamber to avoid contamination.

In contrast, phosphorus, sodium, and silicon show a different evolution compared to O, F and Cl in Figure 92. The sodium and silicon content vary very similarly to each other which might come from variations of residues of the glass-fiber separator as discussed above. In general, the separator sticks better to a cycled electrode where it might be partially pinned between particles and the SEI. This is usually observed during cell disassembly. The strong increase in the phosphorus content after 408 cycles cannot be explained precisely. It is know that LiPF$_6$ can decompose into HF and PF$_3$O in the presence of traces of H$_2$O in the electrolyte [13]. The LiPF$_6$ salt in the electrolyte is the only source for phosphorus in this electrode (see 4.2.2.1).

The differential plot in Figure 93 shows the evolution of the different elements in atomic percent in the different cycling states. All values correspond to the absolute changes and are compared to the pristine electrode. The oxygen amount has been corrected for a decrease of the GOpd43 signal (based on carbon amount from GOpd43, thus, oxygen in Figure 93 does exclude the oxygen from GOpd43 bulk) and the contribution of the glass-fiber separator has been subtracted. Therefore, the oxygen amount in Figure 93 only reflects the oxygen content in the SEI itself without GOpd43 bulk and separator. The fluoride amount has been normalized to the value which was measured for the pristine samples which originates only from the PVDF binder itself. Also sodium and silicon have been corrected for the contribution of the glass-fiber separator assuming that all silicon comes from the separator with a composition of 80:20 wt% SiO$_2$: Na$_2$O as discussed above. To test if these corrections are valid, the values of the third sample at 408 cycles is included in Figure 93. The values of this sample (with the glass-fiber in the center of the

![Figure 92: Summary of atomic composition of GOpd43 electrode at several cycling states extracted from EDX measurements of Table 9.](image-url)
analyzed spot) give the same values for all other elements (C, O, F, Na, Cl, P) after the subtraction of the influence.

From Figure 93 one can see that the oxygen content increases with a factor of two with respect to the fluoride atomic percentage. The ratio of oxygen: fluoride (already corrected for the PVDF binder and oxygen in GOpd43) changes from a ratio of 1: 0.8 in the first cycle to 1: 0.46 after 408 cycles, thus, indicating a strong increase in oxygen content with higher cycle number. The origin could be either further ethylene-carbonate and dimethyl-carbonate decomposition or a partial release of oxygen from the bulk GOpd43 and extrusion on the prismatic surfaces and defect sites on the basal planes. Comparable EDX studies on the SEI of pristine graphite SFG6 could help to judge which mechanism is more probable.

We come to the conclusion that the SEI composition is similar to the one on graphite as suggested from XPS results by Balbuena et al. [13] in the same electrolyte. But here a change to higher oxygen content during long-term cycling can be observed which is unusual for a normal SEI evolution which should be mainly finished after the first cycle. Also traces of chloride increase with cycling on the surface of the electrode. A very significant increase of phosphorus is seen after 408 cycles which cannot be attributed to any process yet but must originate from the salt LiPF₆ in the electrolyte since no other phosphorus source is present in the half-cell. But why both the oxygen and phosphorus content increase in the SEI on the expenses of the fluoride content cannot be explained from this investigation. Further experiments are necessary to understand these changes.

Figure 93: Differential atomic composition of GOpd43 electrode at several cycling states extracted from EDX measurements (subtracted content of oxygen in GOpd43, fluoride in PVDF binder and the influence of glass-fiber separator).
4.2.5 X-ray photoelectron spectroscopy of GOpd43 (XPS)

To detect differences in the SEI and possibly also in the bulk of GOpd43 compared to graphite SFG6, XPS analysis has been carried out for pristine, 1x lithiated and 1x cycled electrodes. The electrodes of GOpd43 consist of 80:10:10 active material: PVDF: SuperP while the graphite SFG6 electrodes consist of 90:10 SFG6: PVDF. Due to the 10% SuperP in the GOpd43 electrodes, XPS has been also performed on SuperP electrodes with 80:20 SuperP: PVDF. The electrodes have been cycled in a capacitor configuration against a counter electrode of activated carbon YP17 in EC: DMC 1:1, 1M LiPF$_6$. A battery configuration against a lithium-metal counter-electrode was avoided to reduce the thickness of the formed SEI in the first cycle to a minimum due to the different potential profiles through the cell keeping less volume of the electrolyte in the reduction potential regime below ~0.8 V.

All XPS spectra of GOpd43, graphite and SuperP electrodes can be found in the appendix 8.3. The XPS spectra of the pristine GOpd43 electrode are presented in Figure 135 with the respective deconvolution summarized in Table 16 for each peak position, FWHM and atomic percentage in the sample. Two spots have been investigated for the lithiated GOpd43 electrode which are shown in Figure 136 and Figure 137 were the deconvolution is summarized in Table 17 and Table 18, respectively. Also, two spots have been evaluated for the delithiated GOpd43 electrodes which have made a full first cycle as shown in Figure 138 and Figure 139. The deconvolution of the different spectra is presented in Table 19 and Table 20, respectively. As mentioned above, also graphite electrodes have been investigated where the pristine XPS spectra are depicted in Figure 140 while the 1x lithiated graphite spectra are shown in Figure 141. The summary of the peak contributions are summarized in Table 21 and Table 22 for the pristine and 1x lithiated graphite sample, respectively. Last, pristine and lithiated SuperP electrodes have been evaluated by XPS (Figure 142 and Figure 143 with summary in Table 23 and Table 24). Hereinafter, the evaluated data from these experiments is used for discussions and to draw conclusions.

First, the evolution of the elemental contributions for the different electrodes can be summarized as shown in Figure 94. For the pristine electrodes, the carbon content is ~83% except for the GOpd43 electrodes with 73% which show a high oxygen content of 6.5% as expected from elemental analysis and EDX shown in the previous paragraphs 4.2.1 and 4.2.4. The fluoride content in all pristine starting electrodes is ~16 at%. To estimate the expected fluoride content in the pristine electrode, one can assume that the electrode consists only of carbon and fluoride (F from PVDF) which is a good approximation for graphite and SuperP electrodes. The 10 wt% PVDF would result in 4 at% of fluoride normalized over the entire bulk. However, XPS is a surface method which is usually restricted to the first 10 nm of the surface.
But to estimate the atomic composition based on the surface ratios, the BET specific surface areas of the respective materials have to be known. SFG6 possesses 17.1 m²/g and SuperP 62 m²/g [156]. The BET of the dispersed PVDF binder is unknown and can be estimated based on the 16 at% by assuming a pure surface signal for the graphite SFG6 and SuperP electrode to be BET (PVDF) ~ 30 m²/g and 44 m²/g, respectively. This is an unusually high BET for PVDF which has only a BET of 4.5 m²/g for electrospray deposited composites [184]. Since both the fluoride content estimated from EDX with ~5.4 at% in Table 9 in paragraph 4.2.4 and the fluoride content estimated from XPS in the pristine electrodes seem to be higher than expected from its bulk and surface area estimated content (4.1 bulk at% and 2.8 BET at%), the electrode might have some higher PVDF content on the surface of the dried pristine electrodes. This might come from the drying procedure since the PVDF is dissolved in NMP which is removed in the vacuum, thus, evaporating preferred on the outer surface of the electrode which is the investigated surface in SEM, EDX, and XPS.

The oxygen content is close to zero in the pristine electrode of SuperP while it contributes 1.8 at% in SFG6 and 6.5 at% in the GOpd43 electrode. The very low oxygen content in the SuperP electrode shows that the surface groups of SuperP are mainly of a different origin than carboxylic or carbonylic character. Both phosphorus and lithium could not be detected in the pristine electrodes since they have not been exposed to the electrolyte.

During the first lithiation to 10 mV, a solid-electrolyte-interphase forms which increases the fluoride content while the XPS signal from the bulk carbon is reduced significantly. Additionally, the lithium content increases to a similar atomic content as the fluoride which might suggest LiF in the SEI (however, PVDF and Li-intercalation might also contribute to the atomic ratio).

![Figure 94: Evolution of elements in XPS measurements of GOpd43, SFG6 and SuperP electrodes at different cycling states (pristine, 1st lithiation, 1st lithiation + delithiation) from the XPS deconvolution in Figure 135 - Figure 143 summarized in Table 16 - Table 24 in the appendix.](image)
The oxygen content at the surfaces of both the SFG6 and SuperP electrodes increases to about ~9.5 at% while the oxygen at the surface of the GOpd43 electrode is much less with only 5.2 at%. Phosphorus content is minimal.

Delithiated electrodes have only been investigated for GOpd43 samples and show a decrease of the fluoride and lithium content while carbon, oxygen and phosphorus content increase. The lithium content decrease is stronger than the fluoride which might show that also compounds other than LiF contribute to the lithium decrease. But these atomic ratios give only a limited insight into the composition of the surface of the different electrodes.

The C1s XPS spectra of the three different electrodes in the pristine electrodes are shown in Figure 95a. The main peak is observed at -284.1 to -284.4 eV with a very small FWHM of ~0.5-0.9 eV which corresponds to the C-C bond energy in GOpd43, SuperP and graphite SFG6. A second main peak can be observed at ~ -285.7 eV which can be assigned in parts to the H-C-H bond in the PVDF binder. The third main peak at ~ -290.3 eV is assigned to the F-C-F bond in the PVDF binder. But if one compares the atomic ratios of the fluoride content to the C1s peak at -285.7 eV and -290.3 eV, small deviations can be observed in comparison to the \((C_2H_2F_2)_n\) composition of PVDF. The pristine SuperP electrode shows a ratio of 15:15:10 at%, the SFG6 electrode 16:10:10 at% and the GOpd43 electrode 20:12:11 at% of F: C1s -285.7 eV: C1s -290.3 eV. This indicates a high error bar of the XPS technique for analytical purpose. But the high ratio of C-H bond in SuperP and the low oxygen content in the electrode let us propose that most surface groups in SuperP could consist of C-H and C-C bonds. The ratios of the SFG6 and GOpd43 electrodes are closer to 2:1:1 at% which is expected from the chemical composition of PVDF.

The C1s spectra of the lithiated electrodes are shown in Figure 95b. Here, a much stronger difference of the spectra can be observed in comparison to the pristine electrodes. The C1s spectrum of graphite SFG6 shifts by 0.3 eV to higher binding energies (-284.7 eV) compared to the SuperP and GOpd43 peaks at -284.4 eV. This shift is known to occur in LiC\(_6\) compared to standard graphite. Both SuperP and SFG6 possess a similar C1s spectrum. The first peak at -284.4 eV (-284.7 eV for LiC\(_6\)) contributes the most. C-O groups are usually located at -286 to -289 eV. One would interpret the very broad double reflexes at ~ -287.1 and ~ -288.6 eV in Figure 95b to be more important for GOpd43 than for SFG6 and SuperP, respectively. But these spectra are misleading. Both peaks sum up to 12-13 at% for all three electrodes. But the C-C peaks is only 1/4th (1.4 at%) in the lithiated GOpd43 electrode compared to 6.8 and 4.5 at% for lithiated SuperP and SFG6, respectively. Also, the peaks at binding energies below -290 eV are similar for the lithiated electrodes of graphite SFG6 and SuperP with ~5-6 at%. Only the GOpd43 electrode shows only 3.4 at% for these high C1s XPS binding energies.
The delithiated GOpd43 electrode (Figure 95c) is almost impossible to deconvolute precisely. The reflex at -284.34 eV shows a very small FWHM of 0.8 eV. However, the C1s spectrum between -285 and -289 eV shows very little features. A deconvolution of the spectrum is shown in Figure 138 and Figure 139 on page IX- XI in the appendix. Three to four different peaks with an FWHM of ~1.5 eV are needed to fit the experimental spectrum reasonably. Since this result is very imprecise, it is only used for comparison to the lithiated and pristine GOpd43 electrode.

The evolution of the various C1s peaks of the GOpd43, SFG6 and SuperP electrodes are displayed in Figure 95d. One can see that the position varies only slightly for the main peaks. Lines are only drawn if the respective peak has been found in both electrodes of the pairs pristine/lithiated or lithiated/delithiated. Some peaks like the one at -291.4 eV could not be found in

Figure 95: C1s spectra of GOpd43, SFG6 and SuperP electrodes in a) pristine, b) first time lithiated, c) once lithiated and delithiated, d) evolution of peak positions of GOpd43, SFG6 and SuperP electrodes with cycling (lines if peaks exist in pristine+lith or lith+delith sample, fits of C1s peaks from Figure 135 - Figure 143 summarized in Table 16 - Table 24).
the pristine electrode but in the cycled ones. A peak should correspond to a certain surface bond and therefore not shift during cycling. Just the relative contributions of the chemical groups are expected to vary. Figure 95d shows that there are several small peak shifts in the deconvoluted spectra which indicate that the spectra cannot be deconvoluted with high precision and shows the relative high experimental error compared to EDX, as discussed in 4.2.4. However, general trends might still be possible to extract based on the C1s peaks but conclusions have to be treated with care.

The evolution of the atomic ratio of the different C1s peaks for the GOpd43, SFG6 and SuperP electrode are shown in Figure 96 where the of the C1s peak at -284.4 eV is shown in Figure 96a. The contribution of this peak decreases drastically for the lithiated electrode which probably indicates the coverage of the carbon active materials by the solid-electrolyte-interphase. An increase of the -284.4 eV C1s peak for the delithiated GOpd43 electrode might indicate the partial decomposition or densification of the SEI which is also observed for other systems when cycled at potentials positive to 1.5 V vs. Li⁺/Li [13, 78].

Additionally, the peaks at -285.7 eV and -290.5 eV decrease for the lithiated electrodes compared to the pristine ones in Figure 96b and Figure 96c, respectively. Since these peaks are attributed to the C-H and C-F bonds in PVDF, one can conclude that the PVDF gets either covered by SEI and/or partially dissolved in the electrolyte. Coverage by SEI might be more realistic since both peaks increase during delithiation which is rather due to SEI decomposition than PVDF crystallization from the electrolyte.

A careful examination of the peaks at ~ -287.1 eV and ~ -288.3 eV in Figure 96b and Figure 96c show some differences for the C-O bonds in lithiated GOpd43 electrode compared to the lithiated SFG6 and SuperP electrodes. It seems that GOpd43 possesses rather more molecular groups with single C-O bonds (~ -287.1 eV) than multiple C-O bonds like in carbonates. This might come from small differences in the bulk since many epoxide and hydroxide groups exist in the pristine GOpd43 electrode. But a precise determination is impossible. The peaks at higher binding energy in the C1s spectra are displayed in Figure 96d and could correspond to different C-F bonds due to the high electronegativity of fluoride causing a high binding energy.

To get more information about the surface groups at the electrodes, the other XPS spectra can be evaluated. The O1s spectra of the three different pristine electrodes are depicted in Figure 97a. As expected, the GOpd43 electrode shows two rich O1s peaks at -531.2 and -533.4 eV and one minor peak at -535.4 eV. The pristine graphite SFG6 electrode has small contributions of O1s which could correspond to the surface groups on the prismatic edge planes. SuperP shows no significant O1s contributions as expected from the evaluated C1s spectrum.
The O1s spectra of the lithiated compounds show fewer differences as depicted in Figure 97b. A peak is located at -533.7 eV while a second one is found at higher binding energy -535.7 eV. The atomic composition and peak shape are very similar for the lithiated graphite SFG6 and SuperP electrodes while the lithiated GOpd43 electrode shows only half of the contribution from the -533.7 eV peak. Additionally, a small contribution can be observed for the GOpd43 electrode at -530.5 eV. The peaks could not yet be assigned to any chemical group.

Additionally, the fluoride F1s spectra are shown for the pristine and lithiated electrodes in Figure 98. While the pristine F1s spectra show mainly a single F1s peak at -687.6 eV which corresponds to the fluoride in the PVDF with F-C-F bond, the lithiated compounds show two distinct peaks. One peak can be detected at -687.1 eV and the second at -689.8 eV. Both fluoride F1s peaks of graphite SFG6 are shifted by 0.6 eV to higher binding energies which is probably due to the standard shift in LiC₆ as also observed for the C1s spectra of LiC₆. The peak of the PVDF

![Grapha](image_a)

![Graphb](image_b)

![Graphc](image_c)

![Graphd](image_d)

Figure 96: Evolution of atomic percentage of different C1s peaks with cycling, colors corresponding to peak positions in Figure 95.
in the pristine sample is now hidden under two new peaks in the lithiated sample. This was also observed in the C1s spectra for the F-C-F peak at -290.5 eV. Like for the C1s and O1s spectra, the F1s spectra are similar for the pristine and lithiated electrodes of graphite SFG6 and SuperP in amount and peak position. In contrast, the F1s peak at -687.1 eV of the lithiated GOpd43 electrode shows significantly more fluoride amount at this binding energy.

Additionally, the Li1s and P2p XPS spectra have been measured for the pristine and lithiated electrodes. The pristine electrodes show no signal for the pristine electrodes as expected. However, the lithiated Li1s spectra are compared in Figure 99a where two main peaks can be found. A minor Li contribution is observed at -56.6 eV with 4.2 at% for SFG6 and 5.8 at% for the GOpd43 electrode. The second peak is observed at -57.8 to -58.2 eV which accounts for 26-32 at% of the total atomic content. The lithiated graphite SFG6 electrode (LiC₆) is probably shifted

Figure 97: O1s XPS spectra of GOpd43, SFG6 and SuperP electrodes in a) pristine, b) first time lithiated configuration.

Figure 98: F1s XPS spectra of GOpd43, SFG6 and SuperP electrodes in a) pristine, b) first time lithiated configuration.
like the C1s, O1s and F1s spectra to higher binding energies. In contrast, no separation of the Li1s spectrum of the SuperP electrode could be made since no significant features are detected in the spectrum.

Also the P2p spectra have been measured for the pristine and lithiated electrodes. Of course, the pristine electrodes show no phosphorus contribution since they have never been exposed to the electrolyte which could be the only source of phosphorus and lithium with its LiPF$_6$ salt. In contrast, the lithiated electrodes show small contributions from the P2p spectra as shown in Figure 99b. The major P2p peak is observed at -139.1 eV which is shifted for the lithiated graphite SFG6 electrode by 0.6 eV to higher binding energy as also observed for all previous spectra (C1s, O1s, F1s, Li1s). Only GOpd43 shows another phosphorus contribution at -136.3 eV which has only an atomic contribution of ~0.1 at%. The noise is very high since the atomic content of phosphorus is very low.

In summary, the XPS analysis gives some extra information about the GOpd43 electrode. It seems that the SEI is similar to the one on SFG6 and SuperP. But some differences can be observed. The XPS C1s spectrum shows much less contributions from C-C bonds in the lithiated state. Also the O1s spectrum shows fewer contributions from the oxygen while more fluoride can be observed in the lithiated GOpd43 electrode. The lithium content is highest in the GOpd43 electrode which might be related to the increased fluoride contents (e.g. LiF) while an extra small P2p peak is observed.

Figure 99: XPS spectra of GOpd43, SFG6 and SuperP electrodes in first time lithiated configuration for a) Li1s spectrum and b) P2p spectrum.
4.2.6 X-ray diffraction of G0pd43

To get a better insight into the bulk properties of partially-disproportionated graphite-oxide, x-ray powder diffraction (XRD) can be helpful. Figure 100 depicts the x-ray diffraction patterns of pristine graphite-oxide, two pristine G0pd’s with 3.6 and 4.3 Å interlayer distances and the precursor graphite SFG6. One can clearly observe the shift of the (002) reflex of P63/mmc space group to higher 2Theta angles from GO to G0pd43 to G0pd36 finally reaching graphite SFG6. All Rietveld refinements have been based on the P63/mmc space group which corresponds to the AB stacking structure in graphite. Based on these refinements, the reflex indexing can been performed and the refined space group parameters are summarized in Table 10 on page 134 in the form for a hexagonal space group (a a c α=90 β=90 γ=120). The stacking defect, ABC-stacking, is observed for pristine graphite SFG6 and is indexed in light green in Figure 100d. The insets in Figure 100 show a zoom on the (100) and (101) reflexes since they show much lower intensity than the (002) reflex. From these reflexes one can evaluate the C-C distance within the graphene-oxide and graphene planes.

The refined space group parameters in Table 10 show the distinct decrease of the distance between the graphene-oxide/ graphene sheets from GO to graphite SFG6 via the intermediate G0pd43 and G0pd36. The trend can be better visualized in Figure 101. The value for the c-axis can be determined very well from the pristine materials since the (002) reflex of an assumed P63/mmc space group shows high intensity and relative low FWHM. In contrast, the a-parameter of GO and G0pd compounds is very weakly defined. One can see that the respective (100) and (101) reflexes do not capture the measured reflex shape in the insets in Figure 100. Especially, a strong broadening between the (100) and (101) reflexes is observed. This “bridge” was suggested to be due to turbostratic disorder between the graphene-oxide sheets [169]. But here, we also suggest the possibility of a C-C distance distortion due to the epoxide and hydroxide “bulk-surface groups” on the graphene sheets. In general, an epoxide stretches the distance between the C-C bonds to 1.47 Å instead of the 1.422 Å in graphite [185]. Although the carbon of the epoxide is sp3-hybridized, it can stay planar to the aromatic structure of graphene [185]. In contrast, the hydroxide “bulk-surface group” forms a tetrahedron and sticks therefore out of the graphene plane [185]. These defects might also contribute to the broad reflex shape of the (10z) reflexes. The (101) reflex possesses a sharp front flank but a broad tail towards higher 2Theta angle.

The reduction of the c-axis can be explained by the decrease in the amount of surface groups in the bulk as shown from the elemental analysis in Table 8 and Figure 75 on page 104. But the variations in the C-C distance in the graphene-oxide planes show a very non-linear evolution compared to the c-axis. The C-C bond in graphene is very strong and does not change much dur-
ing intercalation processes, e.g. C-C distance in LiC₆ is 1.435 Å while 1.42 Å in graphite (1.04% change) as shown in Table 3. For graphite-oxide, a C-C distance of 1.438 Å is observed which decreases to a value much lower than that of graphite for the partially-disproportionated graphite-oxides with 1.41 Å and 1.416 Å for GOpd43 and GOpd36, respectively. This relative small difference in the C-C distance within the graphene-oxide sheets symbolizes very strong elastic energy differences in-plane due to the very strong stiffness of the graphene sheets in a-b-direction of 1036 GPa for c₁₁ (c₃₃ = 40 GPa) [186]. The influence of the epoxide groups seems to be not the reason of this C-C distance evolution since the GOpd compounds show a smaller distance compared to the aromatic graphite C-C distance. The GOpd compounds are believed to contain mainly epoxide groups (Table 8 and Figure 75) and should lead to a stretching of the C-C distance at least in one crystal direction. The chemical origin for these differences cannot be elucidated here.

Figure 100: XRD pattern of a) graphite-oxide, b) GOpd43, c) GOpd36 and d) graphite SFG6 refined and indexed with P63/mmc space group.
To get further insight into the crystallographic changes during cycling, ex situ XRD analysis has been performed on GOpd43 electrodes after the first lithiation and for the lithiated and delithiated state after 70 cycles where the fading of the specific charge during electrochemical cycling saturates, as shown in Figure 78. The respective XRD patterns are depicted in Figure 102 where mainly three different phases can be detected. The refined crystallographic parameters of the different phases are summarized in Table 11. First, the space group of GOpd43 can be detected which is indexed in black in Figure 102. The c-axis of the GOpd43 compound increases from 4.33 Å in pristine GOpd43 to 5.704-5.744 Å after the first lithiation of GOpd43 which is very close to the c-axis distance of the pristine graphite-oxide with 5.744 Å shown for comparison in Figure 101. The same c-axis distance can be found for the GOpd43 after 70 cycles as shown in Figure 102c, however, the respective (002) reflex shows very little intensity. The reflexes (100) and (101) which correspond to the in-plane ordering in the GOpd43 particles cannot be refined for GOpd43 after 70 cycles because their contributions are too weak. For the delithiation GOpd43 after 70 cycles, no contributions of the GOpd43 particles can be detected anymore.

The second phase which can be observed in the cycled GOpd43 electrodes can be assigned to a phase with cubic Fm-3m space group where the a-parameter would be close to 4.05 Å. Compounds which fulfill this condition could be LiH, LiF, Al and many other metals. It is known that the formation of a solid-electrolyte-interphase in EC:DMC 1:1, 1M LiPF₆ leads to the formation

Table 10: Summary of refined space-group parameters of XRD of GO, GOpd43, GOpd36 and graphite SFG6 from Figure 100, graphite shows additional rhombohedral group for ABC stacking defect, a- and c-parameter also calculated for C-C intralayer and C||C interlayer distance.

<table>
<thead>
<tr>
<th></th>
<th>Space group</th>
<th>a-axis [Å]</th>
<th>c-axis [Å]</th>
<th>FWHM</th>
</tr>
</thead>
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<tr>
<td>GO</td>
<td>P6₃/mmc</td>
<td>2.491(1)</td>
<td>11.49(1)</td>
<td>0.28</td>
</tr>
<tr>
<td>GOpd43</td>
<td>P6₃/mmc</td>
<td>2.442(2)</td>
<td>8.67(1)</td>
<td>0.72</td>
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<tr>
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<td>P6₃/mmc</td>
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<td>7.264(6)</td>
<td>0.5</td>
</tr>
<tr>
<td>SFG6</td>
<td>P6₃/mmc</td>
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<td>6.72(1)</td>
<td>0.21</td>
</tr>
<tr>
<td>SFG6</td>
<td>R-3m</td>
<td>2.464(1)</td>
<td>10.08(1)</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Figure 101: Evolution of C-C intralayer and C||C interlayer distance for the different graphitic compounds and during lithiation, error bars included in point size.
of LiF [13] which was also confirmed by the EDX and XPS results discussed in sections 4.2.4 and 4.2.5. Therefore, the second phase is assigned to LiF. The compound can also be detected after 70 cycles in both the lithiated and delithiated state which supports the finding of LiF as it is stable during cycling in the respective potential regime of 0.01-3V [13].

A third phase can be detected in the GOpd43 electrode after the first lithiation which shows very broad and minor reflexes. The identification of the phase is very difficult due to the weak signal but would fit best to the space group of LiOH. The compounds Li$_2$O and Li$_2$CO$_3$ do not match with the detected reflexes. LiOH could form during the chemical reduction of the remaining hydroxide groups in pristine GOpd43 material but should be of rather low amount based on the elemental analysis in Table 8. However, the pristine material could absorb moisture when stored in air which might lead to an increase in hydrogen within the GOpd43 material. LiOH was found in two out of three electrodes after the first lithiation and not observed after 70 cycles.

Figure 102: XRD refinement of GOpd43 after a) first lithiation to 3 mV, b) first lithiation to 0 mV, c) 70 cycles lithiated to 10 mV and d) 70 cycles delithiated to 3 V.
To allow comparison of the found second and third phase with other compounds, the ICSD space groups of LiF, LiH, LiOH, Li$_2$O, and Li$_2$O$_2$ have been added at the end of Table 11 with the corresponding reference. The structure of Li$_2$CO$_3$ is monoclinic base-centered C 1 2/c 1 with $a$=8.36, $b$=4.97, $c$=6.2, $\alpha$=90°, $\beta$=114.8° [187]. Li$_2$O, Li$_2$O$_2$ and Li$_2$CO$_3$ do not correspond to the detected reflexes in Figure 102 as stated above.

Table 11: Summary of refined parameters of GOpd43 after a) first lithiation (3 samples, 1)-3)), b) 70 cycles lithiated in 4) and c) 70 cycles delithiated in 5) corresponding to refinements in Figure 102, phase #2 and #3 assigned to LiF and LiOH, respectively, parameters in black refined while grey left unrefined.

<table>
<thead>
<tr>
<th>GOpd43</th>
<th>Space group</th>
<th>a-axis [Å]</th>
<th>c-axis [Å]</th>
<th>FWHM</th>
<th>Reference</th>
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<tbody>
<tr>
<td>1) cycle 1</td>
<td>P6$_3$/mmc</td>
<td>2.429(2)</td>
<td>11.46(2)</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>1) LiF found</td>
<td>Fm-3m</td>
<td>4.039(3)</td>
<td></td>
<td>1.74</td>
<td></td>
</tr>
<tr>
<td>2) cycle 1</td>
<td>P6$_3$/mmc</td>
<td>2.440(2)</td>
<td>11.41(1)</td>
<td>0.63</td>
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<tr>
<td>2) LiF found</td>
<td>Fm-3m</td>
<td>4.061(4)</td>
<td></td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>2) LiOH found?</td>
<td>P4/nmm</td>
<td>3.550(5)</td>
<td>4.34</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>3) cycle 1</td>
<td>P6$_3$/mmc</td>
<td>2.432(1)</td>
<td>11.49(1)</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>3) LiF found</td>
<td>Fm-3m</td>
<td>4.055(4)</td>
<td></td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>3) LiOH found?</td>
<td>P4/nmm</td>
<td>3.540(5)</td>
<td>4.34</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>4) cycle 70</td>
<td>P6$_3$/mmc</td>
<td>2.44</td>
<td>11.39(5)</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>4) LiF found</td>
<td>Fm-3m</td>
<td>4.036(3)</td>
<td></td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>5) cycle 70,</td>
<td>Fm-3m</td>
<td>4.056(4)</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>delithiated to 3V only</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>LiF found</td>
<td>Fm-3m</td>
<td>4.035</td>
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<td>[188]</td>
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<tr>
<td>LiH</td>
<td>Fm-3m</td>
<td>4.065</td>
<td></td>
<td>[189]</td>
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</tr>
<tr>
<td>LiOH</td>
<td>P4/nmm</td>
<td>3.556</td>
<td>4.343</td>
<td>[190]</td>
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<tr>
<td>Li$_2$O</td>
<td>Fm-3m</td>
<td>4.61</td>
<td></td>
<td>[191]</td>
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</tr>
<tr>
<td>Li$_2$O$_2$</td>
<td>P6$_3$/mmc</td>
<td>3.142</td>
<td>7.65</td>
<td>[192]</td>
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</table>
4.2.7 Electrochemical rate capability

The specific charge of the partially-disproportionated graphite-oxide could be improved compared to standard graphite as shown in paragraph 4.2.2.3. But the main purpose of the chemical modification was the reduction of the elastic energy contribution by introduction of chemical pillars in the bulk graphite to increase the recharge rate performance since standard graphite is usually limited to 2C (30 min charge) to accept 80% of its specific charge galvanostatically [152]. To investigate the rate capability of GOpd, cyclic voltammetry has been chosen since its electrochemical behavior is closer to a capacitor than to an intercalation material. The scan rate was varied between 0.1 – 100 mV/s in the potential window of 0.01-3V vs. a lithium-counter electrode. These scan rates correspond to a charge time of ~8 h and ~30 s (C/8 to 120C in galvanostatic mode, respectively). GOpd43, GOpd36 and pristine graphite-oxide have been investigated with various rates for their electrochemical rate capability.

Figure 103 shows the cyclic voltammetry of the GOpd43 electrode. The activation in the first cycle is depicted in Figure 103a in comparison to the second cycle with the same rate of 1 mV/s. The onset of the activation in the first cycle can be observed to occur at ~1.5V while the activation maximum is observed at ca. 0.38 V. A second process is observed close to 0 V vs. Li⁺/Li. In contrast, the lithiation in the second cycle starts a ~2 V and increases its specific capacitance until 0 V. The delithiation in the first and second cycle are much more similar to each other. During the second delithiation two minor maxima can be observed at 0.44 V and 1.89 V with 630 F/g and 698 F/g, respectively. A reduced specific capacitance (<500 F/g) can be extracted above 2.4 V.

The cyclic voltammetry at various scan rates is depicted in Figure 103b. The lithiation at potentials positive to 1 V is very similar for the scan rates lower than 10 mV/s and show a capacitor-like charge storage behavior. But the lithiation in the potential regime of 0-1 V vs. Li⁺/Li is very strongly dependent on the applied scan rate and appears to be rather an insertion mechanism than an adsorption behavior. The delithiation scan rate of 0.1 mV/s shows a very high specific capacitance, always above 400 F/g except during the transition from lithiation to delithiation. Two major delithiation peaks can be observed during the very low scan rate of 0.1 mV/s at 0.19 V and 1.97 V with 892 F/g and 1180 F/g, respectively. These are very high specific capacitances in comparison to some of the best electrochemical capacitors which use the same GOpd in acetonitrile or propylene-carbonate with a salt of tetraethylammonium-tetrafluoroborate TEABF₄ and deliver 200 F/g which is considered to be a value very high for capacitors [193].

Furthermore, the lithiations seems to be still rate limited as its inserted specific capacitance depends very significantly on the scan rate as observed in Figure 103b. The subsequent delithiation
at the same scan rate is therefore strongly influenced by the preceding lithiation due to the very short constant-potential step which is limited to only 1 min potential hold at either 10 mV or 3V. The first maximum of the specific capacitance during delithiation (~0.19 V for the scan rate of 0.1 mV/s) shifts to more positive potentials with increasing rate, thus, indicating a possible kinetic limitation (diffusion or reaction kinetics). In contrast, the second maximum at 1.97 V for the very low scan rate of 1 mV/s seem not to shift but is suppressed strongly, thus, indicating rather limited available lithium than kinetic influences since the overpotentials do not seem to change.

As discussed above in paragraph 4.2.2.3, a drastic aging is observed during the first 70 cycles during galvanostatic cycling for GOpd43, as shown in Figure 78. As depicted in Figure 103c, the aging was also compared for the scan rates of 1 mV/s in the 2nd, 12th and 22nd cycle which corresponds to the cycle after the formation cycle, first scan rate protocol from 0.1 – 100 mV/s and

Figure 103: Cyclic voltammetry of GOpd43 a) first two cycles with activation cycle, b) rate capability at various scan rates from 0.1 mV/s (= 8h 20min per charge) to 100 mV/s (30 s), c) aging after first and second scan rate test and d) extracted specific charge at different scan rates to determine recharge rate performance.
the second repetition of the scan rate protocol, respectively. A slight aging can be observed as the specific charge decreases from an initial 467 mAh/g in the 2\textsuperscript{nd} cycle to 84\% and 72\% in the 12\textsuperscript{th} and 22\textsuperscript{nd} cycle, respectively. The aging for the galvanostatically cycled GOpd43 electrode with a potentiostatic step deliver 677 mAh/g in the 2\textsuperscript{nd} cycle and decrease to 77 and 63\% of the 677 mAh/g after the 12\textsuperscript{th} and 22\textsuperscript{nd} cycle, respectively. This difference might be related to the time at which the GOpd43 electrode is exposed to reduction potentials below a certain voltage threshold (e.g. \(~0.8\) V for electrolyte reduction or \(~0.44\) V for reactions also causing the activation). The influence of the cycling potential will be investigated in the next section 4.2.8.

The extracted specific charge for the different scan rates is presented in Figure 103d for the performance during the first and second scan rate protocol. The extracted specific charge for both lithiation and delithiation is higher during the first scan rate protocol for rates above 1 mV/s. Interestingly, the low scan rate of 0.1 mV/s delivers higher specific charge in the second protocol despite the aging. Additionally, the delivered specific charge reaches an almost log-linear profile in the second sweep rate test. Therefore, one can conclude that the aging of the material is not only related to a specific charge loss but also to a rate capability loss during cycling.

Another aspect that can be observed in the extracted specific charges in the scan rate tests are the differences between lithiation and delithiation in Figure 103d. For low scan rates lower than 3 mV/s a huge irreversible specific charge is measured in both, the first and second scan rate test. The tests at 0.1 mV/s show a higher specific charge for delithiation than for lithiation which is due to the a little bit faster preceding cycle at 1 mV/s which was not finished and shows therefore a positive current between 2.23 – 3.0 V although lithiation should occur. Therefore, the practical specific charge depends on the previous cycle when measured with cyclic voltammetry. In contrast, the sweep rates >5 mV/s show very little irreversible specific charge. This also supports the hypothesis that the time at which the active GOpd material is exposed to a certain potential regime influences the aging significantly.

The cyclic voltammetry of GOpd36 is presented in Figure 104. The activation cycle shown in Figure 104a resembles a similar profile as the discussed GOpd43. But the onset of the lithiation starts at a more negative potential of \(~1.2\) V vs. Li\textsuperscript{+}/Li. The onset potential was shown to vary linearly with the interlayer distance of the GOpd for capacitors with 1M TEABF\textsubscript{4} in acetonitrile [193]. But the onset potentials are shifted to much more negative potentials in 1M LiPF\textsubscript{6} in EC:DMC 1:1 (wt\%) in comparison to the capacitor electrolyte in Fig. 3 of [193]. Additionally, the maximum of the specific capacitance of the activation of GOpd36 is reached at 0.3 V which is 140 mV more negative than for GOpd43. Also, the delithiation in GOpd36 is similar to the one
of GOpd43 having two minor maxima at 0.43 V and 1.33 V with 722 F/g and 688 F/g in the 2\textsuperscript{nd} cycle, respectively.

The rate capability of GOpd36 is shown in Figure 104b and indicates similar lithiation profiles as the GOpd43 electrode. Most of the insertion occurs at potentials negative to 1 V vs. Li\textsuperscript{+}/Li and depends strongly on the applied scan rate which indicates kinetic limitations as in the GOpd43. During delithiation, however, a difference of the GOpd36 material can be observed. The first delithiation maximum at a scan rate of 0.1 mV/s is located at 0.14 V and shows a higher specific capacitance than the second peak at 1.73 V with 1080 F/g to 939 F/g, respectively. For the GOpd43, the opposite was observed with slightly higher peak potentials of the respective maxima. Here, also a shift of the first peak potential to more positive potentials can be observed with increasing scan rate indicating a kinetically limited process as seen for lithiation and also for the GOpd43 electrode.

![Cyclic voltammetry graphs](image)

Figure 104: Cyclic voltammetry of GOpd36 a) first two cycles with activation, b) rate capability at various sweep rates from 0.1-100 mV/s, c) aging after 1\textsuperscript{st} and 2\textsuperscript{nd} sweep rate test and d) extracted specific charge at different sweep rates showing recharge rate performance.
The aging of the GOpd36 electrode is presented in Figure 104c compared at 1 mV/s. The most severe aging is observed between the 2\textsuperscript{nd} and 12\textsuperscript{th} cycle (first scan rate test) where the specific charge decreases from 417 mAh/g in the second cycle to 81 % and 71 % in the 12\textsuperscript{th} and 22\textsuperscript{nd} cycle, respectively. This is also less severe as the aging observed during galvanostatic cycling of 1C followed by a constant-potential step at 0.01 and 3V as shown in Figure 77.

Figure 104d visualizes the extracted specific charging during the first and second scan rate test at rates between 0.1 – 100 mV/s. The same trends as for the GOpd43 electrode can be observed, however, less total specific charge can be stored in GOpd36 as also seen during galvanostatic cycling in Figure 77. The irreversible specific charge is high for sweep rates <3 mV/s but drastically reduced above 5 mV/s. The second scan rate test shows a log-linear rate performance which is drastically reduced compared to the rate performance during the first sweep rate test. This indicates also an influence of the aging on the rate performance which was also observed for the GOpd43 electrode.

The cyclic voltammetry of pristine graphite-oxide GO is shown in Figure 105. The activation is very different to the partially-disproportionated GOpd’s presented above. The onset of the activation starts at ~2.1 V and possesses two minor maxima for the lithiation at ~1.5 V and ~0.42 V. However, a continuous increase of the specific capacitance can be observed until 0 V vs. Li\textsuperscript{+}/Li. The specific capacitance during delithiation is very low (<150 F/g), thus, indicating a highly irreversible first lithiation. During the second cycle also a high irreversible specific charge can be observed where only 28% of the 193 mAh/g can be extracted. These irreversible specific charges are consistent with the previous findings for galvanostatically cycled GO electrodes in Figure 76.

Cycling at various scan rates is shown in Figure 105b where a high irreversible specific charge can be also measured in the third cycle which was performed at a sweep rate of 0.1 mV/s. The aging of graphite-oxide is shown in Figure 105c where the specific charge of 193 mAh/g in the second cycle decreases to 65 % and 57 % in the 12\textsuperscript{th} and 22\textsuperscript{nd} cycle, respectively. It can be concluded that most of the fading of the specific charge occurs during the first three cycles where the high irreversible specific charge of more than 50% is observed.

The rate performance during the scan rate tests is depicted in Figure 105d. The profile looks similar to the ones of GOpd36 and GOpd43 but delivers much less absolute specific charge. One can also see that the irreversible specific charge equilibrates after the very low rate scan rate of 0.1 mV/s in the third cycle. Additionally, an increased irreversible specific charge can be observed for low sweep rates as discussed for the GOpd electrodes.

When one focuses on the activation cycle, the sweep rate might have an influence on the involved reactions. For standard graphite, the galvanostatic cycling rate is known to influence the
morphology of the SEI [194] and the exfoliation of graphite [195] during the first lithiation. However, no major impact on the intercalation process itself has been observed. To test if the activation of GOpd and GO during the first lithiation depends on the applied current density, the first lithiation was performed at a scan rate of 10 mV/s as shown in Figure 106 for GOpd36 and pristine GO. It can be observed that the increase of the sweep rate by a factor of 10 suppresses the activation cycle significantly. For GOpd36 the onset of the lithiation is shifted to more negative potentials of ~0.9 V vs. Li⁺/Li and shows no activation maximum compared to the activation at 1 mV/s in Figure 104.

Surprisingly, the “normal” activation process can be observed in the second cycle at a low rate of 0.1 mV/s and shows the onset of the lithium insertion at ~1.4 V and an activation maximum at 0.59 V; both more positive than the observed onset and maximum at 1 mV/s in Figure 104.

Figure 105: Electrochemical cyclic voltammetry of GO a) first two cycles with activation, b) rate capability at various sweep rates from 0.1 - 100 mV/s, c) aging after 1st and 2nd sweep rate test and d) extracted specific charge at different sweep rates to determine recharge rate performance.
This potential shift could be due to the lower sweep rate or a slight pre-activation in the first cycle at 10 mV/s. However, a drastic suppression of the activation process cannot be denied if increased current-densities are applied. This indicates that the activation is rather connected to a chemical reaction than a thermodynamic insertion of lithium in GOpd. The reaction kinetics of the activation seems to be limited so that the activation occurs mainly in the subsequent low scan-rate cycle. The rate capabilities of the following rate tests between 0.1 – 100 mV/s shows no difference to the ones plotted in Figure 104d, thus, the delayed activation in the second cycle seems to result in a similar end product.

The increased scan-rate shows also a suppression of the activation in the first lithiation of graphite-oxide in Figure 106b. Here, a negative current is even observed during the intended delithiation from 0.01 V back to 3.0 V in the first cycle. This shows that almost all specific charge in the first cycle is consumed irreversibly. The actual activation occurs in the subsequent second cycle at 0.1 mV/s but shows a different activation profile compared to the one at 1 mV/s for GO in Figure 105a. The onset of the lithiation shifts to slightly more positive potentials of ~2.2 V and only a single local activation maximum can be observed. The activation maximum at ~1.5 V in Figure 105a disappeared while the second one also shifted to slightly more positive potentials at ~0.7 V. A very high irreversible specific charge of 640 mAh/g or 84% of the total specific charge of the lithiation is consumed in the second cycle. As for the GOpd36 electrode, the scan rate capability of the suppressed activation in the first cycle was the same as for the “normal” activated GO electrode as shown in Figure 105d.

Figure 106: High-rate activation in first cycle with a sweep rate of 10 mV/s with subsequent low rate second cycle for a) GOpd36 and b) GO, activation in 2nd cycle observed.
4.2.8 Electrochemical cycling in limited potential window and GITT

To test the influence of the electrochemical cycling potential on the aging of the material, three different potential windows have been chosen for cycling as depicted in Figure 107. First, the galvanostatic cycling window was limited to 1.0-3.0 V vs. Li⁺/Li while the material was lithiated to 10 mV in the first cycle to guarantee complete activation. The aging of the material can mainly be detected in the first few cycles after the activation cycle, as shown in Figure 107a. The inset depicts the cycling profiles of the activation cycles which have been performed every 302 cycles. The decrease of the specific charge is shown in Figure 107b where a very low fading is observed during the first 1200 cycles. Interestingly, a higher specific charge during delithiation can be observed after an activation cycle down to 10 mV as marked by stars in Figure 107b. This means that some extra stored lithium cannot be extracted in the delithiation immediately after the lithiation down to 10 mV and is removed in the subsequent cycles partially. As shown in the inset of Figure 107b, the specific charge during the activation cycles is very high (>400 mAh/g) and the material ages more severely than in the potential regime between 1-3 V. But the total extracted specific charge is limited to only 80 mAh/g which is very low and only as good as today's capacitor materials [170].

The second potential window was chosen to be between 0.01-2 V as shown in Figure 107c and d. A rapid fading of the specific charge can be observed during the first five cycles which is shown in Figure 107c. The inset depicts the activation of the material in the first cycle. The decrease of the specific charge with cycling is shown in Figure 107d and indicates some problems with cycling during the first 150 cycles which is probably related to problems in the cycling device. After the initial problems, a continuous fading is observed where the specific charge drops to 145 mAh/g after the 900th cycle. But the specific charge in the first delithiation (360 mAh/g) drops to circa 233 mAh/g in the fifth cycle by more than 35%. Therefore, it can be concluded that the aging is even more severe for the cycling between 0.01-2 V than the one when GOpd43 is cycled between 0.01-3.0 V as shown in Figure 78 where an fading of 13.6 % is observed from 700 mAh/g to 605 mAh/g between the first and fifth delithiation, respectively.

Additionally, some continuous aging is observed even after 200 cycles, despite the fact that almost no aging is observed during the 70th and 400th cycle of the GOpd43 electrode cycled between 0.01-3.0 V. Usually, the increased potential window should lead to an enhanced fading of the specific charge. But here, it can be concluded that the potential regime close to the lithium-metal potential seems to be very harmful to GOpd43.

Third, the potential window was chosen to be in an intermediate state with a cycling between 0.5-2.5 V. Also, the first activation was only chosen to be performed to 0.5 V to not alter the
Figure 107: Galvanostatic cycling in limited potential regime to determine aging influences on GOδd43, a) cycling and b) aging between 1.0-3.0 V with activation to 0.01 V every 300 cycles, c) cycling and d) aging between 0.01-2.0 V with one activation cycle, e) cycling and f) aging between 0.5-2.5 V potential window (no constant potential steps applied, stars indicate a restart of new cycling protocol, insets show activation in first cycle/cycles).
structure too much. The cycling is shown in Figure 107e and the decrease of the specific charge is shown in Figure 107f. The activation cycle is shown in the inset of Figure 107e). During the first cycles a low aging of 6.8 % can be observed where the specific charge of the delithiation in the first and fifth cycle decreases from 206 to 192 mAh/g. Afterwards, a continuous aging is observed during the next 900 cycles until a specific charge of 130 mAh/g is reached. Therefore, it can be concluded that the potential window of 0.5- 2.5 V leads to much less aging compared to the 0- 2 V potential regime but the material still suffers from fading of specific charge.

Additionally, it can be observed that the hysteresis between lithiation and delithiation decreases for all three investigated potential windows as shown in Figure 107a, c and e which is consistent with previous findings for galvanostatic cycling between 0.01- 3.0V as discussed in 4.2.2.3. To investigate the origin of the hysteresis, galvanostatic-intermittent-titration (GITT) can be used to detect the pseudo-open-circuit potential and overpotentials as described in section 2.6.1c) and already used for pristine graphite electrodes in section 3.5. The GITT of GOpd43 is shown in Figure 108a where the first three cycles are depicted. The specific current was below 0.015 A/g which corresponds to a C-rate of ~C/35 for a respective continuous galvanostatic lithiation. The relaxation time was chosen to be five hours for all GITT experiments in Figure 108.

During the first lithiation of GOpd43 high overpotentials can be detected before and at the beginning of the lithium insertion at 3.0- 1.5 V and 1.5- 1.1 V, respectively, which are lower in the subsequent cycles (Figure 108a). The relaxation is measured to be over 400 mV before the lithium insertion while it decreases to 340 and 270 mV at 1.3 and 1.2 V, respectively. But the overpotentials during the lithiation negative to 1 V are significantly reduced to approximately 100 mV which is still high compared to a few millivolts found for pristine graphite electrodes in section 3.5.

During the delithiation of the GOpd43 electrode (Figure 108a), very low overpotentials of less than 100 mV are observed at potentials between 0- 1 V. But at potentials between 1- 3 V a continuous increase of the overpotential can be observed which has its maximum during the galvanostatic delithiation at potentials of 3 V with more than 780 mV potential relaxation during the five hours. During the galvanostatic discharge, after the 3 V potential cut-off has been reached once, very low specific charge can be withdrawn in every discharge step. These results support the previous findings that there are limitations to extract the specific charge at potentials positive to ~2 V vs. Li+/Li. These limitations are probably not of kinetic origin since the very low rate of C/35 and the long relaxation time allows even very slow diffusion or surface reactions to proceed. It seems that some reaction limitations might govern the system response positive to 2 V. The real origin of these high overpotentials is unknown so far.
During the second and third cycle of the GITT of GOpd43, low overpotentials below 100 mV are measured throughout the entire lithiation. A similar profile is also observed during delithiation. At potentials between 0-1 V, low overpotentials can be detected being less than 100 mV as for the preceding lithiation. But at potentials between 1-3 V, a continuous increasing overpotential can be observed which is 735 mV when the galvanostatic discharge reached the 3 V cut-off potential the first time. Additionally, the hysteresis increases for the second and third cycle compared to the first cycle which can be better seen in Figure 108b where all specific charges are normalized to the SOC interval of [0,1]. This approach introduces an error since irreversible reactions like the activation and SEI formation in the first cycle are also taken into account for the normalization. But one can see that the first lithiation shows a more positive insertion potential compared to the 2nd and 3rd lithiation. However, the first three delithiations appear very similar with small differences at potentials positive to 2V.

Figure 108: Galvanostatic-intermittent-titration-technique (GITT) results for a) GOpd43, b) GOpd43 normalized between SOC of [0,1], c) GOpd36 and d) GO, cycling between 0.01-3 V with 5 hours relaxation at a cycling currents of less than 0.015 A/g.
Additionally, the stored specific charge is significantly enhanced for the second and third cycle compared to galvanostatic cycling at 1 C in Figure 78 where 1025 and 955 mAh/g could be inserted compared to 677 and 674 mAh/g during the second and third cycle in Figure 78. But it can be also seen directly that the fading of specific charge is increased for the GITT compared to galvanostatic cycling at 1C which might be related to the increased exposure to very negative potentials negative to 1 V, as shown above in Figure 107. The potential hysteresis between lithiation and delithiation is 1.21 V at an SOC of 0.5 in the second cycle and is not due to diffusional or surface reaction limitations as discussed above. This high hysteresis would lead to high losses during energy storage and is a substantial disadvantage of this material. But it has been shown that this hysteresis decreases significantly with cycling as presented in Figure 78 and Figure 107.

The GITT result for GOpd36 is shown in Figure 108c and shows similar features like the GOpd43 material discussed above. During the first lithiation, the onset of the lithium insertion is shifted to more negative potentials compared to the GOpd43 electrode, as already discussed during the cyclic voltammetry experiments in section 0. Also, slightly increased overpotentials are observed in the beginning of the lithiation which decrease to less than 100 mV at potentials between 0-0.9 V. The overpotentials are even a bit lower than the ones observed for the GOpd43 electrode in Figure 108a. However, this is not an intrinsic material property of GOpd36 but is the consequence of the smaller galvanostatic current rate which is reduced to C/72 since the electrode loading is about 3 mg while the GOpd43 electrode contained 1.77 mg. For comparison, a GITT result for a GOpd43 electrode with increased loading of 4 mg is presented in the appendix in Figure 144 which indicates reduced overpotentials for both lithiation and delithiation at C/80 compared to the GOpd43 electrode in Figure 108a performed at C/35. The relaxation of the C/80 GITT of GOpd43 is much closer to the one of GOpd36 and shows the differences of these very small rates.

During the delithiation of the GOpd36 electrode in the first cycle, very low overpotentials can be detected for the potential window of 0-1 V as for the GOpd43 electrode. But the relaxation overpotentials at potentials more positive than 1.5 V are significantly enhanced. When the galvanostatic delithiation reaches the 3 V cut-off potential for the first time, a relaxation potential of 1.13 V is observed during the subsequent five hours of relaxation. This is a factor of 1.5 times higher than the one of the GOpd43 electrode. During the delithiation close to the 3 V cut-off potential very low specific charge can be extracted during each galvanostatic charge of 30 min indicating very strong limitation as observed for the GOpd43 electrode. No second cycle could be measured due to time restrictions so that the hysteresis in the second and third cycle cannot be evaluated.
The GITT results for pristine graphite-oxide is presented in Figure 108d and shows severe differences to the partially-disproportionated graphite-oxides. During the first lithiation, the reaction onset is shifted to very positive potentials of ~ 2 V and relaxes by more than 600 mV at potentials positive to circa 1.5 V. Afterwards a decrease of the overpotentials can be detected reaching ~140 mV relaxation at potentials negative to 0.5 V vs. Li⁺/Li. During the delithiation, very low overpotentials can be observed in the potential regime of 0-1 V after which the overpotentials rise continuously as for the GOpd electrodes. At potentials positive to 2 V, high overpotentials can be detected as for the GOpd electrodes. The delithiation of the GO electrode seems to behave similar to the GOpd electrodes, judged from the overpotentials during cycling. However, a significantly enhanced irreversible specific charge is measured consistent with the previous findings in sections 4.2.2.3, 4.2.7 and 4.2.8.

Some miscellaneous side remarks are shortly listed here which might help to get more insight into the material properties. During the preparation of lithiated GOpd powder in a glove box the material showed striking electrostatic charge properties, standing vertically away from the steel spoon and glass beaker. It was very difficult to focus the SEM on GOpd due to charging effects. This indicates that GOpd is most probably an insulating material. However, the SEM images of GOpd after lithiation were very easy to take indicating a better electric conductivity.

No color change was observed at 0 and 3 mV vs. Li⁺/Li indicating very different band structure changes in GOpd and GO compared to standard graphite which has several color changes from black to blue to red and finally to golden for the different lithiated phases, pristine graphite, stage 2L, stage 2 and stage 1, respectively.

The XRD patterns of lithiated GOpd showed high reactivity to air and moisture, even stronger than observed for lithiated graphite. During the XRD experiment with pristine GOpd a c-axis increase was detected during 21h XRD measurement in air with a new appearing and constantly growing second peak at smaller 2Theta angle compared to the (002) reflex. This might be due to H₂O insertion from ambient air since no such new reflex was observed in a sealed capillary.
4.3 Summary of chemical modifications of graphite

Two different approaches have been investigated to increase the interlayer distance between the graphene sheets in graphite. First, a titana te coating was applied on potassiated graphite which should spread the graphene sheets on the prismatic edge planes of graphite. A very thick coating with an excess of approximately 50 times the needed amount of titanate was used to detect the coating in SEM images in Figure 65 to Figure 67 and EDX in Figure 68 and Figure 69. Despite the very thick titanate coating, no bands have been detected in the Raman spectra in Figure 70 and Figure 71. This excess of coating leads to higher overpotentials during galvanostatic cycling compared to pristine graphite, as shown in Figure 72. However, a decreased fading of specific charge of the thin-layer electrodes of titanate-coated graphite SFG6 could be detected compared to the thin-layer electrodes of pristine graphite. A coating of graphite with a very thin surface layer of 3-5 atomic layers would be favorable to detect any influence on the charge rate capability due to the applied surface stress.

A second approach aimed to increase the interlayer distance by a chemical pillaring of the bulk material of graphite. A modified form of graphite, namely graphite-oxide (synthesized by Dr. T. Kaspar), has been taken for this approach. But since the amount of epoxide and hydroxide groups is very high in pristine graphite-oxide which would probably lead to high steric hindering and accumulation of reduction products in the interslabs, a partially-disproportionated form of graphite-oxide (GOpd synthesized by Dr. T. Kaspar) has been chosen. Most of the hydrogen is removed during the thermal disproportionation in Argon atmosphere as shown by the elemental analysis in Table 8. This material is ideal for the pillaring of the graphene sheets which are expected to form lithium-alkoxides and/or lithium oxide from the remaining epoxide and hydroxide groups in the GOpd bulk.

Galvanostatic cycling showed significant thermodynamic differences between GO (Figure 76) and partially-disproportionated GO (GOpd36 in Figure 77 and GOpd43 in Figure 78) compared to pristine graphite (Figure 79). The lithium intercalation process observed in standard graphite was replaced by a process similar to adsorption. But this adsorption possesses some extra features which differ significantly from that known for normal capacitor-like materials. The main lithium-insertion occurs at potentials between 0- 0.5 V vs. Li+/Li while standard capacitor materials show a constant specific capacitance with a linearly decreasing potential vs. specific charge profile. Additionally, the reversibly stored specific charge of GOpd43 and GOpd36 is dramatically enhanced compared to standard graphite. In the first delithiation 677 and 580 mAh/g can be extracted for GOpd43 and GOpd36, respectively, being 1.88 and 1.61 times the specific charge than the practical specific charge of the precursor graphite SFG6.
Additionally, the GOpd material can be used to store anions like PF$_6^-$, as also known for graphite intercalation compounds. The galvanostatic cycling, shown in Figure 80, delivers only very low specific charge of $\sim$100 mAh/g in the first cycles which was also shown in the literature [170].

However, for GOpd and GO during lithium insertion and GOpd for hexafluorophosphate insertion, a severe fading of the specific charge has been observed during the first 70 cycles after which the aging rate is reduced significantly and the material ages only by a few percent during the next 400 cycles. Additionally, an irreversible specific charge is observed during these initial 70 cycles after which a cycling efficiency of over 99% is reached. Thus, it can be concluded that the irreversible specific charge might be directly related to the fading of the specific charge decreasing below the specific charge of standard graphite electrodes, as shown in Figure 79. The specific charges in the hundredth cycle are only 107, 259 and 274 mAh/g for GO, GOpd43 and GOpd36, respectively. The pristine graphite electrode shows still 385 mAh/g (of graphite) which is slightly higher than the practical specific charge of graphite SFG6 due to the 10 wt% of SuperP which was shown to add $\sim$32 mAh/g of extra specific charge in the hundredth cycle. The specific charge of the GOpd43 electrode cycled to positive potentials between 3.0-5.0 V is only 63 mAh/g for storing PF$_6^-$-anions after 100 cycles, which is significantly less than the stage 2 in graphite with a composition of (PF$_6$)$_{0.5}$C$_8$ [123]. However, this stage 2 would be reached at 5.5 V vs. Li$^+$/Li while the cycling window of the GOpd43 electrode was limited to 3.0-5.0 V.

To fulfill some of the requirements for the application of the GOpd material in commercial lithium-ion batteries, exfoliation of the material must be avoided and a homogeneous SEI formation should be guaranteed. Therefore, SEM images have been taken confirming no visible exfoliation after the first and even after 400 cycles for GOpd43. Additionally, a SEI of similar morphology as at graphite is created on the GOpd43 particles as shown in Figure 82, in comparison to a standard graphite electrode in Figure 83. But a very thick SEI can be observed on some prismatic edge planes of the GOpd43 particles after more than 400 cycles which might be of rather polymeric origin judged from visual observations in the SEM images. Additionally, small holes can be observed in a very small percentage of pristine GOpd43 particles, as shown in Figure 84. These holes originate probably from the thermal disproportionation leading to a mass loss of circa 11-23%, as calculated in section 4.2.3.

In contrast, SEM images on GO show some signs of a partial exfoliation during the cycling, as depicted in Figure 85. The GOpd36 electrode shows also no visible signs of exfoliation and a homogeneous morphology of the SEI after more than 100 cycles (Figure 86). In contrast, the SEM images of the GOpd43 electrode cycled between more positive potentials of 3.0-5.0 V vs.
Li⁺/Li show a very thick and woven solid-permeable-interphase (SPI) on the surface of the particles depicted in Figure 87. This SPI is partially permeable for the organic electrolyte components, thus, not fully passivating the surface. This is advantageous for the PF₆⁻ insertion since these ions probably show a very low ionic conductivity through a dense inorganic film (like in the SEI on the negative electrode) but does not prevent the oxidation of the electrolyte in every cycle.

The EDX measurements of the cycled GOpd43 electrodes shown in Figure 88 to Figure 91 of section 4.2.4 correspond to the SEM images displayed in the preceding section 4.2.3. They reveal a continuous decrease of the carbon signal while the oxygen, fluoride and phosphorus signal increase continuously during the cycling progress, as shown in Figure 92 and Figure 93. These results support the picture of a continuous SEI growth on GOpd which is mainly finished after the first cycle and approximately doubles during the consecutive 400 cycles. The increasing oxygen content during the SEI formation might indicate a formation of Li₂CO₃ which is a reduction product of the organic carbonate electrolyte. However, no direct proof of Li₂CO₃ could be made. Additionally, LiF seems to be formed with small contributions of phosphorus, as shown in the EDX elemental analysis. The detected traces of chloride and sodium might originate from the synthesis of graphite-oxide from graphite SFG6 by NaClO₃ in conc. HNO₃, as described in section 4.2.1.

To get further information of the SEI composition, XPS has been measured for GOpd43 electrodes where graphite SFG6 and SuperP electrodes have been used for reference. Three different cycling states have been compared which correspond to the pristine, one time lithiated and one full cycle (1x lithiation + delithiation). The carbon signal is reduced during cycling, as also detected for the EDX experiments. The atomic contribution of fluoride increases during the lithiation while it decreases slightly during delithiation of GOpd43. The lithium content shows a similar evolution during the cycling of GOpd43 electrodes. Interestingly, the relative oxygen content decreases after the first lithiation of GOpd43 while it increases significantly for graphite and SuperP carbon. This is in contrast to the results of EDX which show a continuous increase of the oxygen content. However, EDX delivers information from both the surface and parts of the outer bulk material while XPS can only investigate the outermost ca. 10 nm of the surface. Thus, we can conclude that the SEI of GOpd43 seems to be composed of less oxygen-containing species like Li₂CO₃ or Li₂O as compared to the SEI on graphite and SuperP. These results are in conflict with the EDX results and need to be clarified by a third surface sensitive technique.

Very interestingly, the XPS C1s spectrum of lithiated GOpd43 shows more contributions in the binding energy range of 286-289 eV compared to the C-C binding energy at 284.4 eV as shown
in Figure 95b which might indicate a possible increased amount of C-O bonds. But a conclusive deconvolution is impossible due to the limited amount of reference samples and high amount of peaks making it difficult to deconvolute the C1s spectra precisely (evolution of reflex position and amount shown in Figure 95d and Figure 96). In contrast, the O1s, F1s and Li1s XPS spectra are very similar for the lithiated electrodes of GOpd43, graphite SFG6 and SuperP despite the fact that the initial O1s XPS spectra differ significantly for the different materials due to the different oxygen content.

The XRD results in section 4.2.6 give more insight on the modification of the bulk of the different graphite derivatives. The pristine materials show not only the distinct interlayer distance of 5.74, 4.3, 3.6 and 3.35 Å for GO, GOpd43, GOpd36 and pristine graphite, respectively. But they also indicate a modification of the C-C in-plane distance which is 1.438, 1.41, 1.416 and 1.422 Å for GO, GOpd43, GOpd36 and SFG6, respectively. The defects in the structure due to the hydroxide and epoxide groups are probably responsible for these differences although epoxides should usually stretch the C-C bond. However, a decrease of the C-C bond length below the C-C distance in graphite is observed despite the fact that most bulk groups should be of epoxide origin. The results of the attempted refinements of the XRD patterns in Figure 100 are summarized in Figure 101 and Table 10. Very broad reflexes are observed for the (100) and (101) reflex which was attributed to a possible turbostratic disorder [169] but might also come from the stretching and quenching of the C-C bond length due to the epoxide and hydroxide groups in the pristine material, as proposed in section 4.2.6.

During the lithiation of GOpd43, the interlayer distance increases from 4.33 to 5.73 Å. The lithiated interlayer distance of 5.73 Å is very close to the initial interlayer distance of pristine graphite-oxide. Furthermore, the XRD patterns of the lithiated GOpd43 electrode indicate the formation of LiF during the first charge which is consistent with the findings from EDX and XPS. Some minor and very broad XRD reflexes are detected which cannot be assigned to Li2O, Li2O2 and Li2CO3 but could correspond to LiOH as shown in Table 11 and Figure 102.

The XRD patterns after 70 cycles indicate only a very small diffraction of GOpd43 with an interlayer distance of ~5.7 Å for the lithiated electrode but no information about GOpd43 can be extracted from the diffractogram of delithiated GOpd43 after 70 cycles. Only major contributions of LiF can be detected. Therefore, one can only conclude that the partially and very badly defined crystalline structure of GOpd43 gets almost totally lost during cycling.

To test the influence of the pillaring in graphite, cyclic voltammetry has been used at various scan rates. In the first cycle, an activation process can be detected for the GOpd electrodes (Figure 103a and Figure 104a) which is expected since lithium most probably reduces the epox-
ide and hydroxide groups partially. The cyclic voltammetry of GO reveals a very high irreversible specific charge in the first cycle, as also seen during galvanostatic cycling. The capacitance of GOpd electrodes is very high delivering much more than 500 F/g during low scan rates which is a factor of 2.5 compared to today’s best graphene capacitors with TEABF₄ in AN or PC, as shown in Fig. 6c in [170]. The activation in the first cycle can be partially suppressed by high scan rates which do not allow enough time for the reaction to occur, as shown in Figure 106. The activation can be postponed to the second lithiation if the scan rate is simply increased to 10 mV/s compared to the 1 mV/s of the standard activation for electrodes of GOpd and GO.

The rate performance is significantly improved compared to pristine graphite where GOpd43 delivers ~ 200 mAh/g at a scan rate of 100 mV/s (30 s charge). This is a fundamental improvement compared to standard graphite electrodes which can be charged at ~2C (30 min) for standard electrodes. To determine the correct rate-capability of the GOpd material, a thin-layer electrode would be needed since electrolyte diffusion limitations might severely reduce the rate performance. But even the rate tests with a standard electrode show drastic improvements compared to standard graphite electrodes, which was the goal of the chemical modification of graphite.

However, the material suffers from severe fading of the specific charge which decreases the extracted specific charge during the cyclic voltammetry rate test already after a few cycles. The aging rate is one of the biggest challenges since it needs to be very low for a useful battery material as described in paragraph 4.2.2.2. The aging occurs mainly in the first 70 cycles during galvanostatic cycling with constant potential steps but seems to be reduced during cyclic voltammetry with a short potentiostatic step of one minute after the periodic reduction and oxidation.

To test the influence of the applied potential window on the aging, three different potential ranges have been chosen with 1-3V, 0-2V and 0.5-2.5V, as shown in Figure 107. Very low aging is observed during the cycling between 1-3 V while even an enhanced aging rate is detected during the cycling between 0-2V. The potential window of 0.5-2.5 V indicates also some fading of specific charge but the fading is less drastic than in the 0-2 V potential range. This leads to the conclusion that the operation below 1 V vs. Li⁺/Li seems to be responsible for the capacity fading. No assignment of the aging process to electrolyte reduction and/or possible reduction of the surface groups in GOpd can be done.

A second disadvantage of GOpd concerns the large potential hysteresis of this material during cycling. To detect if the hysteresis is due to kinetic limitations or of thermodynamic origin, GITT has been applied. The GITT of GOpd43 in Figure 108 shows a very high hysteresis of ~1.2 V during the second and third cycle. Additionally, very high polarization of more than 700 mV is detected at delithiation between 2-3 V where still a reasonable specific charge can be extracted.
The hysteresis decreases during cycling/aging of the GOpd material, as shown in Figure 107. This very large hysteresis would lead to reduced energy efficiency in practical applications, e.g. in batteries.

Furthermore, the GITT shows an enhanced specific charge during lithiation and delithiation of more than 1000 mAh/g in the second cycle. It was already shown that there are very slow kinetics close to 0 V and 3 V which usually requires a potentiostatic step to deliver most of the specific charge. But such a high increase to 1025 mAh/g in the GITT experiment compared to the galvanostatic cycling of GOpd43 at 1C with 677 mAh/g might indicate a side reaction which could be partially reversible as the specific charge for delithiation also increases.

It can be concluded that the modification of graphite both on the surface and in the bulk can influence the electrochemistry during lithium storage. Even if the rate capability might be improved while also the total specific charge is increased by a factor of ~1.88 compared to standard graphite SFG6 electrode, severe challenges are encountered. The fading of specific charge, high hysteresis of 1.2 V, kinetic limitations close to 0 and 3 V vs. Li+/Li and, finally, the dangerous and time-consuming material synthesis of GOpd have to be overcome to make this material attractive for future lithium-ion batteries.
5. Thermodynamics of graphite

The kinetic influences on the behavior of graphite electrodes have been investigated with regard to limitations caused by diffusion and surface reactions in section 3. But how do the different stage transitions proceed during the course of lithiation and delithiation? The stages in graphite have been summarized in section 2.5 including the different ordering of the lithium ions within the graphite for the stages/phases. Additionally, some investigations for the transitions between these phases have been discussed. But some aspects are still not fully understood like the transitions between the stages in the lower third of the state-of-charge regime between stages 4L-3L-2L.

This chapter focuses on the attempts to model the open-circuit-potential based on the free energy of these phases. Experimental validation will be done by both in situ x-ray powder diffraction and in situ neutron powder diffraction to get more insight on the stage transitions at low state-of-charge. Additionally, calculation of the orientation of the phase boundaries during the transition will be carried out to complete the thermodynamic picture of graphite.

5.1 Modeling approach for open-circuit-potential of graphite

Several different models have been developed in the past thirty years to describe battery systems. The most complete model describing the kinetic influences in a porous electrode has been developed by researchers around Newman [146, 147]. It includes diffusion in the solid and electrolyte, ohmic losses in the solid matrix and electrolyte, current distribution and surface reactions, as shortly introduced in section 2.7. This model has been extended by impedance models and thermal models accounting for Joule heating [196]. The model can predict performance of lithium-ion batteries very well and can be applied to estimate the aging influences in lithium-ion batteries [197].

However, one of the major disadvantages of this model is the use of the open-circuit-potential as a measured input parameter rather than a derivation from a modeling approach. This issue has been approached by Ceder et al. [63, 151] for olivines, LiMPO₄ (M=Fe, Mn, Co, Ni) in 2004 and further developed to a model predicting electrochemical response under cycling conditions by Bazant et al. [65, 66] with surface reactions and diffusion. This approach will be used and applied to graphite which shows also several different phase separations like the one in LiFePO₄. This approach has been developed by M. Heß and M. Z. Bazant before this PhD work and is only shortly mentioned here.
The free energy of a material can be described by eq (5.1) with a homogeneous free energy \( f(c) \) and an electronic contribution being responsible for the open-circuit-potential offset to a reference electrode, e.g. \( \text{Li}^+/\text{Li} \). Additionally, a gradient energy penalty \( K \) accounts for the energy which is needed to create a phase boundary in the system based on the model by Cahn and Hilliard [132-135]. The free energy \( G(c) \) depends on the normalized concentration of lithium ions \( x \) in the host at each state-of-charge \([0, 1]\), the maximum density of lithium ions in the host material \( \rho \), the electronic potential shift by the electron charge \( e \), and the potential difference \( \Delta \Phi \).

The homogeneous free energy \( f(c) \) is a function of an enthalpy part and entropy of mixing part in eq. (5.2) where “a” is the enthalpy factor and \( k_b \) the Boltzmann constant. If “a” is higher than 2\( k_b T \), the material separates into two different phases while it is forming a solid solution for values smaller than 2\( k_b T \). Note that the temperature \( T \) changes the ratio so that at high temperature the material always forms a solid-solution which is very common as also seen for \( \text{LiFePO}_4 \) [45] and graphite [89, 92].

This concept is extended by an introduction of an enthalpy term for all interlayer interactions for several graphite interslabs, as shown for 12 layers in eq. (5.3). The repulsive enthalpy factor, \( a_j \), is chosen to decrease with distance by an exponent of -5 which is a higher than the one of van-der-Waals forces of \( \exp(-6) \). This value was chosen based on the modeling of Millman et al. [125, 126] while all exponents smaller or equal to -4 work for the repulsive interaction.

\[
G(c) = \int \left( \rho_{hi} (f(c) + e\Delta \Phi c) + \frac{1}{2} \nabla c K \nabla c \right) dV
\]  (5.1)

\[
f(c) = ac(1 - c) + k_b T \left( c \ln c + (1 - c) \ln(1 - c) \right)
\]  (5.2)

\[
\sum_{j=2}^{7} \left( a_j \sum_{i=1}^{12} c_i c_{i+j-1} \right)
\]  (5.3)

\[
a_j = \text{const} \left| i - j \right|^{-5}
\]  (5.4)

The results of the modeling of two interslabs in graphite results in a very simple 2D free energy if one allows the concentration of lithium in the first and second interslab to vary. The free energy landscape based on the concentrations is shown in Figure 109a). One can see that the direct pathway from an SOC of zero to one has a positive free energy. But the path to fill one layer first after which the second layer is filled allows a pathways being less energetically expensive. Since the pathway through stage 2, with only one layer filled while the second is nearly empty, would also need a positive free energy. Thus, phase-separation is favored and the minimal trajectory through the energy landscape is the preferred pathway. Moreover, it can be observed that the fill-
ing of the interslabs is symmetric. If the first or second interslab is filled with lithium ions is energetically the same which shows the symmetry of this calculation.

Additionally, the optimal trajectory is calculated along the minimal free energy and leaves the free energy landscape at the miscibility gap where phase separation is initiated. Usually, a continuation until the spinodal gap is allowed, however, nucleation can occur between the miscibility and spinodal gap. The spinodal gap is characterized by a free energy $\Delta G=0$ while the miscibility gap reflects the energetic minimum of a phase by variation of the concentration. Additionally, one can see that a small solid-solution regime is allowed for each pure phase (graphite, stage 2 and stage 1) at room temperature which is consistent with the phase diagram in Figure 9c on page 17.

The open-circuit-potential can be derived from the optimal trajectory of the free energy from equation (5.5) with the chemical potential $\mu$ and the homogeneous part of the chemical potential symbolized by a bar on $\mu$ in eq. (5.6).

$$\mu = \frac{dG}{dc} = \bar{\mu} - \nabla \cdot KVc$$

(5.5)

$$\bar{\mu} = \frac{df(c)}{dc} = a(1 - 2c) + k_B T \ln \left( \frac{c}{1 - c} \right)$$

(5.6)

The derived potential profile is shown in Figure 109b and matches some of the features of an experimentally determined galvanostatic lithiation of graphite. Both the crystallographic ordering of lithium in every second and every interslab for stage 2 and stage 1 and the allowed solid-

![Figure 109: Modeling of graphite to stage 2 to stage 1 transitions in the Lithium-graphite system, a) free energy of graphite depending on lithium concentration in 1st and 2nd interslab, b) resulting calculated open-circuit-potential compared to experiment.](image-url)
solutions of the pure phases are captured sufficiently. Deviations of this simple mean-field model are observed at the potential profile in the solid-solution regime of the phases and for the low state-of-charge region where several other phases (stage 4L, 3L and 2L) are known to exist.

To include these higher stages, the model has been extended by a simulation with twelve independent interslabs in graphite where the interactions between the layers are of repulsive origin as modeled by eq. (5.3) and (5.4). If one assumes the same in-plane density of LiC₆ for these higher stages, one can calculate the respective open-circuit-potential versus the SOC which is presented in Figure 110a. One can observe that the interactions cannot capture the features of the low state-of-charge region at all.

In contrast, if one allows the concentration of all stages to vary between LiC₆ and LiC₁₄ in-plane density in the interslabs, one can resemble the phase diagram and open-circuit-potentials much better as shown for the OCP in Figure 110b. But also higher stages like stage 5 and stage 6 with LiC₆ in-plane density form with this model. To get a better picture of the stage transitions especially at low state-of-charge, experimental data are needed which might clarify if a certain ordering exists and why higher phases do not form although they form in the potassium-graphite phase diagram until stage 8 [92, 100].

Figure 110: Modeling of graphite stage transitions capturing the full state-of-charge of the Li-graphite system at room temperature, a) stage 6-4-3-2-1 transition, b) stage transitions with reduced in-plane density of LiC₁₄ for higher stages.
5.2 X-ray diffraction of graphite

To study the phase transitions during lithiation of graphite, in situ x-ray powder diffraction has been carried out at the Swiss Light Source of the Paul-Scherrer-Institute. The goal was the detection of the transitions especially at the low state-of-charge. Previous XRD studies on Li-graphite have found a continuous shift of the c-axis during the transitions from stage 4L-3L-2L [88, 97]. However, a continuous shift in the c-axis is theoretically not possible since the lithium is confined to the interslabs in graphite which has a very distinct interlayer distance even during the different stages. Therefore, an own in situ XRD study has been carried out which will be compared to in situ neutron diffraction results on graphite during lithiation. This section will first describe the experimental setup of the experiment, and finally describe the evolution of the measured XRD pattern for galvanostatic and GITT mode.

Self-standing electrodes of graphite SFG44 (Timcal) have been chosen for the experiments due to the high-crystallinity (section 3.4.1) but lower BET specific surface area compared to SFG6, thus, resulting in less SEI formation. Electrode material slurries were prepared by dispersing 80 wt% graphite SFG44 and 20 wt% polyvinylidene fluoride (PVDF, Kynar flex) in acetone. Test electrodes were prepared by doctor-blading the slurries on a PTFE surface at a slurry thickness of 400 µm after which the slurry was allowed to dry at room temperature and ambient pressure for several minutes. The dry film was peeled off the PTFE foil and cut into ~20x20 mm electrodes. A hole of 8 mm diameter was punched into a copper mesh which is used as the current collector. The self-standing electrode was calendared onto the copper mesh after which the composite was dried for >12h at 120 °C in vacuum and assembled in an argon-filled glove box (O₂, N₂, H₂O and active carbon filters). Lithium metal (99.9 %, Sigma Aldrich) served as counter and reference electrode and was also rolled on a copper mesh (also with a center hole in the Cu mesh).

The cells were assembled in a pouch cell configuration where the aluminum casing was punched out in the center and replaced by a polyimide window (kapton). Additionally, a polypropylene window was added. Polyimide hinders oxygen and nitrogen diffusion while polypropylene is prohibiting moisture diffusion through the cell. The electrodes were placed so that the hole in the copper mesh was located at the beam window. A glass-fiber separator was placed between the electrodes and soaked with 1M LiPF₆ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) 1:1 wt%. The pouch cells were vacuum sealed and placed in a metal casing with hard rubber at the electrodes through which a mechanical pressure is applied on the cells. Also samples with the standard pouch cell configuration without a kapton/polypropylene window have been used.
All electrochemical measurements were performed at room temperature using a sample changer especially designed for the MS powder beamline at the Swiss Light Source from PSI [198]. The wavelength of the incident beam was chosen to be $\lambda = 0.7085$ nm which is very close to Mo $K_\alpha$ wavelength. A Mythen detector was used in the range of -60 to -5 and 5 to 60 degree in $2\Theta$.

First, two different sets of electrochemical cycling profiles were chosen for the in situ XRD investigation. Figure 111 show these two different sets with the galvanostatic cycling at C/10 rate until almost full lithiation and a galvanostatic-intermittent-titration-technique GITT (see introduction section 2.6.1c) for reference). The GITT was performed at C/20 rate with galvanostatic steps until the current decreased to C/50 rate followed by a relaxation of ten minutes.

The first set allows analysis of all stage transitions during lithiation between stages 4L, 3L and 2L. The GITT allows a relaxation to detect if changes occur. Differences might indicate metastable phases or kinetic influences which would make ex situ XRD samples different from in situ measured ones. These cells were the first samples measured and used a standard pouch cell configuration without a kapton/polypropylene window. Thus the reflexes from the cubic aluminum do contribute to the diffraction pattern. Additionally, an “amorphous” bump below 10 degree in 2Theta is observed which might come from the glass-fiber separator.

Zooms of the diffraction patterns between 11.4- 12.4° and 18.8- 20.8° are shown in Figure 112 for the galvanostatically cycled graphite SFG44 electrode (first row) and the GITT condition (second row). One can clearly observe the changes of the (00z) reflex starting at $\sim 12.1^\circ$ and shifting to lower angles. This indicates an expansion of the c-axis which is consistent with previous findings (summarized in Table 3 in section 2.5). Additionally, a phase separation can be observed between 0.22- 0.2 V vs. Li$^+$/Li which corresponds to the first potential plateau in Figure 111. Between 3.0- 0.22 V and 0.2- 0.12 V a rather continuous shift of the (00z) reflex can be observed which might indicate a solid-solution-like intercalation behavior.

Figure 111: Electrochemical cycling of graphite SFG44 for in situ x-ray powder diffraction with a) galvanostatic cycling between SOC = [0,1] at C/10 and b) GITT in SOC = [0,~0.3] at C/20 rate with potentiostatic step (ps) and 10 min relaxation (OCP).
The zoom between 18.8- 20.8° in 2Theta of Figure 112 gives even more insight. A phase separation can be clearly observed between 0.11- 0.07 V which corresponds to the stage transition between stage 2L/3L and dense stage 2. Another phase transition can be detected between 0.07-0.04 V corresponding to the stage transition between stage 2 and 1. Both these transitions show a potential plateau during galvanostatic cycling. Special features shows the diffraction pattern between 0.2- 0.11 V where two new reflexes are observed which shift continuously apart from the initial reflex at ~20.1°. These new reflexes might belong to the stages 4L, 3L or 2L.

However, a strong reflex from aluminum can be detected at ~20.2° which is partially superposed to the graphite reflex. The intensity of the aluminum reflex is ~20x more intensive, thus, making the Rietveld refinement of the graphite pattern at this reflex almost impossible. Additionally, the error from the refinement is very high. Therefore, in situ neutron diffraction results have been Rietveld refined and used for the phase identification as shown in the next section.

Figure 112: X-ray diffraction pattern of graphite SFG44 in EC/ DMC 1:1, 1M LiPF₆ at 300K with wavelength λ= 0.7085 nm, a) during galvanostatic charge at C/10 in Figure 111a, b) during GITT measurement as shown in Figure 111b.
5.3 Neutron powder diffraction

This section has been published in parts [199] and [200] and the figures and parts of the text are adapted for the experiments done on graphite. Neutron powder diffraction was conducted at Institut-Laue-Langevin in Grenoble, France. The goal was the investigation of structural transitions during the lithiation of graphite in the state-of-charge range from 7-30 %. The transition should proceed from stage 1L to stage 4L by a phase separation. The next proposed transitions are a bit unclear and involve the transitions to stage 3L and stage 2L where the L in the name of the stages symbolizes the dilute disordered lithium order in the respective stages. The last transitions include dense stage 2 with LiC₆ in-plane order every second interslab. The end structure consists of LiC₆ in-plane ordering in every layer which is dense stage 1. A detailed description of the stage and phase transitions is summarized in the introduction section 2.5.

For the experiment 200 mg of graphite powder, SFG44 (Timcal), was used with deuterated EC: DMC 1:1 (wt) with 1M LiPF₆ containing 6.8 ppm of water (determined by Karl-Fischer-titration). A glass fiber separator and a lithium metal counter electrode were used. Only the first lithiation was investigated. During this cycle a solid-electrolyte-interphase is formed consuming some extra lithium and electrolyte. The SEI formation was performed starting from 3V and also inserting lithium until the potential decreased to 0.22 V vs. Li⁺/Li. During the formation 80 mAh/g were consumed from which ~25 mAh/g are reversible [88].

Figure 113 shows the galvanostatic cycling of the graphite half-cell in deuterated electrolyte. Point 1 indicates the starting point in the beam at ILL in stage 1L after the main SEI formation

![Figure 113: Electrochemical lithiation of graphite SFG44 powder during in situ neutron powder diffraction from point 1-5, continued cycling of the cell done without neutron diffraction due to time restrictions at ILL to show proper cycling behavior, experiment performed at 50°C [199].](image-url)
has been finished. Point 2 refers to a full lithiation of stage 1L with circa 7% lithium inserted as a solid solution in pristine graphite. Point 3 indicates the assumed stage 4L, point 4 depicts assumed stage 3L and point 5 indicates expected stage 2L. These will be used for the Rietveld refinement later on. The markers “x” and “+” indicate the interruption of the cell current due to e.g. transport and a short current density increase, respectively.

These points are also marked in Figure 114 in the same color. Obvious is the phase separation between point 2 and 3 which is accompanied by the phase separation potential plateau in the potential vs. time plot. But interestingly, from point 3 to 5 we see something like a solid solution and no distinct stages as also seen by previous work [88, 97]. It can also be seen that the reflexes

![Diffraction Patterns](image)

Figure 114: Evolution of diffraction patterns during electrochemical lithiation of graphite for a) $2\Theta = 20-56^\circ$ and b) $2\Theta = 76-124^\circ$ with wavelength 1.36 Å (high resolution with a collimator, indexes marked with “x” for titanium container and “*” for graphite P63/mmc starting structure, experiment performed at 50°C [199].
of the titanium container marked with an “x” do not overlap with the most significant reflexes of graphite marked with a “*”. Additionally, the intensities of the titanium reflexes are only of the same order of magnitude as the graphite ones.

However, one needs to evaluate the pure phases before one can investigate the different transitions between them. Therefore, ex situ neutron powder diffraction patterns have been collected on at least 400 mg of lithiated graphite powder for various lithiation degrees. The space groups of dense stage 1 and stage 2 [80], and the ones of the starting material with AB [107] and ABC stacking [109] are known and summarized in Table 3 on page 18. The NPD diffractions patterns of these phases are shown in Figure 115. All diffraction patterns consisted of at least two different phases, e.g. small contributions of dense stage 2 in almost pure stage 1 (94%) for Figure 115a. Stage 2 shows some contributions of stage 1 (32%) in the delithiated sample which was partially discharged from stage 1 as shown in Figure 115b.

![Rietveld refinements of patterns from ex situ NPD](image)

Figure 115: Rietveld refinements of patterns from ex situ NPD for a) charged stage 1, b) discharged stage 2, c) charged stage 2 and d) graphite starting material at $\lambda = 1.36$ Å.
In contrast, the NPD pattern of stage 2 in Figure 115c shows contributions from both stage 2L and stage 3L. This sample was prepared by lithiation of graphite and therefore undergoes the transition from stage 3L-2L-2 in contrast to the sample in in Figure 115b which was delithiated from stage 1. The starting material graphite SFG44 shows two phases with AB stacking (hexagonal P63/mmc) and the metastable defect structure with ABC stacking (rhombohedral R-3m) with a ratio of 72:28 as shown in Figure 115d. This ratio is slightly higher with respect to published data based on XRD with only 17% contribution of the ABC stacking in SFG44 [156].

To facilitate a proper refinement of the measured NPD patterns, a standard (Na2Ca3Al2F14) has been measured before the NPD of the various Li-graphite samples, as shown in the appendix in Figure 145. The Rietveld refinement matched well with literature data of Na2Ca3Al2F14 (I213, a=10.257(1) Å [201] and deviated only on the third digit of the a-parameter. The zero-shift is -0.31 degree which is acceptable for neutron powder diffraction.

The Rietveld refinements of the different NPD patterns of graphite in Figure 115 are summarized in Table 12 on page 169. The crystallographic parameters determined from the refinement show also slight variations on the third digit compared to the parameters from different studies with XRD (Table 3 on page 18). The refinement of stage 1 is the best compared to all other phases. For all other phases, a higher error (Rwp) is determined for the refinement which comes primarily from the different FWHM of the crystallographic directions. The experimental FWHM of the (300) reflex is much smaller compared the one of the (002) direction, however, the reflex width was fitted with the same parameter set. The (xy0) reflexes are well defined and the calculated NPD pattern possesses a higher FWHM. In contrast, the FHWM of the (00z) reflexes are broader than the calculated ones, thus, indicating a higher order in-plane than between the graphene planes. This is very reasonable since the bond is very well defined within the aromatic graphene sheets but bonded less strongly between the different graphene planes by van-der-Waals forces in pure graphite. Since stage 1 does not possess any pure graphite interslab, no such deviation between (xy0) and (00z) reflexes is observed. In contrast, stage 2, 2L, 3L, 4L and graphite have 1, 1, 2, 3, and infinite interslabs of highly lithium-deficient interslabs, thus, showing the anisotropy between the (xy0) and (00z) reflexes.

Next, the diffraction patterns of the remaining stages 2L, 3L, and 4L are investigated in the low state-of-charge region. Despite various attempts to solve the space group of these stages, the respective space groups are still not identified. Usually, single-crystal diffraction is used to determine an unknown space group of a compound, however, only helped to find the a- and c-axis parameters of stage 2L and 3L (Table 3) [90, 91] without a corresponding space group. For stage 4L, only the repeated distance in c-direction could be extracted so far [88, 97].

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The refined patterns of stage 3L, 4L and 1L are shown in Figure 116e-h (a-d are shown in Figure 115 to be compared together in Table 12). The first pattern shows Li-graphite charged to 130 mV which consists of pure stage 3L as shown in Figure 116e despite the fact that stage 2L was expected. The refinement shows the discussed anisotropy of the measured reflex width for the (xy0) and (00z) reflexes. For the first time, a space group could be assigned. Hexagonal P6/mmm with a stacking sequence of A|ABA|A fits the best.

Another sample of Li-graphite which is discharged to 160 mV consists of a composite of stage 3L and 4L where the hexagonal space group P63/mmc with a stacking of A|ABAB|BABA|A and a repeated c-axis of 27.16 Å fits best and indexes all reflexes. The refined diffraction pattern is presented in Figure 116f. For the first time, a reasonable error of Rwp = 4.5 was determined for the refinement.

Figure 116: Rietveld refinements of ex situ NPD patterns of e) pure stage 3L after charge to 130 mV, f) discharge state at 160 mV with stage 3L and 4L, g) charge state at 190 mV with stage 3L and frustrated stage 4L, h) charge state at 220 mV with pure stage 1L (graphite solid-solution).
In contrast, the lithium-graphite sample being charged to 190 mV consisted of stage 3L with a contribution of “frustrated” stage 4L despite the fact that pure stage 4L should be present at this charge condition. The refined diffraction pattern is shown in Figure 116g. The name “frustrated” stage 4L originates from the badly defined peak position of several reflexes of stage 4L during charge compared to discharge. The difference of the diffraction patterns for charge and discharge are shown in Figure 117 where the reflexes are highly broadened for stage 4L during charge (cyan). The charge rate was only C/100 for the sample preparation after which a potentiostatic step of several days was applied with approximately three days of relaxation before the NPD was measured. Despite these very mild conditions, stage 4L does not develop sufficiently during charging. In contrast, the delithiation to 160 mV shows distinct reflexes of stage 4L.

Figure 116b and c give also more details on stage 3L. The c-axis parameter of stage 3L varies strongly for the different state-of-charge conditions (potential cut-offs). The higher the state-of-charge of stage 3L, the higher is the c-axis parameter of stage 3L. This indicates a so-called solid-solution within the phase of stage 3L. This would also explain the sloppy potential profile of the lithium-graphite intercalation compound in the region between ~11-18 % state-of-charge (potential of 200-130 mV) which cannot be due to a phase separation. The finding of the broad solid-solution regime of stage 3L supports the findings of the thermodynamic mean-field model presented in section 5.1 which lead to this investigation.

Last, the NPD pattern of the solid-solution regime of graphite (stage 1L) is presented in Figure 116h. A pure hexagonal phase with AB stacking can be observed. The rhombohedral defect found in the starting material at 3V in Figure 115d cannot be detected anymore. This means that ~5% lithiation within the solid-solution regime of graphite remove the stacking defect to a non-

![Figure 117: Comparison of measured stage 3L and 4L during discharge to 160 mV and charge to 190 mV indicating frustrated stage 4L (weakly developed reflexes of stage 4L in pink).]
detectable amount. The c-axis is slightly expanded compared to the starting material graphite SFG44 which is due to the disordered lithium-insertion in every interslab without the change of the stacking order, as also reported earlier [88-90, 97].

The summary of all refinements of the ex situ neutron powder diffraction patterns of the standard and the various lithium-graphite-intercalation compounds is presented in Table 12. The entries under a)- h) correspond to the diffraction pattern in Figure 115a-d and Figure 116e-h, respectively. The order of the entries shows the highest lithiated phase on top and descends with decreasing lithium content in the respective phase.

To visualize the extracted evolution of the a- and c-axis parameter, the calculated distances have been plotted in Figure 118. The carbon-carbon distance within the graphene sheets can be calculated from the a-axis parameters of the different stages and is depicted in Figure 118a. The state-of-charge in the plot is approximated with respect to a standard cycle, although only the formation cycle has been used to prepare the ex situ samples. Therefore, small errors in state-of-charge determination are expected. However, a clear linear trend can be observed indicated by a dashed line in Figure 118a. This means that the graphene sheets are very slightly expanding with

Table 12: Rietveld refined cell parameters of various ex situ samples of neutron powder diffraction with their respective name, charge/discharge state, space group and refinement parameters.

<table>
<thead>
<tr>
<th></th>
<th>ch/dis, voltage</th>
<th>Space group</th>
<th>a-axis</th>
<th>c-axis</th>
<th>FWHM</th>
<th>fraction [%]</th>
<th>Rwp/zero shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$Ca$_3$Al$<em>2$F$</em>{14}$</td>
<td></td>
<td>1213</td>
<td>10.25049</td>
<td>0.32</td>
<td>100</td>
<td>8/-0.31</td>
<td></td>
</tr>
<tr>
<td>a) Stage 1</td>
<td>ch 0.01V</td>
<td>P6/mmm</td>
<td>4.31694</td>
<td>3.70298</td>
<td>0.37</td>
<td>94</td>
<td>5/-0.28</td>
</tr>
<tr>
<td>a) Stage 2</td>
<td></td>
<td>P6/mmm</td>
<td>4.29028</td>
<td>7.03667</td>
<td>0.48</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>b) Stage 1</td>
<td>dis 0.12V</td>
<td>P6/mmm</td>
<td>4.31785</td>
<td>3.70285</td>
<td>0.35</td>
<td>32</td>
<td>7/-0.25</td>
</tr>
<tr>
<td>b) Stage 2</td>
<td></td>
<td>P6/mmm</td>
<td>4.29204</td>
<td>7.03773</td>
<td>0.45</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>c) Stage 2</td>
<td>ch 0.1V</td>
<td>P6/mmm</td>
<td>4.29117</td>
<td>7.02487</td>
<td>0.55</td>
<td>26</td>
<td>4.5/-0.3</td>
</tr>
<tr>
<td>c) Stage 2L</td>
<td></td>
<td>P63/mmc</td>
<td>2.47135</td>
<td>14.12953</td>
<td>0.46</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>c) Stage 3L</td>
<td></td>
<td>P6/mmm</td>
<td>2.46852</td>
<td>10.40365</td>
<td>0.42</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>e) Stage 3L</td>
<td>ch 0.13V</td>
<td>P6/mmm</td>
<td>2.46708</td>
<td>10.41872</td>
<td>0.42</td>
<td>100</td>
<td>11/-0.28</td>
</tr>
<tr>
<td>Stage 3L</td>
<td>ch 0.16V</td>
<td>P6/mmm</td>
<td>2.46588</td>
<td>10.38789</td>
<td>0.42</td>
<td>100</td>
<td>10/-0.31</td>
</tr>
<tr>
<td>f) Stage 3L</td>
<td>dis 0.16V</td>
<td>P6/mmm</td>
<td>2.46835</td>
<td>10.37033</td>
<td>0.44</td>
<td>44</td>
<td>4.5/-0.24</td>
</tr>
<tr>
<td>f) Stage 4L</td>
<td></td>
<td>P63/mmc</td>
<td>2.46609</td>
<td>27.15605</td>
<td>0.4</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>g) Stage 3L</td>
<td>ch 0.19V</td>
<td>P6/mmm</td>
<td>2.46656</td>
<td>10.33613</td>
<td>0.47</td>
<td>55</td>
<td>8/-0.22</td>
</tr>
<tr>
<td>g) Stage 4L</td>
<td></td>
<td>P63/mmc</td>
<td>2.46585</td>
<td>27.19822</td>
<td>0.33</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>h) Stage 1L</td>
<td>ch 0.22V</td>
<td>P63/mmc</td>
<td>2.46279</td>
<td>6.76532</td>
<td>0.41</td>
<td>100</td>
<td>10/-0.30</td>
</tr>
<tr>
<td>Stage 1L</td>
<td>dis 0.5V</td>
<td>P63/mmc</td>
<td>2.46271</td>
<td>6.74683</td>
<td>0.45</td>
<td>100</td>
<td>8/-0.29</td>
</tr>
<tr>
<td>Stage 1L</td>
<td>dis 0.5V</td>
<td>P63/mmc</td>
<td>2.46283</td>
<td>6.73300</td>
<td>0.46</td>
<td>100</td>
<td>8/-0.29</td>
</tr>
<tr>
<td>d) graphite</td>
<td>pristine ~3V</td>
<td>P63/mmc</td>
<td>2.46290</td>
<td>6.71653</td>
<td>0.32</td>
<td>72</td>
<td>8/-0.27</td>
</tr>
<tr>
<td>d) graphite</td>
<td></td>
<td>R-3m</td>
<td>2.46290</td>
<td>10.07154</td>
<td>0.37</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>dis 3V</td>
<td>P63/mmc</td>
<td>2.46280</td>
<td>6.71542</td>
<td>0.4</td>
<td>100</td>
<td>7/-0.27</td>
</tr>
</tbody>
</table>
increasing lithium content. The slight increase is consistent with a high elastic stiffness factor in-plane of graphite ($c_{11}$ in [186]) and the covalent bond in graphene.

In contrast, the c-axis distance increases significantly with increasing lithium content. The average distance between two graphene layers is calculated by the quotient of the c-parameter and the amount of graphene layers of the respective stacking and averages the lithium-containing and lithium-deficient interslabs. The average c-axis distance is shown in Figure 118b. Two different slopes can be observed. For stages 1L, 3L, and 2L a continuous increase of the average c-axis distance can be observed. However, stages 4L and 2 show a strong deviation from this trend. Most probably this can be attributed to the rearrangement of the stacking sequence of the graphene layers. From stage 1L to 4L every fourth graphene layer shifts to match the next neighbor

Figure 118: Evolution of crystallographic parameters with degree of lithiation/delithiation for Li-graphite stages, a) carbon-carbon in-plane distance in graphene sheets, b) average graphene-graphene interslab ($C||C$) spacing, c) estimated graphene-Li-graphene distance (intercalated layer), d) measured interlayer distance of stage 1L above 700K (Fig. 3a of chapter 3 in [120]).
graphene sheet storing the lithium in the interslab (AB to A|ABAB|BABA|A stacking). Also the stacking sequence changes from stage 2L to 2 with A|AB|B to A|AA|A stacking. However, it is unclear why the average C||C distance of pristine graphite, stage 4L, 2 and 1 are almost on the same line.

One can also estimate the distance of the lithiated interslabs by subtracting the pure graphite C||C distance of 3.358 Å (Table 12) from the repeated c-axis distances. If one compares the evolution of the lithiated interslab distance in Figure 118c with results of the lithium-graphite system at >700K in Figure 118d [120] one can see similarities. However, Figure 118d shows the increase of pure stage 1L since only a homogeneous liquid-like filling of every graphite interslab is observed. One can see that the filling in the respective stages might follow such a solid-solution filling in every, every fourth, and finally every third interslab. Stage 2L possesses already a similar C-Li-C interlayer distance as stage 1. Stage 2 might deviate due to the compression of the empty interslab in the AaAAaA stacking to 3.245 Å instead of 3.358 Å assumed for the calculation which was shown by Billaud et al. [90]. This finding can explain the sloppy potential profile in this SOC regime and support the electrostatic interactions modeled in section 5.1.
5.4 Graphite elastic energy modeling

Graphite intercalation might be possible to be modeled based on the Cahn-Hilliard approach [132-135] where the free energy could be mimicked by a mean-field approach, as shown in section 5.1. But elastic effects seem to have a major contribution towards the formation of stages based on the findings from the overpotentials at very low cycling rate in section 3.5, the modification of graphite with chemical pillars in section 4.2, and the findings of the expansion of the crystallographic space group during lithiation in section 5.2 and 5.3. Therefore, this section focuses on the elastic energy calculations based on the theory of Khachaturyan [202] which have been applied to LiFePO₄ by Cogswell and Bazant [48]. These calculations have been extended to graphite together with these authors with the numerical code of D. Cogswell for Mathematica and Matlab [48] which was adapted for the requirements to model graphite.

The free energy of eq. (5.1) in section 5.1 is extended by an elastic energy contribution, as shown in eq. (5.7) [48] where $e$ is the strain and $C$ the elastic stiffness matrix. The rest of the free energy in eq. (5.7) and the homogeneous free energy in eq. (5.8) are the same as described in section 5.1. The elastic strain in eq. (5.9) can be described as a homogeneous free strain for uniform deformation $\varepsilon(\text{bar})$, a term for inhomogeneous strain due to composition inhomogeneity $u_{i,j}$, and lattice misfit strain between two phases of graphite $\varepsilon_0$ which is assumed to be linear dependent on the concentration in the host structure.

$$G(c) = \int \left( \rho c \left( f(c) + e\Delta\Phi c \right) + \frac{1}{2} \nabla c K \nabla c + \frac{1}{2} \varepsilon_{ij} C_{ijkl} \varepsilon_{kl} - \epsilon_{ij} \epsilon_{ij} \right) dV \quad (5.7)$$

$$f(c) = a c (1 - c) + k_y T \left( c \ln c + (1 - c) \ln (1 - c) \right) \quad (5.8)$$

$$\varepsilon_{ij}(x) = \tilde{\varepsilon}_{ij} + \frac{1}{2} \left( u_{i,j} + u_{j,i} \right) - \varepsilon_{0}^c c(x) \quad (5.9)$$

The electrochemical surface reactions can be described by Butler-Volmer equation, eq. (5.10), and the overpotential is defined as the difference between applied and equilibrium potential in eq. (5.12). Note that the overpotential depends not only on the concentration as in the standard kinetic model by Newman et al. [146, 147] described in section 2.7 but also on its gradient.

$$j = j_0 \left( e^{\frac{-\alpha F \eta}{RT}} - e^{\frac{(1-\alpha) F \eta}{RT}} \right) \quad (5.10)$$

$$I = \int \frac{\partial c}{\partial t} dA \quad (5.11)$$

$$\eta(c, \nabla^2 c) = \Delta\phi - \Delta\phi_{eq} = \frac{\partial G(c, \nabla^2 c)}{\partial c} \quad (5.12)$$
The system needs to be stress free which leads to the boundary conditions:

$$\nabla \cdot \sigma_{ij} = 0 \quad (5.13)$$

$$\int_y C_{ijkl} e_{ij}(x)dV = 0 \quad (5.14)$$

For the phase boundary orientation Khachaturyan [202] developed equation (5.15) to calculate the interfacial energy assuming the same elastic constants for both phases (C_{ijkl}) which is a good approximation in the case of graphite since the elastic constants of graphite and stage 1 LiC₆ vary only by a few percent [186].

$$B(n) = C_{ijkl} e_{ij} e_{kl}^0 - n_j \sigma_{ij}^0 \Omega_{ij} (n) \sigma_{lm}^0 n_m \quad (5.15)$$

Taking the elastic constants from DFT calculation [186] for stage 1 and the lattice constants of stage 1 and stage 2 in graphite [80] we get the minimal elastic energy in (305) direction which is isotropic around this crystallographic angle of 58° vs. the graphene planes as depicted in Figure 119. A 2D zoom into the cross-section in Figure 119 gives us the shape of the elastic energy as depicted in Figure 120. The minimum elastic energy pressure is 29.8 MPa which is relative small compared to LiFePO₄ with 190 MPa [48]. The axis in Figure 120 correspond to the crystal directions a (100) and c-axis (001).

Figure 119: Calculated elastic energy of graphite during stage 1 to stage 2 delithiation, minimum energy in (305) direction and isotropic around the (001) vector due to hexagonal lattice.

Figure 120: 2D cross-section of elastic energy in ac-plane based in Figure 119.
One can test if the minimum is well defined by variation of interfacial energy $B(n)$. If a variation of the elastic energy is allowed to be 1% of the total interfacial energy one can see that the minimum is only slightly perturbed. The crystallographic angle of the minimum energy corresponds to 58 degrees towards the graphene layer. If an energy perturbation of 1% is allowed we get a difference in the angle of $58 \pm 5.2$ degree. The minimum and the perturbation of the energy by 1% to 101% are shown in Figure 121. The orange line indicates the minimum and 1% additional energy. This means that the phase boundary aligns preferably in (1 0 1.64) direction or 58° in the crystal. During lithiation and delithiation the interface between stage 1 and stage 2 tries to align in this crystal direction. The crystal direction (1 0 1.64) corresponds to $\sim 76^\circ$ with respect to the graphene sheets if one observes the interface based on the SEM images or macroscopic dimensions (in crystal direction 58° as discussed above). Insertion of lithium in graphite is mainly confined in (xy0) direction since the graphene layers do not allow lithium diffusion at room temperature and grain boundary diffusion is very slow [160].

The calculation can be performed for all stage transitions. However, the values of the elastic constants are only available for graphite and stage 1 LiC$_6$ [186]. Thus, an assumption is made which averages the respective elastic constants for the different stages by a linear combination of the known end phases. That means that stage 2 is assumed to be half the elastic constants of graphite for the empty interslab and half the elastic constants for the lithium filled interslab (e.g. $c_{11}(\text{stage 4L}) = \frac{3}{4}c_{11}(\text{graphite}) + \frac{1}{4}c_{11}(\text{stage 1})$). This assumption probably deviates for the liquid-like stages since the in-plane density of lithium is reduced compared to stage 1, as shown in section 5.3. But this estimation can give an approximated crystallographic direction of the phase boundary. DFT calculations for the missing phases are needed to calculate precise orientations.

In contrast, the crystallographic expansions for the different stages are well known and summarized in Table 3 of section 2.5. However, the investigation with in situ NPD on graphite in section 5.3 found that the higher stages 4L, 3L, and 2L seem to undergo a solid-solution type of transition which results in slight variations of the crystallographic data found in the literature.
(Table 3). So the systematic error for the calculation for the stage transitions between stages 2L-3L and 3L-4L might be higher. The other transitions should be closer to reality since both crystallographic data and elastic constants are better established.

The calculations for all stage transitions are summarized in Table 13. All transitions show a minimum of the elastic energy at ~70° versus the graphene plane. Additionally, an energy perturbation of 1% would rotate the phase boundary only by a few degrees which indicate that the minimum is very well defined. This calculation is based on a coherent interphase in graphite.

However, small defects and minor dislocations can lead to an incoherent interphase [48] which can influence the alignment of the phase boundary significantly. To calculate the minimum of the elastic energy for an incoherent interphase, two different scenarios have been evaluated. First, an incoherent interphase in c-direction of graphite was assumed which might reflect defects in the stacking of the graphene layers, e.g., turbostratic disorder. Second, an incoherent interphase in-plane of the graphene layers has been considered which might be due to, e.g., point defects or grain boundaries. These incoherencies are modeled by assuming zero strain in (100) and (001) direction for incoherency a- and c-axis direction, respectively.

Figure 122 shows the elastic energy of the phase transition from stage 1 to stage 2 for an incoherent interface in (001) and (100) direction. It can be seen that the shape of the energy graph with respect to the crystal direction changes significantly of the incoherency in (001) while a similar shape is observed for the stage 1-2 transition in the case of an incoherent interface in (100) direction. Additionally, the minimum changes drastically for the first case while the second shows a similar direction as for the coherent interphase calculation. This can be better visualized in Figure 123 where the two-dimensional cross-section of Figure 122 is given in a-c-plane. The outer butterfly-like shape corresponds to the coherent interface while the inner butterfly shape and the small lemon-like shape correspond to the incoherent interface in (100) and (001) direction, respectively. The minimum of the elastic energy rotates significantly for the incoherent interface in c-direction while the other stays almost the same as for the coherent interface.

Table 13: Calculated angle of phase boundary between coherent phase during the stage transitions, 1% energy variation to the minimal energy shows rotation by small energy perturbations.

<table>
<thead>
<tr>
<th></th>
<th>Phase boundary vs. graphene plane</th>
<th>1% energy variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage 1 - 2</td>
<td>76.7°</td>
<td>74°-79°</td>
</tr>
<tr>
<td>Stage 2 - 2L</td>
<td>66.3°</td>
<td>62°-70°</td>
</tr>
<tr>
<td>Stage 2L- 3L</td>
<td>73.3°</td>
<td>70°-76°</td>
</tr>
<tr>
<td>Stage 3L- 4L</td>
<td>65.1°</td>
<td>59°-70°</td>
</tr>
<tr>
<td>Stage 4L- 1L</td>
<td>74.7°</td>
<td>71°-77°</td>
</tr>
</tbody>
</table>
This calculation can also be extended for the five different stage transitions as shown in Table 14. One can clearly see that the phase rotates to ~20° in the case of an incoherent interface in c-direction. Additionally, the minimum is very badly defined as the broad range of the geometric angles shows which is between circa -45° to 45° due to symmetry reasons around 0°. In contrast, an incoherent interface in a-direction does not influence the alignment of the phase boundary much. The rotation is less than 2° to higher angles and the minimum is well defined as in the case of the coherent interface.

These calculations have to be validated experimentally. For LiFePO$_4$, the phase boundary alignment is quiet well studied [46, 203] and the calculations by Cogswell and Bazant [48] agree very well with these experiments. In the case of graphite, only one study could be found which measured the phase boundary movement for the transition from stage 1L to stage 4L in highly-

![Figure 122: Elastic energy of graphite during stage 1 to stage 2 delithiation for an incoherent interface a) in c-direction and b) in a-direction.](image)

![Figure 123: 2D cross-section of elastic energy for an incoherent interface based on Figure 122, minimum energy indicated by red arrow, incoherent interface in (001) changes minimum.](image)
oriented pyrolytic graphite HOPG [204, 205] which is usually not the best model material for intercalation kinetics and thermodynamics for standard small graphite particles like SFG6 and SFG44. However, some observations of this study can be compared with the calculations of the phase boundary alignment for graphite.

Figure 124 shows the observations of Funabiki et al. [204] for HOPG. The left images a)-d) show the propagation of the interface during lithiation. The images focus on the basal plane where the phase boundary seems to align isotropically in ab-direction as calculated and due to the hexagonal symmetry of the phases. A line defect can be observed in the figure which forms probably an incoherent interface in at least (100) direction. Here an alignment of the phase boundary can be observed. However, no depth information is available which would be needed to confirm the calculation conclusively.

Table 14: Calculated angle of phase boundary for incoherent interface during the stage transitions, 1% energy variation to the minimal energy shows rotation by small energy perturbations.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Loss in (001) ε3= 0</th>
<th>Loss in (100) ε1= 0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phase boundary vs. graphene plane</td>
<td>1% energy variation</td>
</tr>
<tr>
<td>Stage 1 - 2</td>
<td>15°</td>
<td>0°- 40°</td>
</tr>
<tr>
<td>Stage 2 - 2L</td>
<td>20°</td>
<td>0°- 46°</td>
</tr>
<tr>
<td>Stage 2L- 3L</td>
<td>20°</td>
<td>0°- 46°</td>
</tr>
<tr>
<td>Stage 3L- 4L</td>
<td>22°</td>
<td>0°- 49°</td>
</tr>
<tr>
<td>Stage 4L- 1L</td>
<td>23°</td>
<td>0°- 51°</td>
</tr>
</tbody>
</table>

Figure 124: Microscopy images of highly-oriented-pyrolytic-graphite (HOPG) with stage 1L in light gray and stage 4L in dark gray (taken from [204]).
Taking the full equation set with the free energy in eq. (5.7), the surface reaction with the over-potential (eq. (5.10) and (5.12)), and the boundary conditions in eq. (5.13) and (5.14), one can simulate the behavior of graphite for the different stage transitions including the elastic contribution. Here, a coherent interface between stage 1 and stage 2 has been chosen. The interfacial energy penalty tensor $K$ is not known for graphite so that the one of LiFePO$_4$ had to be taken as this might be the best available estimate [48]. Furthermore, no higher order terms could be included in the homogeneous free energy in eq. (5.8) to separate between the different stages since the model in section 5.1 was not able to capture the open-circuit-potential and phase diagram of lithium-graphite sufficiently. Furthermore, the modeling is done in 2D while the development in in-plane direction would be helpful to investigate the ordering due to the hexagonal symmetry of the system to compare the calculations to the findings by Funabiki et al. in Figure 124.

However, interesting features can still be accessed by the model. The chosen parameter for the enthalpy term is a best fit to the phase diagram in Figure 9c and OCP as described in section 5.1. Three different scenarios are chosen for the investigation. First, a relaxation at a SOC of 75% lithiated graphite is calculated. Second, the lithium intercalation starting from stage 2 and continued to stage 1 is performed. Last, the reverse process, delithiation from stage 1 to stage 2, is investigated. The numerical calculations have been based on a finite difference method of first order with a backward time stepping [48]. The grid was chosen to be 1200x 200 in $a$- and $c$-axis, respectively due to the flake like particle shape of graphite SFG6 as an experimental counterpart. However, the dimensions of graphite are circa 3300x 500 nm; however, the computer is limited to a smaller grid.

The first scenario concerns the relaxation of a graphite particle at an SOC of 1:1 of stage 1 and 2 equivalent to 75% total state-of-charge. No lithium flux is applied externally but lithium could formally exit the particle at the left and right edges and reinsert at the same time. Figure 125 shows the evolution of the concentration in the graphite particle during the relaxation. The concentration is visualized on a grey scale where black relates to stage 2 (50% of total SOC) and white reflects full lithiation being stage 1 (100% SOC). The time is normalized to a virtual charge rate of C/2.

At the beginning, $t = 0$, a homogeneous concentration profile was set with 75% total SOC. After the first time stepping a very inhomogeneous concentration profile can be observed which separates in stage 1 and stage 2 after the second time stepping ($t = 0.008$). However, the phases do not align and a typical Cahn-Hilliard type of phase separation can be observed. During progressing relaxation of the graphite ($t = 0.25$), small islands of phases grow together to bigger ones and the phases begin to align in the direction of minimal elastic energy which was calculat-
ed to be 76.7° for the coexistence of stage 1 and 2. At the end of the relaxation the islands are completely formed and align in the direction of minimal elastic energy as calculated before, Table 13. This relaxation shows that elastic energy might play a significant role on how the phases align to each other. The findings can be combined with the investigations on graphite rate kinetics in section 3.2 to develop a sketch for phase distributions in graphite (see section 6.1).

Figure 125: Evolution and distribution of lithium concentration during relaxation of graphite starting at 75% state-of-charge (grey), separation into lithium-rich phase (stage1) and lithium-poorer phase (stage 2) with characteristic alignment of phase boundaries, time normalized to C/2.
The second scenario focuses on the lithiation of graphite during the transition from stage 2 to the end phase, stage 1 LiC$_6$. 100% stage 2 is present at the beginning of the lithiation at $t = 0$ in Figure 126. During the lithiation, the concentration increases homogeneously which corresponds to the solid-solution regime of pure stage 2, as also found by the above described XRD and NPD experiments in sections 5.2 and 5.3. At $t = 0.22$ or an SOC of circa 0.61 of the total SOC, stage 1 nucleates spontaneously due to the spinodal decomposition. It has to be stressed that nucleation is not modeled here but the spinodal gap is reached, thus, a tiny numerical perturbation leads to phase separation. In reality, nucleation starts probably at much lower SOC due to possible nucleation events and inhomogeneous concentrations within the particle. The region around the new formed stage 1 decreases its concentration closer to the original stage 2 concentration, thus, indicating a relaxation of the concentration close to the spinodal gap back to the miscibility gap.

During progressing lithiation, the phase boundary between stage 1 and stage 2 tries to align as much as possible to the direction of minimal elastic energy as shown in Table 13 and also observed during the relaxation. Finally, stage 1 (white) occupies more and more graphite as lithiation progresses. At the time $t = 0.92$ which is equivalent to an SOC of 0.96, finally only stage 1 fills the graphite particle. However, the concentration at this point is only Li$_{0.96}$C$_6$, thus, reflecting the solid-solution regime of stage 1 at room temperature. At $t = 1$ full LiC$_6$ is reached where the image had to be framed to allow judgment. The solid-solution range of stage 1 is smaller compared to the one of stage 2 which is not a thermodynamic difference but rather the real solid-solution since no nucleation is needed for the extinction of stage 2. This shows the clear difference between the spinodal and miscibility gap. These calculations are the first ones for graphite to the best of my knowledge and give good insight into the thermodynamics during the graphite stage transitions.
Figure 126: Evolution and distribution of lithium concentration during galvanostatic lithiation of graphite from stage 2 (black) at $t = 0$ to stage 1 (white), time normalized to C/2 rate.
5.5 Summary of thermodynamic stage transitions of graphite

This chapter focuses on the phases and phase transitions of the lithium-graphite system. Since graphite undergoes five different stage transitions at room temperature during lithiation, a model has been developed based on a mean-field approach in section 5.1. The free energy of graphite has been modeled which captures the characteristics of the phase diagram and open-circuit-potential of graphite. The approach found several unexplained features in the lower state-of-charge regime of the phase diagram/OCP. The model indicated a reduced in-plane density of lithium for stages 4L and 3L and some hindering of the stage 2L formation. Additionally, a normal phase separation like in the case of stage 1-2 could not be validated by the model for the liquid-like stage transitions.

These findings lead to the investigation of the phases and phase transitions by in situ XRD and in situ and ex situ NPD in sections 5.2 and 5.3, respectively. A continuous shift of the c-axis can be observed in Figure 112 for the transitions between stages 4L-3L-2L while a phase separation can be observed for the stage transitions 1L-4L, 2L-2, and 2-1. However, the XRD patterns showed very low intensity and were very difficult to refine due to much stronger aluminum reflexes overlapping with the (110) reflex of graphite.

In contrast, the NPD diffraction data showed very good results. For the first time, all space groups could be refined. Stage 1, stage 2, and graphite are known from the literature [80, 107, 109]. However, only the repeated distance and in-plane carbon-carbon distance is known for stages 2L, 3L, and 4L as summarized in Table 3. The refined space group parameters of these stages could be identified and correspond to an AA stacking for the lithiated interslab while AB stacking is observed for the empty interslabs. Another interesting feature was detected. The stages 3L and 4L show a solid-solution behavior where the a- and c-axis parameters vary with degree of lithiation. These findings support the model in section 5.1. The sloppy potential profile in the regime between stage 4L-3L-2L can be explained by a solid-solution in the respective stage as shown in Figure 118.

Furthermore, a frustration of stage 4L was found during the lithiation of graphite as shown in Figure 117. The reflexes of stage 4L are badly defined during lithiation with shoulders and strong peak broadening while stage 3L shows well defined reflexes. In contrast, during the delithiation of graphite at a potential of 160 mV, both stage 3L and 4L are very well-defined and show distinct reflexes. This can explain the sloppy potential profile for the transition of stage 1L to 4L since stage 3L might already develop. This means that the transition starts from stage 1L and phase-separates to a mix of stage 4L/3L. These findings need to be included in the model in section 5.1 to describe the phase diagram and OCP precisely.
The last part of this section focused on the orientation of phase boundary between the five different stage transitions in section 5.4. Based on the calculations of Khachaturyan [202] it could be found that the minimal elastic energy for a coherent interface aligns around 70° for all coexisting phases as summarized in Table 13. Additionally, the minimum is very well defined which could be estimated by an energy perturbation of 1% compared to the minimum.

Furthermore, the influence of an incoherent interface in a) (001) direction and b) (100) direction has been investigated. For an incoherent interface in c-direction, the phase boundary rotates to circa 20° for the different stage as summarized in Table 14. However, the minimum is very badly defined so that an energy perturbation of just 1% could rotate the phase boundary between circa -45 to +45° with respect to the graphene planes. In contrast, an incoherent interface in (100) direction shifts the minimum only by two degrees to more inclined angles and is as well-defined as the minimum for the coherent interphase.

Last, a model for phase separation was combined with the elastic energy contributions based on the work of Cogswell and Bazant [48]. The adaptation of their model to graphite allowed the study of the alignment of stage 1 and 2 to each other during relaxation and galvanostatic lithiation. It could be found that the stages try to align close to the minimum energy as calculated above. However, deviations from this alignment can be observed during the beginning of the relaxation and partially during the lithiation which show that the phases can often not align due to reasons of forming a continuous phase boundary. These finding might help to understand the progression of the stages in the bulk of graphite and will be used in combination with the experiments of the rate kinetics of graphite in the next section.
6. Models for graphite

This chapter focuses on the combination of the previously collected experimental and calculated results for graphite from chapters 3, 4, and 5 to draw conclusions on several mechanisms. In the first part, the kinetics of graphite during galvanostatic cycling (section 3.2) will be combined with knowledge about the thermodynamic stage transition from sections 5.2 and 5.3, while information about the phase boundary will be included as well (section 5.4).

In the second part, a sketch of the reaction mechanism in partially-disproportionated graphite-oxide will be discussed. Both the electrochemical and analytical experiments from section 4.2 will be combined with the previous findings for graphite (e.g., section 3.5) to draw conclusions why graphite-oxide possesses an increased rate capability combined with 1.8 times the specific charge of pristine graphite.

The last section focuses on the phase transitions in the liquid-like stages of lithium-intercalated graphite. Literature data and the findings in section 5 will be combined to describe the transitions between the stages.

6.1 Diffusion pathway model

It has been found that the different stage transitions contribute differently to the total rate capability of graphite, as shown in section 3.2.3. The transitions towards the dense stages (stage 1 and 2 with LiC₆ in-plane density) are limited and deliver only ~40% of their specific charge at 20C. However, the transitions towards the liquid-like stages (lower in-plane density and disordered) deliver more than 80% of their respective specific charge at 20C charge rate. Surprisingly, the transitions between stages 2-2L-3L-4L deliver even more specific charge during 20C discharge as compared to C/20 rate. This is obviously thermodynamically impossible; however, the previously very limited stage transition stage 1 to stage 2 can further progress into the graphite particle while the next phases propagate into the particle, thus, withdrawing more specific charge than at low discharge rate.

This difference might probably be due to the different diffusion coefficients for the dense and liquid-like stages. It was found that the diffusion coefficient of the liquid-like stages is enhanced by a factor of ~10x compared to the dense stages [153, 159]. But how can the different diffusion coefficients and the order of the respective stage transition lead to such a tremendous difference in rate capability for charge and discharge?

To visualize this behavior, an arbitrary single particle of graphite was marked with the different stage colors using gold for stage 1, red for stage 2, and blue for stage 2L in Figure 127. Nuclea-
tion of a new phase is assumed to occur at the edge-plane and subsequently propagate into the center of the particle. At high rates of lithiation, the stage 2L-2 transitions cannot deliver the full specific charge (Figure 20). Therefore, as the total overpotential increases due to diffusion limitation, the surface of the particle will reach the thermodynamic potential of the next stage transition, stage 2-1. When the nucleation of the new stage 1 is initiated at the edge plane, it also propagates into the particle, taking over more and more of the edge-plane. The different stages in the particle distribute in a similar manner as the annuli of trees. This is due to the fact that lithium ions can only diffuse in the interslabs of the graphene layers. Grain boundary diffusion can occur but it was shown to be five orders of magnitude slower than the in-plane diffusion of lithium ions [160].

The phase distribution along the radial vector in Figure 127 is displayed in Figure 128. The black line indicates the phase boundary between stage 1 and stage 2, while the red one illustrates the stage 2 to 2L phase boundary. Phase boundaries in graphite are expected to be isotropic along the a- and b-axis due to the hexagonal symmetry of the structure as discussed in section 5.4. But there is an alignment along the c-axis to minimize elastic energy, which is indicated in the figure (the calculations are presented in section 5.4). One can see that, although the particle appears to be composed of more than 50% of stage 1 from the outside (the golden phase seen from the basal plane at the top in Figure 127), the actual fraction of stage 1 is very small in the entire particle, as shown in Figure 128. This would imply that one cannot judge the real state-of-charge of a single particle directly from colorimetry. Also, the Daumas-Herold domains are indicated in Figure 128 for stage 2 and 2L, where local domains of the respective stage exist but alternate after a certain island length [131]. The annuli model is an adaptation of the shrinking core model for LiFePO$_4$ [61], which has been developed further, including information of the phase boundary alignment and using the Cahn-Hilliard phase separation model [65, 133]. The sketch is also consistent with previous models of graphite staging based on the Cahn-Hilliard approach [131].

Plotting the concentration profile along the interslab third from the top in Figure 128, which includes the phase boundaries, one can sketch the profile of the interslab concentration (Figure 129). One can see that the standard Fick’s diffusion equation is not applicable over the entire particle when phase boundaries are present. Fick’s law can be used in the solid-solution regime of each pure phase that develops a standard diffusion profile over the single phase regime (including many Daumas-Herold domains). But at the phase boundaries, two different diffusion mechanisms can take place. On the one hand, lithium ions could diffuse from the solid-solution phase (e.g., pure stage 1) to the interface, which then propagates further (concentration gradient in the Daumas-Herold domains which propagates macroscopically into the particle). On the other hand,
lithium ions could diffuse along the phase boundary, which was found to be the main diffusion pathway for LiFePO₄ [65]. At low rates, we cannot estimate the relative contribution of both diffusion pathways to the overall process, which depends on several different factors such as interfacial energy, gradient energy penalty, etc. But at high rates, diffusion limits the propagation of stages 2 and 1, as shown in section 3.2.3. High rates lead to full coverage of the new phase at the edge plane, allowing only diffusion through the solid-solution regime of each single phase. This results in the formation of the depicted annuli.

Figure 127: Shrinking annuli sketch of a single graphite particle (stage 1 gold, stage 2 red, stage 2L blue), the arrow indicates the radial direction of the 2D cross-section shown in Figure 128.

Figure 128: Sketch of a simplified 2D phase distribution profile along the arrow indicated in Figure 127 (phase boundary of stage 2L to 2 in red, phase boundary of stage 1 to 2 in black).

Figure 129: Sketch of the concentration profile along the 3rd interslab from the top of Figure 128 from the edge (r = R = 1.6 µm) to the center (r = 0) in a graphite particle with phase boundaries.

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For delithiation, a similar mechanism can be suggested. First, the stage 1 to 2 transition takes place, which is diffusion limited for the model particles with diameters of 3.3 µm. When diffusion becomes limiting in stage 2, the imposed diffusion overpotential allows the nucleation of the next phase, stage 2L, which is only 30 mV more positive than the thermodynamic potential of the stage 1 to 2 transition. Thus, the new phase, stage 2L, nucleates at the edge plane as depicted in Figure 130a. Due to the higher diffusion coefficient of this liquid-like stage 2L (as discussed above) this phase boundary progresses faster into the particle. This leads to a decrease of the stage 2 regime (Figure 130b), which increases the lithium diffusion rate due to a smaller Δr of stage 2, which in turn increases the concentration gradient dc/dr. Therefore, a higher practical specific charge can be withdrawn from the stage 2 to 2L phase transition as shown above (Figure 22), because the process facilitates the stage 2 phase boundary propagation and releases its charge. The stage 2 to 2L transition finally becomes limited by the further propagation of both stage 1 and stage 2, and therefore drops at a rate of ~32C below its low rate specific charge (Figure 22).

The next stages, 3L as well as 4L, also nucleate at the edge plane when their respective thermodynamic potential is reached. They propagate into the particle with a higher diffusion coefficient, withdrawing additional charge from all the previously uncompleted stage transitions so that almost all stored lithium ions can be released at rates of up to 680C. At about 1000C, our experiments as well as those of Dokko et al. [157] show a major decrease in specific charge delivered galvanostatically. In our case, one knows that the current density is above the diffusion-mass-transfer-limited current density of the electrolyte (see the theoretical considerations in section 3.1.2). Therefore, we can conclude that graphite can be delithiated with at least 680C while at higher rates electrolyte limitations govern the response of our system.

Figure 130: Simplified course of the propagation of the phase boundary during delithiation at a) the beginning and b) the end of the stage 2 to 3L transition.
Due to the faster diffusion of lithium in the liquid-like stages, many phase boundaries can agglomerate during delithiation. But the phase boundaries are unlikely to collide, which would mean an infinitely high flux just before the collision would occur. This is due to an infinitely high concentration gradient within the pure phase dc/dr (first Fick’s law). Therefore, the graphite particles are likely to possess more annuli simultaneously during delithiation.

In addition to the proposed diffusion pathway for medium and high rates there exists also an influence of the temperature on the rate capability of graphite. At higher rates, when the entire edge plane is assumed to be covered with a pure phase, only the diffusion through the solid-solution of each phase governs the kinetics. But both the diffusion coefficient and the solid-solution miscibility regime depend on temperature, as shown in the binary phase diagram of the lithium-graphite system [89]. Therefore, when the temperature decreases the flux per area (Fick’s law \( J = -D \frac{dc}{dr} \)) would be significantly reduced due to a decrease in the permissible \( \Delta c \) for the miscibility regime and a lower diffusion coefficient.

Both the experimental findings of the rate kinetics of graphite from section 3.2.3 and the developed shrinking annuli model have several implications for experiments with highly crystalline graphite electrodes (excluding MCMB and HOPG). First, the diffusion coefficient cannot be extracted by applying Fick’s law over the entire particle when a phase boundary is present. Second, two different diffusion pathways are possible, i.e., the diffusion of lithium through the solid-solution regime of each pure phase (including the Daumas-Herold domains), and the diffusion along the phase boundaries between two pure phases. For high rates, the diffusion through the solid-solution regimes seems to be the main diffusion mechanism. Third, the diffusion coefficient of the dense stages 1 and 2 seem to be lower than that for the liquid-like stages, supporting the previously published trends of Levi et al. [153] and Umeda et al. [159]. Last, based on the proposed shrinking annuli model, the asymmetry in the rate capability of graphite can be explained. However, one has to keep in mind that the maximum overpotential is very limited for lithiation (~90 mV). Otherwise, lithium-plating would occur.

Some conclusions can also be drawn for the application of graphite electrodes in lithium-ion batteries. Highly crystalline standard graphite electrodes with ideally engineered porosity and electronic conductivity will probably not exceed 6C charge rate (10 min) for particles of diameters of more than 3 µm. However, a discharge at very high rate is feasible for practical applications.
6.2 Proposed mechanism for lithium storage in partially-disproportionated graphite-oxide

The intended purpose of the development of chemically modified graphite was the stretching of the interlayer distance by either surface-coating or pillaring in the interslabs between the graphene layers of graphite. GOpd was used as one of the options since it possesses several different oxygen-containing “bulk-surface” groups. We use here the new term “bulk-surface” since the actual bulk would be graphite which is chemically oxidized to create “bulk-surface” groups containing oxygen. The “normal” surface is still similar to the one of the precursor SFG6, as seen in Figure 81. But how could these “bulk-surface” groups possibly pillar the normal structure of graphite?

Two different scenarios can be imagined for the pillaring which are sketched in Figure 131. The starting material GOpd contains many epoxide and hydroxide groups as shown in Figure 131a. However, also some other groups can be present like carbonyl, carboxyl, and hydrogen groups. During the first lithiation the GOpd could be reduced electrochemically by lithium to form Li₂O. Since this reaction product is solid it precipitates in the interslabs of the GOpd structure as shown schematically in Figure 131b. The diffusion rate of the molecule Li₂O is probably very low in the bulk material so that it might stay at its reduction location and forms, thus, a pillar between the graphene layers. Due to the increased spacing between the graphene sheets, more lithium could be stored, e.g., in a bi-layer of lithium.

The second scenario would also involve a reduction of the “bulk-surface” groups of GOpd. However, the reduction of epoxides and hydroxides would end after the formation of lithium-alkoxide bonded to the graphene sheets (Li-O-graphene). These alkoxides would stay in the interslabs between the graphene sheets, thus, pillaring the structure as sketched in Figure 131c. Due to the interlayer distance increase, more lithium ions could be stored from steric point of view. In contrast to the full reduction to Li₂O, the lithium-alkoxide cannot move in the interslab due to the covalent bond to the graphene sheets.

The increased specific charge of GOpd in respect to pristine graphite, as shown in Figure 77 and Figure 78, suffers from a rapid aging over the first 50 cycles after which the cycling efficiency reaches more than 99.8%, which is shown in the same figures. This phenomenon could be explained by the proposed sketch in Figure 131d. The lithium-alkoxide could reduce finally to Li₂O at very negative potentials (Figure 131c) or would be already present (Figure 131b). Due to the cycling, the normally immobile Li₂O molecules would be pushed back and forth so that they might form aggregates of Li₂O in the interslabs. These can be imagined like regularly observed the Daumas-Herold domains of intercalates in graphite [100]. Due to the agglomeration, the pil-
laring effect would disappear so that only the standard specific charge of graphite minus the sites blocked by Li$_2$O agglomerates could be cycled reversible. The collapse of the structure would be irreversible because the aggregates of Li$_2$O could bond to one another forming something close to a local monolayer. Additionally, the elastic energy might also prohibit a redistribution of the Li$_2$O, thus, leaving an irreversibly collapsed structure behind.

Figure 131: Proposed mechanism for the pillaring effect in GOpd43, a) pristine GOpd, b) Li$_2$O in the interslabs of graphite, c) LiO-graphene, in both structures two layers of Li$^+$ could be stored sterically, d) proposed aging by movement of Li$_2$O pillars during cycling forming isolated islands (like Daumas-Herold domains) while the remaining structure collapses back to graphite.
Neither one of the two proposed pillaring mechanisms nor the aging mechanism could be proven directly. However, some hints could be derived from the different experimental methods, as discussed in section 4.2 where several different electrochemical and analytical methods have been used.

First, the changes of specific charge of GOpd during reversible cycling can be analyzed. In the first cycle, a SEI formation and the activation of the material takes place as shown in Figure 82 and Figure 103, respectively. This leads to a high irreversible specific charge in the first cycle. To separate both influences in the first cycle from each other, a similar graphite electrode has been prepared with a ratio of 80:10:10 of graphite SFG6: PVDF: SuperP and cycled under the same conditions (same mass, thickness, and cycling conditions). The extra specific charge in the first cycle compared to the practical specific charge of SFG6 (~360 mAh/g) was attributed to the insertion of lithium in SuperP and the SEI formation on SuperP, Cu current collector, and graphite SFG6. This superposition is based on the results of section 3.2.2 where this kind of superposition worked well for graphite thin-layer electrodes.

However, it cannot be guaranteed that GOpd forms the exact same SEI as the precursor graphite SFG6. But the investigations with SEM (section 4.2.3), EDX (section 4.2.4), and XPS (4.2.5) show a relative similar SEI morphology with slight variations in the composition. The oxygen content in XPS measurement was slightly lower for lithiated GOpd43 compared to both SuperP and graphite SFG6 electrodes (Figure 94 and Figure 96). But the difference was very small and might be partially due to the increased lithium content of GOpd43 electrodes in the XPS measurements which reduces the relative amount of oxygen and carbon, as shown in Figure 94. Therefore, it will be assumed that the SEI of GOpd43 electrodes is very similar to the one on graphite SFG6. This will be used to get a rough estimate of the reversible and irreversible charge during electrochemical cycling. During the subsequent cycles, mainly the reversible insertion of lithium in SuperP needs to be taken into account, as shown in Figure 16 on page 34.

The number of exchanged electrons is directly correlated with the specific charge by Faraday’s law in eq. (6.1). With the above discussed assumption of similar SEI formation on graphite SFG6 electrodes, the total specific charge of the GOpd43 electrode can be corrected for the SEI and SuperP influence by a linear superposition of the charges, as shown in eq. (6.2).

\[
Q = zF \frac{m}{M} \quad (6.1)
\]

\[
z = \frac{M}{mF} \left( Q_{GOpd} - Q_{same LiC} \right) \quad (6.2)
\]
The results of the estimated exchanged electrons are summarized in Table 15. On the left hand side, the exchanged electrons per C$_6$O$_{0.96}$(OH)$_{0.05}$ are displayed for each lithiation and delithiation. It can be directly seen that the number of electrons in the first lithiation is substantially higher compared to the subsequent cycles despite the fact that the contributions from SEI and SuperP have already been subtracted. This means that the observed activation during the first lithiation as seen by both galvanostatic cycling and cyclic voltammetry (Figure 78 and Figure 103) consumes some charge irreversibly. The following calculations are based on the cycling of GOpd43 shown in Figure 78.

During the cycles 2-5 very low irreversible charge loss can be detected. However, a small contribution of an average of $z_{irr}$(lith-delith) = 0.04 and $z_{irr}$(delith-lith) = 0.02 can be observed during each half-cycle. This might indicate a more significant aging for lithiation than for delithiation which would be consistent with the findings of the restricted cycling potential window in section 4.2.8 where an increased aging rate was detected at very negative potentials. Lithiations usually stay a longer period of time in the negative potential regime while the delithiation shows a capacitor like potential profile as shown in the cyclic voltammetry and GITT experiments in sections 0 and 4.2.8, respectively.

One can calculate the charge necessary to form lithium-alkoxides from the epoxide and hydroxide “bulk-surface” groups based on the elemental analysis in Table 8. Approximately, 1.065 electrons will be transferred to form Li-O-graphene in the first cycle for GOpd43 shown in Table 15b. The experimentally found irreversible specific charge corresponds to a $z_{irr}$ of ~1.1. Therefore, the pillaring mechanism based on Li-O-graphene formation in Figure 131c might be more reasonable. In contrast, the complete reduction of GOpd43 to form Li$_2$O in the interslabs in Figure 131b would consume $z_{irr} = 2.13$ electrons (neglecting the possible formation of LiOH as a side product).

Table 15: Transferred electrons z per C$_6$O$_{0.96}$(OH)$_{0.05}$ during cycling of GOpd43 based on Faraday’s law in eq. (6.2) for a) total z for GOpd43 corrected for SEI and SuperP influence based on identical graphite SFG6 system, b) comparison of experimental and theoretical irreversible and reversible charge loss ($z$(theory) based on complete reaction of results of elemental analysis in Table 8).

<table>
<thead>
<tr>
<th>cycle</th>
<th>$z$(lith)</th>
<th>$z$(delith)</th>
<th>$z_{irr}$(cycle)</th>
<th>$z_{rev}$(cycle)</th>
</tr>
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<tr>
<td>1</td>
<td>3.36</td>
<td>2.25</td>
<td>1.065</td>
<td>1.10</td>
</tr>
<tr>
<td>2</td>
<td>2.11</td>
<td>2.12</td>
<td>2.11</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.11</td>
<td>2.08</td>
<td>2.08</td>
<td>2.41</td>
</tr>
<tr>
<td>4</td>
<td>2.05</td>
<td>1.97</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.95</td>
<td>1.89</td>
<td></td>
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</table>
The reversible specific charge in the second cycle corresponds to $z = \sim 2.11$ electrons per $C_6O_{0.96}(OH)_{0.05}$ stored in the system (Table 15b), which would be more than double the electrons stored in lithiated graphite $LiC_6$ ($z = 1$). However, the specific charge of GOpd43 is less than double the specific charge of graphite due to the increased molecular weight of GOpd43. These 2.11 electrons can either be stored by a reversible chemical reaction, by storage of extra lithium in the cavities of the GOpd, or stored in a bilayer of lithium ions between two adjacent graphene layers. Also other possibilities are possible and will be discussed hereafter.

As shown for the first cycle, the irreversible specific charge can also be estimated for all subsequent cycles. If one sums all irreversible specific charges/exchanged electrons in the first fifty cycles, a total amount of 2.41 electrons per $C_6O_{0.96}(OH)_{0.05}$ are “consumed” irreversibly. Since the SEI and SuperP contribution was subtracted before this analysis, this amount most probably origins almost only from reactions in the GOpd43. If one calculates the formation of pure $Li_2O$ and $Li_2O+LiOH$ from the results of the elemental analysis in Table 8 for these fifty cycles, one would get a $z_{irr}$ (cycle 1-50) of 2.13 and 2.08, respectively. Here, the experimental irreversible charge deviates much more to the calculated one compared to the first cycle. This might be due to a slightly different SEI composition but cannot be proven. However, one can judge that the lithium-alkoxide from the first cycle might reduce completely to $Li_2O$. This would be consistent with the findings for a limited cycling potential window as shown in section 4.2.8. Li-O-graphene will probably be reduced further at very negative potentials. Therefore avoiding these potentials could help to decrease the aging aret significantly, as shown in Figure 107a for cycling between 1-3 V vs. $Li^+/Li$.

The number of experimentally estimated reversibly exchanged electrons, however, decreases to $z_{rev}$ of circa 0.84, as shown in Table 15b. The stored charge is now smaller than the one of graphite. This would be consistent with the aging mechanism proposed in Figure 131d. The reduction product $Li_2O$ would be pushed periodically back and forth so that an agglomeration could occur. This would lead to the discussed collapse of the interlayer spacing back to graphite, thus, allowing only a single lithium-ion layer between two adjacent graphene sheets. The precipitate $L_2O$ would further reduce the available specific charge due to steric blocking of lithium-ion sites. Also some extrusion of $Li_2O$ could be possible especially near the edge planes which would result in increased oxygen content at the prismatic edge surface. An increase amount of oxygen is observed in the XPS spectra of cycled GOpd43 electrodes compared to graphite SFG6 and SuperP electrodes, as discussed in section 4.2.5.

Another evidence can be extracted from the XRD data on lithiated GOpd43 in section 4.2.6. The initial c-axis parameter of 4.33 Å increases to 5.704- 5.744 Å for the lithiated GOpd43, as
shown in Table 11. This value is very close to the one of pristine graphite-oxide with 5.74 Å in Table 10. Graphite-oxide possesses a significant amount of hydroxide “bulk-surface” groups which increase the c-axis distance due to the sp3-hybridization and vertical orientation of the hydroxide to the graphene sheets [185]. In contrast, epoxides keep the planar structure of graphene intact, thus, allowing smaller c-axis distances [185]. This interpretation is consistent with the elemental analysis and XRD data of GO, GOpd, and graphite in Table 8 and Table 10, respectively. Since lithium-alkoxide forms a similar steric structure like hydroxide, the increased interlayer-spacing could be due to these pillars. This would also support the proposed mechanism in Figure 131c as the Faraday law did. The estimated interlayer distance based on Li₂O pillars cannot be judged since the orientation of the molecules in the interslabs are unknown.

The second main challenge is the description of the charge storage mechanism in GOpd. It was found that the electrochemical delithiation behaves very close to a capacitor-type as observed during galvanostatic cycling and cyclic voltammetry (Figure 78 and Figure 103). The lithiation mechanism shows initially also a capacitor-like behavior. However, at potentials negative to 0.5 V vs. Li⁺/Li an additional diffusion limited insertion of lithium is detected. Furthermore, a very high hysteresis between lithiation and delithiation can be observed with ~1.2 V at 50% SOC of GOpd43. These two special features clearly indicate a significant difference to capacitor-like materials. But how can GOpd43 store more than two electrons reversibly?

To get an insight, one can search for possible other carbon based systems that might perform similar to GOpd. Obviously, graphite shows an intercalation mechanism and is, despite the structural similarities, not a good model material for lithium storage in GOpd. Coke is an amorphous carbon and shows also not many similarities as only ~0.6 Li per C₆ can be inserted reversibly with a low hysteresis (Fig. 11 in [1]). Also other soft-carbons differ significantly from GOpd.

In contrast, hard carbons show many similarities compared to GOpd. These carbons are essentially non-graphitizable which means that they do not form a well-defined graphitic stacking during heat-treatment. They possess a specific charge between 400-2000 mAh/g combined with a large hysteresis between charge and discharge [1]. Additionally, the galvanostatic cycling profile of GOpd in Figure 108 looks very similar to the one of hard carbon (Fig. 13 in [1]). However, the potential where the specific charge is inserted and extracted in GOpd seems to be stretched by a factor of ~2 with respect to the potential of hard carbons. This means that the lithium insertion reactions of GOpd occur mainly between 0-2.5 V while hard carbons store lithium mainly between 0-1.2 V. However, the main lithium insertion occurs at potentials close to metallic lithium like in the case of GOpd. Therefore, hard carbons seem to be one of the closest relative in the family of carbons regarding many aspects of the possible mechanism for lithium storage.
Several different mechanisms have been proposed in the literature how the extra specific charge with respect to LiC₆ can be accommodated in hard carbons. The first one was proposed by Sato et al. [81] who found covalently bonded lithium in hard carbons by NMR studies. They proposed that lithium could occupy every hexagon of a graphene layer in contrast to every third hexagon for LiC₆ in-plane density in graphite [81]. Another possibility was proposed by Mabuchi [206] who indicated that the extra specific charge might come from lithium storage in the cavities of hard carbons. A third approach discussed the possibility of lithium adsorption at the zig-zag and arm-chair edge planes of graphene layers [207]. A fourth modeled is based on the house-of-cards approach which means that very short graphene layers are stacked randomly. Xue and Dahn proposed that lithium ions can be stored in nano-cavities of ~15 Å and adsorb on both sides of graphene, thus, increasing the specific charge significantly [208]. They also found that the amount of oxygen groups from chemical oxidation increases the hysteresis [208]. But which of these storage mechanisms might be the main contribution for GOpd?

It was found by XRD in 4.2.6 that the interlayer spacing increases from 4.33 Å to ~5.73 Å for GOpd43. Therefore, steric hindrance should not play a role so that the high-density storage of lithium by Sato et al. [81] should be less probable. However, their findings of possibly covalently bonded lithium cannot be excluded.

The second approach discussed the possibilities of lithium storage in small cavities of hard carbons [206]. GOpd probably possesses many cavities and small holes in the graphene sheets. These cavities can originate from the thermal disproportionation under inert atmosphere where H₂O, CO, and CO₂ are some of the gaseous disproportionation products. Both CO and CO₂ leave point defects in the graphene sheets except if they get released at the edge or basal plane. These point defects may grow to cavities during progressing disproportionation or even holes in the structure as shown in Figure 84. The estimated mass loss of GOpd43 is circa 10.5-23 % of carbon compared to the starting material graphite-oxide as estimated in eq. (3.14) and (3.15) for pure CO and CO₂ release, respectively. Thus, these cavities in the bulk structure could be a preferred storage site for lithium. However, the reversible specific charge of GOpd36 is less than that of GOpd43 although more or bigger cavities should be present due to a higher carbon loss (EA in Table 8). Therefore, either the cavity size is determining the extra specific charge or cavities are not the main storage mechanism.

The third approach focused on the adsorption of lithium ions on the edge planes of graphene and grain boundaries of graphitic domains [207]. The amount of these sites in GOpd, however, should be not more than maximum 10.5-23 % due to the carbon mass loss. If one assumes that only a single lithium ion could reside in a point defect site, only a slight increase in specific
charge could be explained. However, these lithium sites could be a part of the storage of lithium ions in cavities as proposed by Mabuchi [206].

The model by Xue and Dahn [208] proposed the storage of lithium in cavities of ~15 Å between small graphene sheets stacked as a “house-of-cards”. They allowed also the storage of lithium on both sides of graphene without a neighboring screening layer of graphene. They showed that the pore size towards the cavities determines the reversible and irreversible specific charge in their pyrolyzed epoxy-resins at 600°C [208]. Their experiments showed also a high potential hysteresis for pyrolyzed epoxy-resins. This model seems to be the closest to the experimental observations for the GOpd materials since an irreversible specific charge is observed which also depends on the amount of “bulk-surface” groups and a potential hysteresis of ~1.2 V can be detected while GOpd possesses still a high oxygen content of circa 1:6 of O: C (Table 8).

However, the GOpd is still partially ordered and shows few and broad Bragg reflexes as discussed in section 4.2.6. Thus, the “house-of-cards” sketch does not fully describe the structure of GOpd. Additionally, the pore size is predefined by the disproportionation temperature (4.2.1). Therefore, the GOpd might be an “ordered” form of hard carbon in a very broad perspective. The adsorption of lithium ions on both sides of graphene sheets might also be a possible storage mechanism in GOpd while cavities could contribute significantly. Thus, the model of Xue and Dahn [208] seems to be the closest to our experiments. However, the idea of a bilayer of lithium between the GOpd sheets as presented in Figure 131b) and c) seems to be more probable since a certain ordering of the GOpd sheets is preserved. Direct experimental validation is still lacking to judge if cavities or a bilayer of lithium is responsible for the high specific charge of GOpd compared to graphite.

6.3 Proposed mechanism for stage transitions in graphite

The in situ x-ray and neutron diffraction data in sections 5.2 and 5.3 revealed the ordering of the graphene layers in stages 4L, 3L, and 2L. Additionally, the expansion of the average and lithiated interslabs could be extracted as summarized in Figure 118. It was found that the liquid-like stages possess a solid-solution regime like graphite, stage 2 and stage 1. This was expected from thermodynamic point of view but never described sufficiently in literature.

There can be commensurated and incommensurated ordering of intercalates in graphite intercalation compounds. For example, the potassium-graphite system possesses a commensurated stage 1 with KC_{8} in-plane order while stage 2 possesses a KC_{12} in-plane density which does not match with the underlaying graphite structure [100]. Commensurated ordering of intercalates
occurs with a ratio of intercalate: graphite in ratios of one to 2, 6, 8, 14, 18, etc. The distance between neighboring intercalates would be equidistant for those ratios.

Figure 118c showed the evolution of the interlayer distance of the lithiated interslabs. It could be observed that the interlayer spacing increases constantly for stage 4L and 3L with degree of lithiation. If one compares the evolution of the interlayer distance of stage 1L (graphite solid-solution) at elevated temperatures (>700K), one can observe a similar trend as shown in Figure 118d [120]. However, the stacking order is unknown for stage 1L since it should transform from AB stacking to AA stacking during the course of lithiation.

If one uses the evolution of the c-axis interlayer distance of stage 1L determined at >700 K for the stages 1L, 4L, 3L, and 2L at room temperature (~300 K) as a rough estimate, one could extract approximated in-plane concentrations of lithium for the different stages. It has to be stressed that this approach is very uncommon and might involve significant errors, however, could help to determine the responsible forces causing the ordering and transitions.

Based on these assumptions, the concentration regime for stage 1L would range from 0- 6.8 % of lithiation compared to LiC₆ (100%). Stage 4L would exist from 7.2- 8.1% SOC with an in-plane density of LiC₁₈.₄- LiC₂₀.₇ in every fourth interslab. Stage 3L would range from circa 16.5-21.6 % SOC with LiC₁₂- LiC₉.₂ in-plane density. Stage 2L would be at a SOC of approximately 35% with LiC₈.₆ in-plane density.

However, the calculated SOC regimes deviate from the experimentally determined ones of section 3.2.3. The estimated concentration regime of stage 1L extends to 6.8-7 % SOC which is consistent with the calculated range. In contrast, stage 4L is observed electrochemically at circa 12.6 and 12.8 % SOC for charge and discharge, respectively. Stage 3L is observed at circa 18-18.8 % SOC, and stage 2L at circa 24 and 26.6 % SOC for charge and discharge, respectively. The electrochemically observed solid-solution regime of dense stage 2 is between 47.2-52.8 % SOC.

The solubility limit of stage 1L with circa 6.8 % agrees well between the electrochemical observed and calculated one from NPD. Also the estimated regime of pure stage 3L matches. In contrast, stage 4L would need an increased in-plane density while stage 2L would need a decreased in-plane density to match the electrochemically observed values. It has to be stressed that also only stage 1L and 3L were found as a pure single phase while stages 2L and 4L were always mixed with stage 3L (and stage 2 in the case of stage 2L in Table 12). The necessary in-plane density of stage 4L and 2L would be circa LiC₁₁.₇-₁₁.₉ and LiC₁₁.₃-₁₂.₅ to match the electrochemically observed SOC, respectively.
It has to be stressed that stages 1, 2, 3L, and 1L are the only stages where the lithiated interslab match with the next lithiated interslab. This means that the stacking is \( \text{A|A...A|A} \) or \( \text{A|B|A|B} \) stacking for stage 1, 2, 3L, and 1L, respectively. Thus, the lithium ions could order in their preferred column structure [80]. In contrast, stages 2L and 4L have an \( \text{A|A...B|B} \) stacking of next neighbor lithiated interslabs, thus, disturbing the lithium column order significantly. The influences of these matching and unmatched stacking sequences on the development of a pure phase are unknown so far. Further research is necessary to shed light.

However, a simple model can be developed to describe the transitions between the different stages including the new information extracted from the diffraction experiments in section 5.2 and 5.3. To sketch the transition, the previously known information from the introduction section 2.5 can be used and extended by the new information. Therefore, Figure 132 shows the proposed transitions between the different phases of graphite which is adapted from Figure 7.

![Diagram of thermodynamic stage transitions of graphite during lithium intercalation](image)

Figure 132: Schematic of thermodynamic stage transitions of graphite during lithium intercalation, adapted from Figure 7.
The starting material is graphite as shown in Figure 132a). It can be filled up to ~6.8% SOC with lithium in the miscibility region of the phase diagram at room temperature. This phase is called stage 1L since every layer is filled with ~6.8% lithium. Next, a stage transition occurs to form stage 4L as described in section 2.5. This transition seems to be triggered by elastic energy because the average layer spacing decreases compared to stage 1L as shown in Figure 118. However, now a solid-solution of stage 4L occurs which means that the in-plane density of lithium in every fourth layer increases continuously. This densification can occur until the electrostatic repulsion of the lithium ions is stronger than the electrostatic repulsion in c-direction plus the elastic energy to form an expanded lithiated interslab every third layer instead of every fourth one.

Now, stage 3L shows a similar solid-solution regime where a densification within every third interslab is expected. However, the in-plane density should be increased compared to stage 4L due to the mentioned electrostatic repulsion. After a certain in-plane density is reached, it is energetically preferred to undergo a transition to stage 2L where every other interslab is filled liquid-like. Stage 2L should also show a solid-solution with an increase of the in-plane density of lithium in every other interslab compared to stage 3L and 4L. However, this densification is limited to a certain in-plane density around LiC₈.₅ to LiC₀ before a phase transition occurs forming LiC₆ in-plane density in very other interslab as stage 2. This abrupt densification towards stage 2 is in contrast to the previously described transitions where a homogeneous concentration increase is detected. The transition from stage 2L to stage 2 seems to be mainly due to elastic energy since the average layer spacing is decreasing drastically as shown in Figure 118. This decrease of c-axis spacing coincides with the shift from A|AB|B stacking to A|AA|A stacking which was found to compress the empty interslab to only 3.24 Å instead of the standard 3.35 Å for standard graphite AB stacking [90].

The following stage transitions are well understood. Stage 2 undergoes a phase transition to stage 1 where the stacking and in-plane density stay constant (AA, LiC₆) [80]. However, it is not understood why the lithium ions order in columns for stage 2 and stage 1 while all other intercalated alkali and earth-alkali metals order in helix form [100]. Electrostatic repulsion should rather favor the helix form, however, the column ordering is even observed for stage 2 with an empty interslab between the lithiated interslabs. DFT calculations would be necessary to explain the lithium ordering in columns. However, current DFT calculations have problems with the correct incorporation of the van-der-Waals forces in the empty interslabs [136, 186, 209, 210]. Further, research in this field is necessary to allow the completion of the model in section 5.1.
6.4 Summary of sketched mechanisms for graphite and GOpd

This chapter focused on the combination of experimental data and modeling approaches to get an insight into the kinetic and thermodynamic behavior of graphite and its derivatives. The first section 6.1 combined the results from the rate capability tests of thin-layer graphite electrodes in section 3.2 with the stage transitions of graphite in sections 2.5, 5.2, and 5.3. Additionally, the calculations of the orientation of the phase boundary in section 5.4 were included to describe the stage progression during cycling. Figure 127 sketched this progression which resembles the shape of the annuli of trees. The propagation of the phase boundary into the particle is described in Figure 128 where the concentration profile along the radial direction is sketched in Figure 129. This model is able to explain the differences of the rate capability of graphite based on the order of the stage transitions in graphite. The dense stages (stage 1 and 2) possess a lower diffusion coefficient which prohibits full lithiation at elevated rates. Thus, especially the specific charge of the stage transitions stage 2L-2 and 2-1 cannot deliver their expected charge. In contrast, the delithiation starts with the transition from stage 1 towards dense stage 2 which is as diffusion-limited as during charge. However, the subsequent liquid-like stage transitions can compensate for this loss allowing not only a longer diffusion period for the stage 1-2 phase boundary but also increasing the diffusion by reducing the phase width in radial direction. This increases the concentration gradient dc/dr, thus, increasing the diffusion rate based on Fick’s law. This model is able to explain the long known asymmetry between charge and discharge of graphite besides the limited overpotential available for charge of circa 80 mV.

Section 6.2 focused on the description of possible mechanisms for the improved rate capability and specific charge of partially-disproportionated graphite-oxide. Two different scenarios were proposed assuming the formation of either Li₂O or lithium-alkoxide groups to pillar the graphite structure as sketched in Figure 131. This probably leads to a reduction of the elastic stress during lithium intercalation as intended. It was found by application of Faraday’s law on the galvanostatic cycling of GOpd43 and XRD measurements that the formation of Li-O-graphene “bulk-surface” groups is more probable.

The strong aging of this material during the first 50-70 cycles (Figure 78) could also be sketched. The reduction of the Li-alkoxides to Li₂O might be the first step of the aging mechanism. These mostly “single” molecules are pushed back and forth periodically during lithium insertion and deinsertion, thus, possibly forming agglomerates similar to the Daumas-Herold domains of graphite. Due to the removal of the rather homogeneously distributed pillars to local domains, the structure might collapse and try to form graphite-like domains. This would lead to a decrease of the specific charge below the one of pristine graphite due to the blocking of many
lithium sites by \( \text{Li}_2\text{O} \) in the interslabs. This aging mechanism would be consistent with the findings for a significantly suppressed aging if cycling is limited to potentials between 1-3 V, as shown in section 4.2.8. However, direct evidence of the pillars in GOpd and the aging mechanism could not be found yet. Further research is necessary to confirm these hypotheses.

The last section 6.3 extended the known information about the thermodynamic stage transitions in graphite (summarized in section 2.5) by the experimental observations described in sections 5.2 and 5.3. All Li-graphite stages show a certain solid-solution regime at room temperature which is included in the phase diagram in Figure 9 but has not been parameterized crystallographically. A densification of the lithium in-plane density is observed before the next stage is formed, as sketched in Figure 132. Especially, the formation of stages 4L and 2 seem to be triggered by elastic energy which is accompanied by a decrease of the average interlayer distance, as shown in Figure 118. In contrast, the transitions from stage 4L-3L, 3L-2L, and 2-1 seem to depend rather on electrostatic repulsion. However, DFT calculations would be needed to estimate the contributions from elastic and electrostatic forces for the different stages.
7. Conclusions and outlook

Several conclusions have been given in the respective summaries of the chapters in sections 3.6, 4.3, 5.5, and 6.4. This chapter summarizes the most important results and conclusions from the combination of different experiments and models of all sections. Additionally, an outlook will be discussed to guide further research on unsolved or newly found challenges.

7.1 General conclusion

7.1.1 Kinetics of graphite as a negative electrode in lithium-ion batteries

The experimental chapter 3 investigated the kinetics of lithium intercalation in graphite. With the help of the newly developed thin-layer technique for electrodes, several different properties of graphite could be investigated. It could be proven that highly-crystalline graphite is one of the fastest lithium-ion intercalation materials described up to now. Delithiation can be performed at rates up to 680C for 3.3 μm big particles above which diffusion limitation in the electrolyte hinder further investigations. However, lithiation can be done only up to ca. 6C rates based on a galvanostatically extracted specific charge of 82% of the total specific charge (see section 3.2).

Besides the limited overpotential for the lithiation of graphite of ~80 mV, the order of the stage transitions seems to be important. Due to the reduced diffusion coefficient in the dense stages of graphite [136] compared to the liquid-like stages [153, 159], significantly less practical specific charge can be stored during galvanostatic lithiation. The transitions towards the dense stages, namely stage 1 and 2, deliver only ~40% of their specific charge at rates of 20C. In contrast, the transitions towards the liquid-like stages, namely 2L, 3L, 4L, and 1L, deliver more than 80% of their respective specific charge during lithiation. During delithiation, these liquid-like stage transitions can even compensate for the initial specific charge loss of the dense stage transitions, thus, allowing rates of at least 680C when high overpotentials are allowed (section 3.2.3). Usually, such high rates are only seen if the intercalation material is nanosized which reduces the diffusion length drastically. But the investigated graphite has a median diameter of 3.3 μm which is two-orders of magnitude higher than comparably fast intercalation hosts [52].

To describe this charge-discharge asymmetry in graphite, a shrinking annuli model has been developed in sect. 6.1. Knowledge about the stage transitions from both, literature and experimental findings from the in situ x-ray and neutron powder diffraction in 5.2 and 5.3 were combined with the calculations of the phase boundary orientation in sect. 5.4 to develop a lithiation-delithiation mechanism (Figure 127 - Figure 129). This mechanism can describe why more than 100% of practical specific charge can be withdrawn for the delithiation between 3- 32 C for the
transitions between stages 2-2L-3L-4L. Additionally, this model can describe the asymmetry between charge and discharge and was a necessary tool to guide possible modifications of graphite to change the performance towards a faster charge rate capability in chapter 4.

Furthermore, some kinetic bottlenecks of graphite could be determined for different specific currents. For very low specific currents of <0.5 A/g, an unknown phenomenon dominates the overpotentials of graphite which saturates at ~8 mV for both lithiation and delithiation. For specific currents ranging from 4 to ~50 A/g, surface-reactions dominate the overpotential contribution while at higher specific currents of more than 160 A/g both ohmic potential drops in the SEI and surface reactions contribute almost equally to the total overpotentials. A hysteresis is measured to be 6.6 mV for the transition of stage 1-2 and 12-13 mV for the transitions of stage 2-2L and 4L-1L. The hysteresis and the phenomenon at very low current density might lead to very strong nonlinearity for the electrochemical impedance spectroscopy in the ±10 mV potential regime around the OCP which could be an explanation for the failed deconvolution of the Li-graphite EIS and would be important to consider for EIS on graphite in general.

An activation process of the Li-graphite and Li-Li cell can be observed during the first two to three high-current-density discharges (section 3.3). Both high-rate experiments and electrochemical impedance spectroscopy found that the decrease is due to a resistance decrease on the lithium-metal electrode. The reduction of the resistance of the solid-electrolyte-interphase seems to be the dominating process to improve the cell performance.

The particle properties of different carbons dominate the electrochemical response of a thin-layer electrode since electrolyte diffusion limitations are suppressed (section 3.1.2). Therefore, bigger particles show a worse rate performance in the thin-layer electrode as shown for highly crystalline graphite particles in section 3.4.1. However, in standard electrodes, these properties contribute minor to the overall response since electrolyte diffusion limitations become dominating. Therefore, the particle shape seems to become the most important property of graphite since it defines the pore structure and connection between different pores in standard electrodes.

Difference in the polarization at very low rates can be detected by the galvanostatic-intermittent-titration-technique. Higher overpotentials are observed for lithiation compared to delithiation. Additionally, very uncommon relaxation phenomena can be observed on top of the initial ohmic potential drop and diffusional relaxation, as discussed in section 3.5. These overpotentials might originate from elastic energy contributions. These findings and the rate capability guided the research on the chemical modification of graphite described in chapter 4.
7.1.2 Chemical modifications of graphite to enhance the recharge rate capability

Two different approaches have been investigated to increase the interlayer distance between the graphene sheets in graphite in chapter 4 based on the findings for the rate kinetics in chapter 3. First, a titanate coating was applied on potassiated graphite which should spread the graphene sheets on the prismatic edge planes of graphite. A very thick coating with an excess of approximately 50 times the amount of titanate was used to confirm the coating by SEM images and EDX. This excess of coating lead to higher overpotentials during galvanostatic cycling, as shown in Figure 72. However, a decreased fading of specific charge of the thin-layer electrodes of titanate-coated graphite SFG6 could be detected compared to the thin-layer electrodes of pristine graphite. A coating of graphite with a very thin surface layer of 3-5 atomic layers would be necessary to detect any influence on the charge rate capability.

A second approach aimed to increase the interlayer distance by pillaring the bulk material of graphite (section 4.2). A modified form of graphite, namely partially-disproportionated graphite-oxide (GOpd synthesized by Dr. T. Kaspar, ETHZ) has been chosen. This material is ideal for the pillaring of the graphene sheets which are expected to form lithium-alkoxides and/or lithium oxide from the remaining epoxide and hydroxide groups in the GOpd bulk. Also the precursor, graphite oxide, (GO synthesized by Dr. T. Kaspar) was investigated for comparison.

Galvanostatic cycling showed significant thermodynamic differences between GO and partially-disproportionated GO compared to pristine graphite. The intercalation process observed in standard graphite was replaced by a process similar to adsorption. But this adsorption shows some extra features which differ significantly from those of normal capacitor-like materials. The main lithium-insertion occurs at potentials between 0 - 0.5 V vs. Li+/Li while standard capacitor materials show a constant specific capacitance. Additionally, the reversibly stored specific charge of GOpd43 and GOpd36 is significantly enhanced compared to standard graphite. During the first delithiation 677 and 580 mAh/g can be extracted for GOpd43 and GOpd36, respectively, being 1.88 and 1.61 times the specific charge than that of the precursor graphite.

However, a severe fading of the specific charge has been observed during the first 70 cycles of GOpd after which the aging is reduced significantly and ages only by a few percent during the next 400 cycles. Additionally, an irreversible specific charge is observed during these initial 70 cycles after which a cycling efficiency of over 99 % is reached. Thus, it can be concluded that the irreversible specific charge might be directly connected to the fading of the specific charge decreasing below the specific charge of standard graphite electrodes. The specific charge in the hundredth cycle are only 107, 259, and 274 mAh/g for GO, GOpd43 and GOpd36, respectively.
An investigation with three different potential ranges (1-3V, 0-2V, and 0.5-2.5V) revealed that the operation negative to 1 V vs. Li+/Li seems to be mainly responsible for the capacity fading.

No visible exfoliation has been observed for GOpd particles after the first and even after 400 cycles. Additionally, a SEI is created on the GOpd particles which possesses a similar morphology in comparison to standard graphite electrode which was also confirmed by EDX and XPS measurements. But a very thick SEI can be observed on some prismatic edge planes of the GOpd43 particles after more than 400 cycles which might be of rather polymeric origin based on visual observations in the SEM images. In contrast, SEM images on GO show some signs of partial exfoliation during the cycling as depicted in Figure 85.

To get further information about the SEI composition, EDX and XPS measurements of the cycled GOpd43 electrodes have been measured (sections 4.2.4 and 4.2.5). The EDX results support the picture of a continuous SEI growth on GOpd which is almost finished after the first cycle but its thickness approximately doubles during the consecutive 400 cycles. Very interestingly, the XPS C1s spectra of lithiated GOpd43 shows more contributions in the binding energy range of 286-289 eV compared to the C-C binding energy at 284.4 eV as shown in Figure 95b which indicates a possible increased amount of C-O bonds. This could indicate a possible lithium-alkoxide formation. But a conclusive deconvolution was impossible due to the limited amount of reference samples and high number of peaks making it difficult to deconvolute the C1s spectra.

The XRD results in section 4.2.6 give more insight into the modification of the bulk of the different graphite derivatives. The pristine materials show not only the distinct interlayer distance of 5.74, 4.3, 3.6, and 3.35 Å for GO, GOpd43, GOpd36, and pristine graphite, respectively. But they also indicate a modification of the C-C in-plane distance which is 1.438, 1.41, 1.416, and 1.422 Å for GO, GOpd43, GOpd36, and SFG6, respectively. Very broad reflexes are observed for the (100) and (101) reflexes which was attributed to a possible turbostratic disorder [169] but might also come from the stretching and quenching of the C-C bond length due to the epoxide and hydroxide groups in the pristine material as proposed in section 4.2.6.

During the lithiation of GOpd43, an increase of the interlayer distance is observed which increases from 4.33 to 5.73 Å corresponding to the initial interlayer distance of pristine graphite-oxide. This interlayer distance also indicates a possible formation of lithium-alkoxide pillars which are isostructural to the hydroxide groups of pristine graphite-oxide.

To test the influence of the pillaring in graphite, cyclic voltammetry has been used at various sweep rates. In the first cycle, an activation process can be detected for the GOpd electrodes (Figure 103a and Figure 104a) which is expected since lithium most probably reduces the epoxide and hydroxide groups partially. The rate capability of GOpd electrodes is very high deliver-
ing much more than 500 F/g during low sweep rates which is a factor of 2.5 compared to today’s best graphene based capacitors with TEABF₄ in AN or PC (Fig. 6c in [170]). The activation can be partially suppressed by increased sweep rates of 10 mV/s compared to 1 mV/s of a standard activation which allow not enough time for the reaction to occur.

The rate performance is significantly improved compared to pristine graphite delivering ~ 200 mAh/g at a sweep rate of 100 mV/s (30 s charge). This is a fundamental improvement compared to standard graphite electrodes which can be charged at ~2C (30 min) for standard electrodes. To determine the true rate-capability of the GOpd material, a thin-layer electrode would be needed since diffusion limitations in the electrolyte might severally reduce the overall rate performance. But even the rate tests with a standard electrode show drastic improvements compared to standard graphite electrodes, which, in fact, was the goal of the chemical modification of graphite.

The material GOpd shows a large hysteresis of ~1.2 V between charge and discharge (Figure 108) which is not due to kinetic limitations but an intrinsic property of the material itself. Additionally, very high polarization of more than 700 mV is detected at delithiation potentials between 2-3 V where still a reasonable specific charge can be extracted. However, the hysteresis shrinks during cycling/aging of the GOpd material as shown in Figure 107. This very large hysteresis would lead to a reduced energy efficiency during cycling.

A mechanistic sketch could be developed in section 6.2 where it was found that the formation of lithium-alkoxide seems to be the most probable pillaring mechanism. Faraday’s law applied to galvanostatic cycling and XRD measurements support this hypothesis. The aging might come from a reduction of Li-O-graphene to Li₂O which could agglomerate during cycling. This could lead to the collapse of the expanded interlayer distance. However, direct evidence of the activation and aging mechanism is still needed.

It can be concluded that the modification of graphite, both on the surface and in the bulk, can influence the electrochemistry during lithium storage. Even if the rate capability might be improved significantly while also the total specific charge increased by a factor of ~1.88 compared to standard graphite SFG6 electrode, severe challenges are encountered. The fading of specific charge, high hysteresis of ~1.2 V, kinetic limitations close to 0 and 3 V vs. Li⁺/Li, and dangerous and time-consuming material synthesis of GOpd have to be overcome to make this material promising for future lithium-ion batteries.
7.1.3 Thermodynamic phase transitions in the lithium-graphite system

Chapter 5 focused on the lithiated phases of graphite and phase transitions. Since lithiated graphite undergoes five different phase transitions at room temperature, a model was developed based on a mean-field approach in section 5.1. The modeled free energy of graphite mimics the phase diagram and open-circuit-potential and revealed that there are several unexplained features in the lower state-of-charge regime of the phase diagram/OCP. The model indicated a reduced in-plane density of lithium for stages 4L and 3L, and some hindering of the stage 2L formation. Additionally, pure phase separation could only be confirmed for the stage transition 2-1.

These findings lead to the investigation of the phase transitions by in situ XRD and in and ex situ NPD in section 5.2 and 5.3, respectively. For the first time, all space groups could be assigned. The structure of stage 1, 2, and graphite are known [80, 107, 109]. However, only the repeated distance and in-plane carbon-carbon distance were known for stages 2L, 3L, and 4L, as summarized in Table 3. The refined space group parameters of these stages could be identified and correspond to an AA stacking for the lithiated interslab while AB stacking is observed for the empty interslabs. Another interesting feature was also detected. The stages 3L and 4L show a solid-solution behavior where the a- and c-axis parameters vary with degree of lithiation. These findings support the model in section 5.1. The sloppy potential profile in the regime between stage 4L-3L-2L can be explained by a solid-solution in the respective stage (Figure 118).

Furthermore, stages 3L and 4L are very well-defined and show distinct reflexes during electrochemical delithiation. In contrast, a frustration of stage 4L was found during lithiation as shown in Figure 117. The reflexes of stage 4L are badly defined for lithiation while stage 3L is well-established. This can explain the sloppy potential profile for the transition of stage 1L to 4L since stage 3L might already develop so that the transition forms a phase mix with 1L to 4L/3L.

The last part of this section focused on the orientation of phase boundary between all five different stage transitions described in section 5.4. Based on the calculations of Khachaturyan [202] it could be found that the minimal elastic energy for a coherent interface aligns around 70° with respect to the graphene sheets (summary in Table 13). Furthermore, the influence of an incoherent interface in a) (001) direction and b) (100) direction has been investigated. For an incoherent interface in c-direction, the phase boundary rotates to circa 20° for the different stages. In contrast, an incoherent interface in (100) direction shifts the minimum only by two degrees.

Last, a model for phase separation was combined with the elastic energy contributions based on the work of Cogswell et al. [48]. The adaptation of their model to graphite allowed the study of the alignment of stage 1 and 2 to each other during relaxation and galvanostatic lithiation. It
could be found that the stages try to align close to the minimal elastic energy as calculated. These findings help to understand the progression of the stages into the bulk of graphite.

The new findings about the liquid-like stages 4L, 3L, and 2L helped to describe the transitions in graphite in more detail, as discussed in section 6.3. The transitions seem to be triggered by elastic and electrostatic forces. For the transition of stage 1L-4L and 2L-2 the elastic energy seems to be the dominant driving-force which can be seen by a decrease of the average interlayer distance in Figure 118 and a reordering of the stacking in graphite. In contrast, the transitions of 4L-3L, 3L-2L, and 2-1 seem to be dominated by electrostatic repulsion of the intercalated lithium ions.

7.2 Outline

Some aspects could not be solved in this work. For the rate kinetics of graphite described in section 3, the unsolved aspects concern the electrochemical impedance spectroscopy. A three-electrode cell would be necessary to detect if the high-rate discharge also improves the cycling on the graphite electrode. Especially, the decrease of the SEI resistance after high current densities would be important to confirm. This would be helpful to give guidelines for the formation cycles of graphite electrodes for high-power applications. Additionally, the thin-layer electrode technique could be applied to other materials for which electrolyte diffusion limitations seem to govern the electrochemical response during high rates. A thin-layer electrode with LiFePO₄ showed already good results.

The modification of graphite in chapter 4 shows very high potential for further development. First, the titanate coating needs to be synthesized forming a thin coating of only a few atomic layers to evaluate if the charge rate capability can be improved. Second, the partially-disproportionated graphite-oxide needs to be studied in more detail. Especially, a direct evidence of the chemical modification and aging mechanism is necessary. Li-NMR could be crucial to shed a light on the chemical bonds in the activated GOpd.

The raw material GOpd leaves also many possibilities to be modified chemically. Titanates could be included in the structure which could be validated already in preliminary experiments in Prof. Nesper's group at ETH. Additionally, the gap between an interlayer distance of 5.7 Å for GO and 4.6-3.3 Å for GOpd could be closed by applying a stoichiometric chemical reduction by hydrazine. Preliminary experiments in the group of Prof. Nesper showed already promising results. Moreover, a partially-reduced graphite-oxide GOpr instead of a partially-disproportionated graphite-oxide would be very helpful to determine the amount of lithium stored in cavities in
GOpd. A preferred partial-reduction should reduce the graphene-oxide sheets without the introduction of point defects or cavities due to CO and CO$_2$ release. If a similar specific charge can be stored in GOpri as in GOpd, cavities would play a minor role.

Additionally, other cations like Na and K could be stored in GOpd. Preliminary experiments showed a similar potential profile during cycling, however, a lower specific charge could be extracted compared to Li-GOpd. Especially, the sodium insertion is very important since Na does almost not intercalate in pristine graphite showing only 35-40 mAh/g of specific charge [100]. This material could make a significant impact in the field of sodium batteries due to its advantages, if aging could be avoided.

For the investigations of the thermodynamic stage transitions in graphite in chapter 5, complete evaluation of the in situ XRD and NPD data could help to clarify the mismatch of calculated and measured in-plane concentrations of lithium in stages 4L, 3L, and 2L, as discussed in section 6.3. This issue might be due to phase-mixing as discussed but needs to be validated.

Additionally, the refined phases should be used to develop the model in section 5.1 further which actually initiated the research on the transitions at low SOC. The model would help to understand graphite better and develop the model of Newman et al. [146] further including thermodynamic information on the actual phase equilibria, as done for LiFePO$_4$ [65]. A complete three-dimensional model of the stage transitions based on the Cahn-Hilliard approach would help to confirm the shrinking annuli model in section 6.1, however, the calculations might be very time-consuming.

Last, the influence of temperature would be interesting to be studied with respect to the proposed influence of both the diffusion coefficient and the solubility limit determining the maximum concentration gradient in a single phase regime in graphite. These experiments could be helpful to understand the performance of graphite under severe temperature conditions for vehicle applications at -20 to 60°C.
List of symbols

a  enthalpy factor
A  area, m^2
c  concentration, mol m^-3
ce  concentration of salt in electrolyte, mol m^-3
co  concentration of solvent, mol m^-3
De, Ds  diffusion coefficient in electrolyte, solid m^2 s^{-1}
e  electron charge
E  energy, J
f  activity coefficient, mol m^{-3}
f(c)  homogeneous free energy, J
F  Faraday’s constant, 96485 C mol^{-1}
h  porous electrode thickness, m
i  current density, A m^{-2}
i0  exchange current density, A m^{-2}
I  superficial current density, A m^{-2}
J  diffusion flux, mol m^{-2} s^{-1}
K  gradient energy penalty tensor
kB  Boltzmann constant
m  mass, g
OF  oxidation factor
Q  charge, mAh
r  particle radius, m
R  universal gas constant, 8.3143 J mol^{-1} K^{-1}
R0  contact resistance, \Omega
RSEI  resistance of solid-electrolyte interphase, \Omega
S  dimensionless number for diffusion influence
t^0  transference number
T  temperature, K
u  composition inhomogeneity
U_{OCP}  open-circuit potential, V
V  volume, m^3
z  number of electrons
\alpha_{a,c}  transfer coefficient, anodic/cathodic
\varepsilon  porosity or elastic strain
\rho_{Li}  maximum density of lithium in the host material
\eta  surface overpotential, V
\lambda  wavelength, nm
\mu  chemical potential, V
\kappa  conductivity of electrolyte, S m^{-1}
\sigma  conductivity of solid matrix, S m^{-1} or stress, N
\Phi  electrical potential, V
\Theta  diffraction angle Theta, °

Subscripts
e  electrolyte in separator and porous electrode
s  solid phase
n  normal direction
TL  thin layer
List of abbreviation

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>AC</td>
<td>alternating current</td>
</tr>
<tr>
<td>AN</td>
<td>acetonitril</td>
</tr>
<tr>
<td>ASA</td>
<td>active surface area</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller surface area</td>
</tr>
<tr>
<td>CMC</td>
<td>carboxymethylcelluloose</td>
</tr>
<tr>
<td>CNT</td>
<td>carbon nanotubes</td>
</tr>
<tr>
<td>DC</td>
<td>direct current</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DMC</td>
<td>dimethyl carbonate</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>DRT</td>
<td>distributed relaxation times</td>
</tr>
<tr>
<td>EC</td>
<td>ethylene carbonate</td>
</tr>
<tr>
<td>EDX</td>
<td>energy-dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>ETH</td>
<td>Eidgenössische Technische Hochschule</td>
</tr>
<tr>
<td>EV</td>
<td>electric vehicle</td>
</tr>
<tr>
<td>FEM</td>
<td>finite element method</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>GITT</td>
<td>galvanostatic-intermittent-titration-technique</td>
</tr>
<tr>
<td>GOpd</td>
<td>graphite-oxide partially disproportionated</td>
</tr>
<tr>
<td>HCD</td>
<td>high-current density</td>
</tr>
<tr>
<td>HCDFC</td>
<td>high-current density formation cycle</td>
</tr>
<tr>
<td>HEV</td>
<td>hybrid electric vehicle</td>
</tr>
<tr>
<td>HOPG</td>
<td>highly-oriented pyrolytic graphite</td>
</tr>
<tr>
<td>IC</td>
<td>internal combustion</td>
</tr>
<tr>
<td>MCMB</td>
<td>mesocarbon microbead</td>
</tr>
<tr>
<td>MIT</td>
<td>Massachusetts Institute of Technology</td>
</tr>
<tr>
<td>NCA</td>
<td>NiCoAl-oxide</td>
</tr>
<tr>
<td>NMC</td>
<td>NiMnCo-oxide</td>
</tr>
<tr>
<td>NMP</td>
<td>n-methyl-pyrolidone</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NPD</td>
<td>neutron powder diffraction</td>
</tr>
<tr>
<td>OCP</td>
<td>open-circuit potential</td>
</tr>
<tr>
<td>PHEV</td>
<td>plugin-hybrid electric vehicle</td>
</tr>
<tr>
<td>PSI</td>
<td>Paul-Scherrer-Institute</td>
</tr>
<tr>
<td>PTC</td>
<td>positive temperature coefficient</td>
</tr>
<tr>
<td>PTFE</td>
<td>polytetrafluoroethylene</td>
</tr>
<tr>
<td>PVDF</td>
<td>polyvinylidene fluoride</td>
</tr>
<tr>
<td>SEI</td>
<td>solid-electrolyte-interphase</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SOC</td>
<td>state-of-charge</td>
</tr>
<tr>
<td>SPI</td>
<td>solid-permeable interface</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>VdW</td>
<td>van-der-Waals</td>
</tr>
<tr>
<td>wt%</td>
<td>weight percent</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>x-ray diffraction</td>
</tr>
</tbody>
</table>
8. Appendix

8.1 Aging of thin-layer electrodes of graphite SFG6 during high rate cycling

The five different samples in section 3.2 and 3.3 underwent electronic particle loss during the high rate cycling as shown in Figure 133. This aging has been included in the calculations for rate, galvanostatically extracted specific charge and current densities.

![Figure 133: Aging of thin-layer electrodes of pristine SFG6 graphite during cycling for five different samples corresponding to the galvanostatic cycling in Figure 23.](image)

8.2 Raman spectroscopy of KC₈

The titanate coating in section 4.1 used potassium intercalated graphite in stage 1 with a composition of KC₈. The golden powder was investigated by Raman spectroscopy to see its influences on the phonons in graphite and detect if potassium remains in graphite.

![Figure 134: Raman spectroscopy of KC₈, a) light microscope image of KC₈ powder, b) Raman spectroscopy results of potassiated graphite SFG6.](image)
8.3 X-ray photoelectron spectroscopy (XPS) of partially-disproportionated graphite-oxide (GOpd43), graphite SFG6 and SuperP electrodes

The XPS spectra in section 4.2.5 have been taken for GOpd43, SFG6, and Super electrodes in three different cycling states. Pristine and one time lithiated electrodes have been measured for all three electrodes while GOpd43 was also measured in the delithiated state after one cycle. The GOpd43 electrode is composed of 80:10:10 of GOpd43: PVDF: SuperP while the graphite SFG6 electrode consists of 90:10 SFG6: PVDF and the SuperP one of 80:20 SuperP: PVDF due to the very small particle size of SuperP. Both SFG6 and SuperP electrodes are used as reference samples. All electrodes where assembled in a capacitor configuration versus YP17 activated carbon in EC:DMC 1:1 (wt), 1M LiPF₆ with an excess of YP17. The electrodes were disassembled and washed three times with DMC to remove remaining salt in an Argon-filled glove box and transferred with an air-tight transfer-chamber to the XPS. After the measurement, the electrodes have been transferred back to the glove box in XPS transfer chamber after which they have been transferred to the SEM machine in another transfer chamber to be tested by SEM and EDX.

8.3.1 XPS of pristine GOpd43 electrode:

![XPS Spectrum](image)

![Density of States](image)

![C1s Spectrum](image)

![O1s Spectrum](image)
Figure 135: XPS of pristine GOpd43 electrode a) full XPS pattern, b) valence pattern, c) C1s spectrum, d) O1s spectrum and e) F1s spectrum.

Table 16: Summary of deconvolution of XPS spectra of pristine GOpd43 electrode.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s reflex 1</td>
<td>284.43</td>
<td>0.87</td>
<td>37.54</td>
</tr>
<tr>
<td>C1s reflex 2</td>
<td>285.69</td>
<td>1.25</td>
<td>12.34</td>
</tr>
<tr>
<td>C1s reflex 3</td>
<td>286.4</td>
<td>1.5</td>
<td>7.19</td>
</tr>
<tr>
<td>C1s reflex 4</td>
<td>288.22</td>
<td>1.74</td>
<td>4.35</td>
</tr>
<tr>
<td>C1s reflex 5</td>
<td>290.44</td>
<td>1.49</td>
<td>10.95</td>
</tr>
<tr>
<td>C1s reflex 6</td>
<td>293.03</td>
<td>1.46</td>
<td>1.09</td>
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<tr>
<td>O1s reflex 1</td>
<td>531.2</td>
<td>1.81</td>
<td>2.82</td>
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<td>O1s reflex 2</td>
<td>533.35</td>
<td>1.58</td>
<td>3.49</td>
</tr>
<tr>
<td>O1s reflex 3</td>
<td>535.71</td>
<td>1.56</td>
<td>0.23</td>
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<tr>
<td>F1s reflex 1</td>
<td>687.42</td>
<td>1.41</td>
<td>12.63</td>
</tr>
<tr>
<td>F1s reflex 2</td>
<td>688.44</td>
<td>1.47</td>
<td>7.37</td>
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8.3.2 XPS of GOpd43 after first lithiation, sample 1:
Figure 136: XPS of GOpd43 after 1st lithiation a) full XPS pattern, b) valence pattern, c) C1s spectrum, d) O1s spectrum, e) F1s spectrum, f) Li1s spectrum, g) P2p spectrum and h) C1s spectrum comparison at beginning of XPS measurement and after all other spectra (O1s, F1s, Li1s, P2p, Valence) have been taken to determined sample changes in ultra-high vacuum over experimental period.
Table 17: Summary of deconvolution of XPS spectra of GOpd43 after the 1st lithiation, sample 1.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position</th>
<th>FWHM</th>
<th>At %</th>
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<tr>
<td></td>
<td>[eV]</td>
<td>[eV]</td>
<td>%</td>
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<td>C1s reflex 1</td>
<td>284.45</td>
<td>0.97</td>
<td>1.72</td>
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<td>C1s reflex 2</td>
<td>285.96</td>
<td>1.44</td>
<td>3.02</td>
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<td>C1s reflex 3</td>
<td>287.17</td>
<td>1.44</td>
<td>8.33</td>
</tr>
<tr>
<td>C1s reflex 4</td>
<td>288.76</td>
<td>1.44</td>
<td>3.28</td>
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<td>C1s reflex 5</td>
<td>292.15</td>
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<td>3.58</td>
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<tr>
<td>O1s reflex 1</td>
<td>533.65</td>
<td>2.32</td>
<td>2.56</td>
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<tr>
<td>O1s reflex 2</td>
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<tr>
<td>Li1s reflex 1</td>
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<tr>
<td>Li1s reflex 2</td>
<td>57.71</td>
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<td>34.31</td>
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<tr>
<td>P2p reflex 1</td>
<td>138.95</td>
<td>2.77</td>
<td>0.4</td>
</tr>
</tbody>
</table>

8.3.3 XPS of GOpd43 after first lithiation, sample 2:

a) 4x10^5

b) 1200

A C1s spectrum reflects the convolution residuals.

c) 6000

d) 12000

A C1s spectrum shows the convolution residuals.
Table 18: Summary of deconvolution of XPS spectra of GOpd43 after the 1\textsuperscript{st} lithiation, sample 2.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
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<td>C1s reflex 1</td>
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<td>C1s reflex 2</td>
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<td>288.52</td>
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<td>291.55</td>
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<td>1.39</td>
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<td>C1s reflex 6</td>
<td>292.69</td>
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<td>Li1s reflex 2</td>
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<td>P2p reflex 1</td>
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<td>1.82</td>
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8.3.4 XPS of GOpd43 after first lithiation + delithiation, sample 1:
Figure 138: XPS of GOpd43 after 1st lith- + delithiation a) full XPS pattern, b) valence pattern, c) C1s spectrum, d) O1s spectrum, e) F1s spectrum, f) Li1s spectrum and g) P2p spectrum.

Table 19: Summary of deconvolution of XPS spectra of GOpd43 after the 1st lithiation and delithiation, sample 1.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position</th>
<th>FWHM</th>
<th>At %</th>
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</thead>
<tbody>
<tr>
<td>C1s reflex 1</td>
<td>284.34</td>
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<td>C1s reflex 2</td>
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<td>2.15</td>
<td>5.36</td>
</tr>
<tr>
<td>O1s reflex 2</td>
<td>534.76</td>
<td>2.15</td>
<td>3.02</td>
</tr>
<tr>
<td>F1s reflex 1</td>
<td>685.98</td>
<td>1.52</td>
<td>16.54</td>
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<tr>
<td>F1s reflex 2</td>
<td>688.55</td>
<td>2.2</td>
<td>14.35</td>
</tr>
<tr>
<td>Li1s reflex 1</td>
<td>56.63</td>
<td>1.41</td>
<td>21.23</td>
</tr>
<tr>
<td>P2p reflex 1</td>
<td>135.55</td>
<td>1.65</td>
<td>0.25</td>
</tr>
<tr>
<td>P2p reflex 2</td>
<td>137.98</td>
<td>1.64</td>
<td>0.76</td>
</tr>
</tbody>
</table>
8.3.5 XPS of GOpd43 after first lithiation + delithiation, sample 2:

Figure 139: XPS of GOpd43 after 1st lith- + delithiation a) full XPS pattern, b) C1s spectrum.

Table 20: Summary of deconvolution of XPS spectra of GOpd43 after the 1st lithiation and delithiation, sample 2.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s reflex 1</td>
<td>284.36</td>
<td>0.84</td>
<td>7.92</td>
</tr>
<tr>
<td>C1s reflex 2</td>
<td>285.3</td>
<td>1.5</td>
<td>12.8</td>
</tr>
<tr>
<td>C1s reflex 3</td>
<td>286.64</td>
<td>1.5</td>
<td>6.36</td>
</tr>
<tr>
<td>C1s reflex 4</td>
<td>287.71</td>
<td>1.51</td>
<td>3.95</td>
</tr>
<tr>
<td>C1s reflex 5</td>
<td>289.63</td>
<td>1.5</td>
<td>1.41</td>
</tr>
<tr>
<td>C1s reflex 6</td>
<td>291.35</td>
<td>1.5</td>
<td>4.74</td>
</tr>
<tr>
<td>O1s reflex 1</td>
<td>533.11</td>
<td>1.98</td>
<td>4.94</td>
</tr>
<tr>
<td>O1s reflex 2</td>
<td>534.55</td>
<td>1.98</td>
<td>3.51</td>
</tr>
<tr>
<td>F1s reflex 1</td>
<td>685.98</td>
<td>1.44</td>
<td>17.35</td>
</tr>
<tr>
<td>F1s reflex 2</td>
<td>688.5</td>
<td>2.09</td>
<td>14.44</td>
</tr>
<tr>
<td>Li1s reflex 1</td>
<td>56.63</td>
<td>1.37</td>
<td>21.53</td>
</tr>
<tr>
<td>P2p reflex 1</td>
<td>135.28</td>
<td>1.61</td>
<td>0.25</td>
</tr>
<tr>
<td>P2p reflex 2</td>
<td>137.93</td>
<td>1.77</td>
<td>0.8</td>
</tr>
</tbody>
</table>
8.3.6 XPS of pristine graphite SFG6:

(a) XPS spectrum

(b) Density-of-states

(c) C1s spectrum

(d) O1s spectrum

(e) F1s spectrum

(f) Li1s spectrum
Figure 140: XPS of pristine graphite SFG6 electrode a) full XPS pattern, b) valence pattern, c) C1s spectrum, d) O1s spectrum, e) F1s spectrum, f) Li1s spectrum and g) P2p spectrum.

Table 21: Summary of deconvolution of XPS spectra of pristine graphite SFG6 electrode.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position</th>
<th>FWHM</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[eV]</td>
<td>[eV]</td>
<td>%</td>
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<tr>
<td>C1s reflex 1</td>
<td>284.11</td>
<td>0.55</td>
<td>41.75</td>
</tr>
<tr>
<td>C1s reflex 2</td>
<td>284.42</td>
<td>1.44</td>
<td>20.77</td>
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<td>285.91</td>
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<td>9.75</td>
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<tr>
<td>C1s reflex 4</td>
<td>290.14</td>
<td>2.06</td>
<td>9.79</td>
</tr>
<tr>
<td>O1s reflex 1</td>
<td>531.24</td>
<td>2.4</td>
<td>0.94</td>
</tr>
<tr>
<td>O1s reflex 2</td>
<td>532.93</td>
<td>2.4</td>
<td>0.85</td>
</tr>
<tr>
<td>F1s reflex 1</td>
<td>687.62</td>
<td>2.05</td>
<td>16.15</td>
</tr>
</tbody>
</table>

8.3.7 XPS of lithiated graphite SFG6 electrode in first cycle:
Figure 141: XPS of lithiated graphite SFG6 electrode in first cycle a) full XPS pattern, b) valence pattern, c) C1s spectrum, d) O1s spectrum, e) F1s spectrum, f) Li1s spectrum and g) P2p spectrum.
Table 22: Summary of deconvolution of XPS spectra of lithiated graphite SFG6 electrode.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s reflex 1</td>
<td>284.72</td>
<td>0.62</td>
<td>4.5</td>
</tr>
<tr>
<td>C1s reflex 2</td>
<td>285.32</td>
<td>1.29</td>
<td>4.88</td>
</tr>
<tr>
<td>C1s reflex 3</td>
<td>287.4</td>
<td>1.59</td>
<td>7.05</td>
</tr>
<tr>
<td>C1s reflex 4</td>
<td>288.85</td>
<td>1.75</td>
<td>6.35</td>
</tr>
<tr>
<td>C1s reflex 5</td>
<td>292.07</td>
<td>2.03</td>
<td>2.59</td>
</tr>
<tr>
<td>C1s reflex 6</td>
<td>293.28</td>
<td>1.12</td>
<td>2.77</td>
</tr>
<tr>
<td>O1s reflex 1</td>
<td>530.47</td>
<td>1.14</td>
<td>0.34</td>
</tr>
<tr>
<td>O1s reflex 2</td>
<td>534</td>
<td>2.31</td>
<td>7.61</td>
</tr>
<tr>
<td>O1s reflex 3</td>
<td>535.97</td>
<td>2.31</td>
<td>1.88</td>
</tr>
<tr>
<td>F1s reflex 1</td>
<td>687.67</td>
<td>1.46</td>
<td>20.09</td>
</tr>
<tr>
<td>F1s reflex 2</td>
<td>690.42</td>
<td>2.12</td>
<td>11.9</td>
</tr>
<tr>
<td>Li1s reflex 1</td>
<td>56.64</td>
<td>1.44</td>
<td>4.06</td>
</tr>
<tr>
<td>Li1s reflex 2</td>
<td>58.16</td>
<td>1.44</td>
<td>25.54</td>
</tr>
<tr>
<td>P2p total</td>
<td>139.74</td>
<td>1.56</td>
<td>0.43</td>
</tr>
</tbody>
</table>

8.3.8 XPS of pristine SuperP electrode:

a) XPS spectrum
b) density-of-states
c) C1s spectrum, reflexes, convolution, residuals
d) O1s spectrum, reflexes, convolution, residuals
Figure 142: XPS of pristine SuperP electrode in first cycle a) full XPS pattern, b) valence pattern, c) C1s spectrum, d) O1s spectrum, e) F1s spectrum, f) Li1s spectrum and g) P2p spectrum.

Table 23: Summary of deconvolution of XPS spectra of pristine SuperP electrode.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s reflex 1</td>
<td>284.13</td>
<td>0.92</td>
<td>56.3</td>
</tr>
<tr>
<td>C1s reflex 2</td>
<td>287.52</td>
<td>1.44</td>
<td>3.04</td>
</tr>
<tr>
<td>C1s reflex 3</td>
<td>285.69</td>
<td>1.44</td>
<td>14.8</td>
</tr>
<tr>
<td>C1s reflex 4</td>
<td>290.34</td>
<td>1.8</td>
<td>10.43</td>
</tr>
<tr>
<td>O1s reflex 1</td>
<td>531.93</td>
<td>3.15</td>
<td>0.3</td>
</tr>
<tr>
<td>F1s reflex 1</td>
<td>687.82</td>
<td>1.98</td>
<td>15.14</td>
</tr>
</tbody>
</table>
8.3.9 XPS of lithiated SuperP electrode:

![Graphs showing XPS spectra and binding energy distributions for different elements and their respective states: C1s, O1s, F1s, and Li1s.]

- **a)** XPS spectrum with counts on the y-axis and binding energy in eV on the x-axis for C1s.
- **b)** Density-of-states graph with counts on the y-axis and binding energy in eV on the x-axis.
- **c)** C1s spectrum showing the resolved peaks with reflexes, convolution, and residuals.
- **d)** O1s spectrum with similar components as in (c).
- **e)** F1s spectrum, again with reflexes, convolution, and residuals.
- **f)** Li1s spectrum, indicating the convolution and residuals.
Figure 143: XPS of lithiated SuperP electrode in first cycle a) full XPS pattern, b) valence pattern, c) C1s spectrum, d) O1s spectrum, e) F1s spectrum, f) Li1s spectrum and g) P2p spectrum.

Table 24: Summary of deconvolution of XPS spectra of lithiated SuperP electrode.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s reflex 1</td>
<td>284.43</td>
<td>0.96</td>
<td>6.75</td>
</tr>
<tr>
<td>C1s reflex 2</td>
<td>285.4</td>
<td>1.44</td>
<td>3.04</td>
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<tr>
<td>C1s reflex 3</td>
<td>286.92</td>
<td>1.44</td>
<td>5.62</td>
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<td>C1s reflex 4</td>
<td>288.29</td>
<td>1.44</td>
<td>6.42</td>
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<tr>
<td>C1s reflex 5</td>
<td>290.64</td>
<td>1.44</td>
<td>1.6</td>
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<tr>
<td>C1s reflex 6</td>
<td>292.39</td>
<td>1.44</td>
<td>5.09</td>
</tr>
<tr>
<td>O1s reflex 1</td>
<td>533.7</td>
<td>2.16</td>
<td>7.74</td>
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<td>O1s reflex 2</td>
<td>535.74</td>
<td>2.12</td>
<td>1.62</td>
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<tr>
<td>F1s reflex 1</td>
<td>686.99</td>
<td>1.45</td>
<td>20.3</td>
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<td>F1s reflex 2</td>
<td>689.72</td>
<td>2.04</td>
<td>13.91</td>
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<tr>
<td>Li1s reflex 1</td>
<td>57.46</td>
<td>1.51</td>
<td>27.3</td>
</tr>
<tr>
<td>P2p total</td>
<td>139.28</td>
<td>1.56</td>
<td>0.62</td>
</tr>
</tbody>
</table>
8.4 GITT of GOpd43 with C/80

![GITT cycle 1 and GITT cycle 2 comparison](image)

Figure 144: Galvanostatic-intermittent-titration-technique of GOpd43 electrode at reduced current density compared to GITT of GOpd43 in Figure 108.

8.5 Neutron powder diffraction

To extract the zero shift and several other machine parameters, a standard material was measured which is Na$_2$Ca$_3$Al$_2$F$_{14}$. The cubic space group I2$_1$3 with a refined crystal parameter of a=10.2505 gives a zero shift of -0.3134 at a wavelength of 1.8679 Å. This zero shift is quite high but possible for neutron diffraction. The refined NPD pattern is shown in Figure 145 with a refinement value of Rwp = 7.72 which is quite high despite of the good fit.

![NPD diffraction pattern](image)

Figure 145: NPD diffraction pattern of Na$_2$Ca$_3$Al$_2$F$_{14}$. Used as a standard to determine machine parameters like zero shift and reflex broadening (performed by Thomas Hansen, ILL D20).
8.6 Used machinery

Galvanostats: Bat-small, Astrol Electronic AG, Switzerland
VMP3, Biologic, France
Bettscben Electronik AG, Switzerland
Electrochemical impedance spectrooscope: VMP3, Biologic, France
Scanning electron microscope: Ultra55VP, Carl Zeiss, Germany
X-ray diffractometer: Empyrea, Panalytical, Netherlands
in situ x-ray powder diffraction: Materials Science Beamline at SLS, PSI Villigen, Switzerland
in situ neutron powder diffraction: D20 beamline at Institut-Laue-Langevin, Grenoble, France
X-ray photoelectron spectrometer: Escalab 220i XL, Thermo Scientific, United States
Raman spectroscopy: LabRAM HR 800, Horiba Jobin Yvon, Japan

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Bibliography


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XXVI


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