Doctoral Thesis

Electrochemical and chemical surface modifications of carbons for Li-ion batteries

Author(s):
Verma, Pallavi

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ELECTROCHEMICAL AND CHEMICAL SURFACE MODIFICATIONS OF CARBONS FOR Li-ION BATTERIES

A dissertation submitted to

ETH ZURICH

for the degree of

Doctor of Sciences

presented by

PALLAVI VERMA

Master of Science, Université de Toulouse III, France

born on June 25th, 1985

citizen of India

accepted on the recommendation of

Prof. Dr. Alexander Wokaun (ETH Zurich/PSI)

Prof. Dr. Petr Novák (ETH Zurich/PSI)

Prof. Dr. Thomas Schmidt (ETH Zurich/PSI)

2011
This thesis is dedicated to my mother Sarita Verma.

She is my idol and inspiration. My achievements are solely a result of her blessings and persistent encouragement. She makes me believe in myself, and motivates me to keep striving even in trying times. Being a single parent she has selflessly provided for me beyond any daughter's expectation. It is her belief and trust in me that has made me self-confident and independent. I am grateful to God, for blessing me with the strongest mother on earth. I hope I have made her proud and lived up to her and my father's expectations.

I bow before my father, Sushil Kumar, and Lord Almighty and pray that they will continue to shower their blessings upon me!
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Abstract

Safety and energy efficiency are the main challenges faced by Li-ion battery technology for application in electric vehicles. On the graphite negative electrode these properties are mainly governed by the solid electrolyte interphase (SEI). Though the natural SEI electronically passivates the surface of the electrode material, and ensures cyclability by virtue of Li-ion conduction; it is normally inhomogeneous, partially soluble, and does not prevent exfoliation of graphite in propylene carbonate based electrolyte (important for low temperature applications). Hence, the surface of graphite is modified before cycling, to tune its morphology and reactivity for controlled SEI properties. Two methods of surface modification developed here are: grafting followed by terminal functional group reduction, and tuning reactivity of surface groups existing on graphite.

Grafting is used for covalent immobilization of organic moieties on the surface of graphite. It allows control over SEI morphology, decreases charge consumption for SEI formation, and prevents exfoliation of graphite in PC based electrolyte. The reactivity of the grafted layer is further tuned by a consecutive reduction step. The resulting material exhibits further decreased charge consumption for SEI formation. Owing to the covalent nature of attachment the surface layers formed by this method are stable throughout cycling. However, the modification obtained by grafting is multilayered rather than monolayered and hence adversely affects the specific energy of the material.

To minimize surface layer thickness, the surface groups already existing on graphite were modified by chemical pretreatments. Chemically pre-reduced graphites show less irreversible charge loss, whereas chemically pre-oxidized graphites show higher irreversible charge loss. Treatment of graphite by n-butyl lithium resulted in exclusively edge covered particles. This material exhibits good reversible cycling in PC based electrolyte as well as homogeneous and flexible SEI. Cyclability of this material in standard electrolyte was improved by stabilizing the surface chemical composition by use of ethylene carbonate as additive.

Surface modification methods are ideal for tuning surface properties of electrode materials, which enables a precise control over SEI. Challenges like safety, cycling efficiency, and loss of specific charge can be surmounted by this approach.
Zusammenfassung


Diese Methoden sind ideal, um die Oberflächeneigenschaften von Elektrodenmaterialien anzupassen, was eine präzise Kontrolle des SEI ermöglicht. Herausforderungen wie Sicherheit, Zyklisierungseffizienz und irreversibler Ladungsverlust wurden überwunden.
Résumé

Les deux verrous actuels au développement des véhicules électriques sont la sécurité et l’efficacité énergétique des batteries Li-ion. Les propriétés de l’électrode négative (graphite) sont gouvernées par une couche de passivation (nommée Solid Electrolyte Interphase ou SEI). La passivation électronique de la surface de l’électrode est spontanée et elle permet d’obtenir une bonne cyclabilité tout en maintenant la conduction des ions lithium. Cette couche de passivation est normalement inhomogène, partiellement soluble et ne prévient en aucune manière de l’exfoliation du graphite dans les électrolytes à base de carbonate de propylène (PC) (important pour les applications à basses températures). Ainsi, la surface du graphite se retrouve modifiée avant le cyclage sans pour autant avoir un contrôle sur les propriétés morphologiques ni même sur la réactivité de cette couche. Dans ce manuscrit, deux méthodes de modification de surface ont été développées : (1) le greffage suivi de la réduction d’espèces organiques, (2) la modification des groupes préexistant à la surface du graphite.

La technique de greffage est utilisée pour les immobilisations covalentes de composés organiques à la surface du graphite. La réactivité de la couche greffée est ensuite adaptée par une étape de réduction. Cette technique permet de contrôler la morphologie de la SEI, de diminuer la consommation de charges utilisées pour la formation de la SEI naturelle et de prévenir de l'exfoliation des feuillets de graphites (électrolytes à base de PC). La nature covalente du greffage lui permet d’être stable durant le cyclage. Cependant, contrairement à la réaction spontanée, la modification par greffage affecte plusieurs feuillets ce qui empiète sur l’énergie spécifique du matériau.

Afin de minimiser l’épaisseur de la couche en surface, les groupes existant en surface ont été modifiés par des traitements chimiques. Un graphite pré-réduit chimiquement présente une moindre perte en capacité, alors qu’un graphite pré-oxydé chimiquement montre une perte accrue. Le traitement du graphite par du n-butylate de lithium permet de couvrir exclusivement les arêtes des particules de graphite. Le matériau montre ainsi une bonne réversibilité durant le cyclage dans des électrolytes à base de PC, mais également une SEI homogène et flexible. La cyclabilité du matériau dans les électrolytes standards a été améliorée en utilisant du carbonate d’éthylène comme additif permettant ainsi une stabilisation de la surface.
En résumé, les méthodes de modification de surface sont idéales pour adapter les propriétés des matériaux d’électrodes, ce qui permet d’avoir un contrôle précis des propriétés de la SEI. Les défis comme la sécurité, l’efficacité énergétique et la perte de la capacité spécifique peuvent être surmontés par l’approche développée dans ce manuscrit.
SECTION I

INTRODUCTION
Chapter 1. The current energy scenario

Energy in crude terms is just a thermodynamic quantity but the underlining fact is that it is a mandatory input needed to propel any process. The demand for energy is on a perennial surge due to the overwhelming technological developments worldwide. Collaterally, the energy market is currently confronted with two major issues. The first one being, severe dearth of conventional fossil fuels like gasoline and coal, and the second one being atmospheric pollution due to perpetual CO₂ emissions. These concerns render the conventional fuel driven stop and go automobile systems unsuitable for the future. Therefore, the market is witnessing an upsurge of hybrid vehicles (HV) for example Prius by Toyota. Hybrid technology employs both battery and fuel in the power train of a car. Energy efficiency is maximized by using the battery for initiation, motor assist, and regenerative breaking functions. There is a spectrum of systems based on the extent of contribution from the battery. It ranges from idling stop HV, where the battery is used only for regenerative breaking, to mild HV where it is also used for motor assist, until the strong hybrid where it is also possible to run the car on only the battery. HVs ushered the plug in hybrid vehicles (PHV) and electric vehicles (EV) into the market. PHVs can be charged by both fuel as well as electricity, whereas EVs run exclusively on battery. Many automobile companies are now releasing EVs and the domain of electromobility is expanding at an overwhelming rate.

The common bottleneck of HV, PHV, and EV technology is the battery performance. For optimum performance of the EV, the battery system should deliver high energy density for extended driving range (achievable with one charge), and high power density which is required for initiation, acceleration, and breaking. One of the most promising battery systems capable of meeting these requirements is Li-ion battery [1]. Li-ion battery has an edge over other contemporary battery systems such as Ni-MH battery due to its higher energy density (Li-ion battery: 250-360 Wh/L, 100-160 Wh/kg; Ni-MH battery: 140-300 Wh/L, 30-80 Wh/kg) and higher voltage (Li-ion battery: 3.6 V; Ni-MH battery: 1.2 V). The inherent reasons behind these virtues is the low molar mass (6.941 Da) and very negative potential (-3.04 V vs. standard hydrogen electrode (SHE)) of Li metal. Due to poor cyclability of Li metal battery, the industry and research rather use Li-ion battery. The working principles and the state of the art system will be detailed in chapter 2.

The current Li-ion battery technology faces some crucial challenges, which need to be surmounted. Firstly, the specific energy of the battery needs to be increased. For this the
research is focused on designing high capacity materials, making thicker electrodes, and minimizing dead mass. A few examples are the new generation active materials which employ alloy electrodes [2], conversion reactions [3], and the discovery of a large number of new materials [4]. However, each of these technologies is quite nascent and need further improvement. For example, alloy electrodes exhibit large capacity (up to 4.4 Li per Si) but concomitantly the 400% volume expansion results in poor cyclability [5]. Conversion reaction materials [3] exchange up to 6 Li per 3d metal but the large polarization and irreversible loss is yet to be resolved. Many of the new materials are insulating or semi-conducting like LiFePO₄ [6] and Li₂FeSiO₄ [7]. Secondly, the specific power of the battery needs to be increased. To tackle this, research is directed towards enhancing the conductivity of the materials and the porosity of the electrodes. The most prevalent way of obtaining high power is by making thin films [8], however that comes at the cost of energy. The third issue is that of sustainability, for which energy efficient production, recycling, and using bio-materials are potential pathways. There are reports of using organic materials [9] and low energy active material synthesis [10] in the literature. But, further research is mandatory in this direction. And finally, the most paramount issue is that of safety. Due to large voltage of Li-ion battery, non-aqueous electrolytes are employed. This raises concerns regarding the flammability of the electrolyte and reaction of the activated electrode materials with the electrolyte. There have been incidents of laptops batteries catching fire in the past, and the consequences will be catastrophic if this occurred for the huge battery packs (~100 kg battery pack) contained in EVs. Thus, it is imperative that the safety problems be solved. An external method of avoiding accidents is by using auxiliary components such as power control units and sensors in the battery management systems. However, these devices demand additional space and weight, which are very constrained in EVs. Therefore, research has to be oriented to intrinsically avert hazardous reactions of the active materials with the electrolyte within a battery. This requires the reactivity of the materials to be tuned. And since most of the reactions are triggered from the interface of the material and the electrolyte, it is fundamentally important to tune the reactivity of the surface. One such substantial reaction occurring in a Li-ion battery is electrolyte reduction on the surface of graphite, which results in the formation of a passive layer as interphase which is called solid electrolyte interphase (SEI). SEI is explained in details in chapter 3.

The aim here is to prepare surface modified carbons (negative electrode material) with tuned reactivity towards non-aqueous electrolytes. The surface modified carbons would comprise of tailor-made surfaces in terms of reactivity and morphology and will play a predominant role in determining the properties of the SEI, and consequently the performance of the battery in terms of safety, irreversible charge “loss” (ICL), exfoliation of graphite, and cyclability.
A Li-ion battery is also called a “rocking chair” battery [11], because unlike the Li metal battery this battery does not contain any metallic Li. Li-ion battery comprises of insertion active materials on positive as well as negative side [12]. These materials are capable of accommodating Li-ions in specific sites in their structure without undergoing significant distortion. The Li-ions shuttle back and forth between the positive and negative electrodes during cycling. A typical Li-ion battery is illustrated in figure 2.1.

![Figure 2.1. Schematic illustration of a typical Li-ion battery: a) aluminum current collector b) oxide positive electrode material; c) porous separator soaked with liquid electrolyte; d) inhomogeneous SEI layer; e) graphite negative electrode material; f) copper current collector.](image)

As shown in figure 2.1, a Li-ion battery comprises of Cu and Al metal current collectors for the negative and positive electrode respectively, active materials, separator (glass fiber or celgard), and electrolyte. Normally each electrode is a composite comprising of active material powder, conductive carbon (needed for insulating materials), and binder for mechanical stability. Composite electrodes ensure electronic as well as ionic conduction pathways during cycling. The electrolytes typically used in Li-ion battery are Li salts in carbonate based solvents. One of the most widely used electrolytes is 1 M LiPF₆ in ethylene carbonate (EC): dimethyl carbonate (DMC). Effect of electrolyte on battery performance will be discussed in details in chapter 3. Typically various kinds of carbons are used [13] as negative electrode materials, out of which graphite is most common, because it is cheap, abundant, undergoes lithiation at low potential, and suffers minimal
active material breathing. As positive electrode materials mostly transition metal oxides [14] and phosphates [15] are employed, out of which LiCoO$_2$ [16], LiMn$_2$O$_4$ [17], and LiFePO$_4$ [6] are the most common ones. The redox reactions involved in a typical Li-ion battery are:

**Negative:** $C_6 + Li^+ + e^- \rightleftharpoons LiC_6 \quad E = 0.1 \text{ V vs. } Li^+/Li$

**Positive:** $2 \text{LiCoO}_2 \rightleftharpoons 2 \text{Li}_{0.5}\text{CoO}_2 + e^- + Li^+ \quad E = 3.7 \text{ V vs. } Li^+/Li$

**Cell:** $2 \text{LiCoO}_2 + C_6 \rightleftharpoons 2 \text{Li}_{0.5}\text{CoO}_2 + LiC_6 \quad \Delta E = 3.6 \text{ V}$

As lithiated carbons are not stable in air, a Li-ion battery is always assembled in its discharged state, with graphite and lithiated positive electrode material. During charge the positive electrode undergoes oxidation and the Li-ions travel from the positive material to the negative. During discharge the negative electrode undergoes oxidation and the ions flow in the reverse direction. Due to the structural stability of intercalation materials cycling lifetime of Li-ion battery is longer than that of conventional lead acid battery or Ni-MH battery.

In spite of the instability of the electrolyte at low and very high potentials (vs. Li$^+/Li$), formation of a passive layer called solid electrolyte interphase on the negative material during first lithiation, makes the cycling of Li-ion battery feasible. This will be discussed in full length in chapter 3.
Chapter 3. The solid electrolyte interphase

During first charge of a Li-ion battery, the electrolyte undergoes reduction at the negatively polarized graphite surface. Competing and parallel solvent and salt reduction processes result in deposition of a number of organic and inorganic decomposition products on the surface of graphite in form of a passive layer. This layer is called the solid electrolyte interphase or SEI [18]. SEI on a typical negative electrode is diagrammatically shown in figure 3.1.

Figure 3.1. Sketch of a lithiated graphite electrode covered by inhomogeneous SEI. The SEI components shown in darker shades of grey are mainly inorganic while those shown in lighter shades of grey are organic.

3.1. Advantages of the SEI

- SEI is typically electronically insulating and hence prevents further electrolyte degradation after it is formed in the first cycle. It imparts kinetic stability to the electrolyte against further reductions in the successive cycles and thereby ensures good cycling of the battery.
- It is ionically conducting and thus allows Li-ions to travel across itself, thereby ensuring good cyclability.
- Normally, in propylene carbonate (PC) based electrolytes [19], natural SEI cannot prevent solvent co-intercalation and hence exfoliation of graphites. However, by using some additives an effective SEI can be formed which is capable of averting exfoliation of graphite [20]. Cycling in PC based electrolytes is of utmost importance for low temperature applications of the battery.

Some solvents such as cyclic alkyl carbonates [21] form effective passive layers that ensure good cycling stability of the negative electrodes. It is essential to understand the features, functions, significance, and chemical composition of the SEI in order to be able to tune it. Thus, the foundation stone of this work is a thorough literature study of the SEI. This study is published as a review article [22]. This chapter has been derived from this
publication. Here, some vital features of the SEI on graphitic carbons will be described. Some fundamental questions will be discussed, like what factors affect the SEI and how the SEI affects battery performance. Substantial work has been done in the past few decades on analyzing the SEI and spelling out its components. In this chapter, the literature on SEI on carbons is compiled including detailed X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) data of the SEI components.

### 3.2. Formation and features of the SEI

SEI is a very complicated layer comprising of inorganic components which are normally salt degradation products and organic components which are partial or complete reduction products of the solvent of the electrolyte. The thickness of the SEI may vary from few Å to tens or hundreds of Å [23, 24]. It is difficult to distinctly measure the SEI thickness as some of the components are partially soluble in the electrolyte [25]. But as formation of a new phase between active material and the electrolyte modifies the interphase resistance, the average thickness was estimated using electrochemical impedance spectroscopy (EIS) [26]. The picture of a real SEI inside the battery has always been blur. Models of the SEI on graphite were proposed by Peled [27], Aurbach [26, 28], and Edström et al. [23, 29]. They all suggest SEI to be a dense layer of inorganic components close to the carbon, followed by a porous organic or polymeric layer close to the electrolyte phase. In some cases crystals of LiF were also detected [30].

The onset potential of SEI formation is not a fixed value. Literature offers values such as 2 V vs. Li⁺/Li [31], 1.7 V Li⁺/Li [32], or 1 V Li⁺/Li [19]; but 0.8 V Li⁺/Li [23, 33] is the most widely adopted practical value. SEI formation may also continue up to few cycles. However, this parameter cannot be normalized because it depends on a number of factors like nature and composition of electrolyte, nature of additives used in the electrolyte [34], sweep rates [35] etc. It is desirable to have complete SEI formation before Li-ion intercalation begins (> 0.3 V Li⁺/Li [28]). It is more difficult to achieve this for disordered carbons as the intercalation begins from 1.5 V Li⁺/Li as compared to ordered carbons where it begins at 0.25 V Li⁺/Li [31].

#### 3.2.1. Components of SEI

The composition of the SEI is a highly debated subject in the literature. It is dependent on numerous factors, which are detailed in section 3.3. Proposed composition of SEI varies from one research group to another as operating conditions in different laboratories are
different. Thus it is impossible to normalize or generalize the composition or even contents of SEI. Table 3.1 lists the major components of the SEI reported by various research groups. Since, a large number of inorganic salts (precipitates) from salt reductions can be present in the SEI, these are not listed in table 3.1. We list the most plausible and common SEI components along with corresponding references to the best of our knowledge.
<table>
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<th>Component</th>
<th>Present</th>
<th>Not present</th>
<th>Notes</th>
</tr>
</thead>
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<tr>
<td>(CH$_2$OCO$_2$Li)$_2$</td>
<td>[21, 31, 36, 37, 38]</td>
<td></td>
<td>Being a two electron reduction product of EC; it is found mostly in the SEI formed in EC based electrolytes.</td>
</tr>
<tr>
<td>ROCO$_2$Li</td>
<td>[21, 31, 34, 37, 39]</td>
<td></td>
<td>They are present in the outer layer of the SEI and are absent near Li [40]. They occur in most PC containing electrolytes, especially when the concentration of PC in the electrolyte is high.</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>[21, 36, 39, 40, 41]</td>
<td>[30, 31, 32, 34, 36, 42, 43]</td>
<td>Not always present [23]. Normally present in the SEI formed in EC or PC based electrolytes. It may also appear as a reaction product of semicarbonates with HF, water, or CO$_2$.</td>
</tr>
<tr>
<td>ROLi</td>
<td>[31, 32, 43, 44, 45, 46, 47]</td>
<td></td>
<td>Most commonly found in the SEI formed in ether electrolytes like tetrahydrofuran (THF), but may also appear as DMC or ethyl methyl carbonate (EMC) reduction product [48]. It is soluble and may undergo further reactions [49].</td>
</tr>
<tr>
<td>LiF</td>
<td>[30, 40, 42]</td>
<td></td>
<td>Mostly found in electrolytes comprising of fluorinated salts like LiAsF$_6$, LiPF$_6$, LiBF$_4$. It is a major salt reduction product. HF contaminant also reacts with semicarbonates to give LiF byproduct. Amount of LiF increases during storage [50].</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>[42, 51, 52]</td>
<td>[23, 29, 30, 53]</td>
<td>It may be a degradation product of Li$_2$CO$_3$ during Ar$^+$ sputtering in the XPS experiment.</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>[30, 54]</td>
<td></td>
<td>Present in the outermost layer of the SEI, close to the electrolyte phase. This part imparts flexibility to the SEI.</td>
</tr>
<tr>
<td>LiOH</td>
<td>[38, 55, 30]</td>
<td></td>
<td>It is mainly formed due to water contamination</td>
</tr>
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</table>
It may also result from reaction of Li$_2$O with water or with ageing [43].

| Li$_2$C$_2$O$_4$ | [43, 47] | It is found to be present in 18650 cells assembled in Argonne National Labs containing 1.2 M LiPF$_6$ in EC:EMC (3:7) electrolyte. Li carboxylate and Li methoxide were also found in their SEI [43].
| HCOLi | [34] | It is present when methyl formate is used as co-solvent or additive.

3.2.2. Changes in SEI at elevated temperatures

The SEI composition and thickness does not stay constant throughout cycling or storage [59]. There are many different ways in which it can transform. It may partially dissolve in a solvent of the electrolyte, e.g., DMC [60]. Its thickness may also vary during cycling. SEI is believed to be thicker at lower potentials (lithiated state of carbon) and thinner at higher potentials (delithiated state) [33]. However, the changes appearing in the SEI are more pronounced at elevated temperatures [61, 62]. There are two prime reactions that occur on elevating battery temperature. First transformation of SEI occurs. Here, the components like lithium alkyl carbonates and semicarbonates convert to the stable components like Li$_2$CO$_3$. The temperature at which this occurs is highly dependent on the salt and solvent of the electrolyte, type of carbon material, and its specific surface area. For 1 M LiPF$_6$ in EC and diethylcarbonate (DEC) the onset temperature was found to be 105 ºC [63]. Whereas for LiBF$_4$ containing electrolytes it was as low as 60 ºC [64]. The second process occurring at high temperature is the reaction of active material with the SEI, or SEI with the electrolyte, or active material with the electrolyte. This begins at 120-140 ºC [64]. At this temperature, the transformed SEI allows Li from carbon to come into contact with the electrolyte and electrons to pass through the SEI. Beyond this temperature, even more exothermic reactions like that of lithiated carbon with binders (e.g. polyvinylidene difluoride-hexafluoropropylene (PVDF-HFP) at 350 ºC) occur [60]. These exothermic processes are detrimental for the performance of a Li-ion battery and are critical from safety point of view. They can be carefully examined by thermo analytical technique such as differential scanning calorimetry [65] and accelerated rate calorimetry [66].
3.2.3. Influence of SEI on battery performance

Each property of the SEI significantly affects battery performance. The composition, thickness, morphology, and compactness are a few to name. ICL in the first cycle occurs due to solvent reduction and SEI formation and is hence a characteristic of SEI [67]. Detrimental processes occurring during storage (self-discharge) also depend on the ability of the SEI to passivate active material surface. Therefore, shelf-life of a battery also depends on SEI [68]. As mentioned above SEI may also dissolve and/or evolve during cycling. Thus, effective and stable SEI is mandatory for good cycling life of the battery [69]. It becomes even more important during cycling at high rates and at deeper depth of discharge [70]. SEI components are highly temperature sensitive. Thus, performance of the battery at high/low temperature is also dependent on the SEI [71]. However, the most important consequence of SEI is on the safety of the battery [72, 73].

3.2.4. Influence of SEI on exfoliation of graphite

The mechanism of SEI passivating the active material surface imparting kinetic stability and ensuring good cycling may sometimes fail. The effective SEI formation may be hindered by the other chemical reactions. One of the causes of this failure is exfoliation of graphite which is a common occurrence in PC based electrolytes [41]. Two mechanisms have been proposed in the literature explaining the reason and mechanism of exfoliation of graphite. The first model was given by Besenhard et al. [19]. They proposed that solvent molecules co-intercalate along with Li-ions between the graphene sheets of graphite. Then the secondary reactions of graphite intercalated compounds distort the ordered structure of the graphite [19]. The second model by Aurbach [48] argues that solvent co-intercalation is only limited to ether electrolytes, PC based electrolytes rather reduce on crevices of the edge planes to release gaseous byproducts (propylene). The pressure of the gas cracks the particles and exposes fresh surface for further reactions. Their supporting argument is that exfoliation is highly dependent on the morphology and 3-D structure of the carbon [48]. But both the authors conclude by suggesting the use of film forming additives like CO₂, N₂O, S₂⁻ [74], and vinylene carbonate (VC) or Li disalicylatoborate salt [75] for averting exfoliation.

3.3. Factors affecting SEI

Many vital factors contribute to properties of the SEI. There is no absolute parameter circumscribing the SEI. It’s the combination and concomitant effect of all these factors
which dictates the properties, quality, and efficiency of SEI. Hence, the resulting influence of many factors listed in this section is collective and interdependent rather than independent.

3.3.1. Type of carbon

SEI is essentially formed on the surface of the carbonaceous negative active material, thus the type of carbon significantly affects the SEI. Winter et al. showed that ICL attributed to SEI formation is linearly proportional to the BET (Brunauer Emmett Teller) specific surface area of the carbon [76]. Zheng et al. found that the crystallographic structure and particle morphology are as influential as BET specific surface area [59]. They showed that coke and graphite powders having same BET specific surface area exhibit different ICL [59]. In addition, edges and surface imperfections like defects, crevices, and active sites act as catalytic sites for solvent reduction. Hence, they play an important role in solvent reduction kinetics. Dangling bonds and high current density on these sites favor electrolyte reduction. Thus concentration and nature of defects, and edge to basal plane ratio [77] are also critical factors affecting SEI properties. On similar lines active surface area of the graphites was correlated with film formation and ICL [78, 79, 80]. In general, the SEI on the cross-section of the electrode and the edges of graphite particles contain more inorganic components like LiF whereas the SEI on the graphene sheets contain soft organic compounds [42] as shown in a schematic sketch of SEI in figure 3.1. Even though the surface is very important for SEI formation, the importance of the crystallographic structure of the carbon should not be underestimated. Highly crystalline carbons are more vulnerable to exfoliation and are thus more sensitive to electrolyte composition. Therefore, crystallographic order significantly affects the extent of exfoliation and co-intercalation of solvents [31, 41].

3.3.2. Pretreatment of carbon

Once the importance of the surface properties of the material was understood, efforts were made to modify the surface morphology and chemistry of the carbons by various methods. Surface treatments of vast diversity were experimented upon. Scott et al. [81] performed reduction of their electrodes in butyl-lithium solutions for varying durations of time to decrease the ICL. The SEI formed was thicker but more brittle. Ein-Eli and Koch [82] oxidized the graphite powders with HNO₃ and (NH₄)₂S₂O₈ and enhanced the specific charge capacity of graphite. This was attributed to the formation of cavities or nanovoids
during oxidation (etching). Pan et al. used a different approach of chemical treatment. Instead of altering the surface groups already present on the carbon surface, they immobilized aryl functional groups onto carbon to facilitate the SEI formation on these groups [83, 84]. But the success was limited in terms of suppression of the ICL. Electrochemical treatments like electroless plating of graphite by Cu were also tried. The discharge capacity and columbic efficiency were found to improve [85].

Another category of the surface treatments of carbons is the thermal treatments. The main target of these treatments is to obtain high specific charge capacity carbons, which would accommodate more than one Li\(^+\) per C\(_6\). It was mainly done by pyrolysis of different organic precursors at various temperatures. Work done in this field has been reviewed by Zheng et al. [86]. There are also treatments combining two or more methods. For example, Ohzuku et al. [87] improved the performance of graphite fiber negative material by heat treating acetylene black and graphite at 700 °C. They ascribed the amelioration to removal of hydroxyl groups and water from the surface. Aiming at similar targets many other methods were reported. The literature cited above and the references within are a few examples to illustrate the wide variety of treatments performed. A detailed discussion of this subject is beyond the scope of this thesis.

### 3.3.3. Electrolyte composition

The SEI composition and contents are a direct consequence of the electrolyte composition. Thermodynamic instability and kinetic reactivity of the electrolyte culminates into the SEI. Some features can be derived from table 3.1. For example, lithium alkoxides appear in the SEI formed in ether electrolytes, semicarbonates and Li\(_2\)CO\(_3\) appear in SEI formed in carbonate electrolytes (EC, PC) [31], while lithium formate occurs in SEI formed in methyl formate electrolyte [34]. The decomposition products of various solvents depend on the solvents dielectric constant, polarity, reactivity [34], viscosity [19], etc. These parameters are also vital selection criteria of the solvents for suitable electrolytes. Reactivity of common carbonate based electrolytes are in the order EC>PC>DMC>DEC [34].

A study specifically on EC and PC showed that when the EC or PC concentration in the electrolyte is high, \((\text{CH}_2\text{OCO}_2\text{Li})_2\) or \(\text{ROCO}_2\text{Li}\) are the major reduction products respectively. However at low EC or PC concentration \(\text{Li}_2\text{CO}_3\) is the major reduction product [31]. Presence of \(\text{Li}_2\text{CO}_3\) was extensively studied in the 1990's. Most of the studies
by Aurbach’s group [21, 36, 39, 41] showed presence of Li$_2$CO$_3$. In another they showed that Li$_2$CO$_3$ was absent in the SEI formed in dry THF or PC solutions, but on addition of water or PC, Li$_2$CO$_3$ precipitates [31]. In contrast, the studies in 2000’s reported much less Li$_2$CO$_3$ in the SEI owing to more controlled conditions of analyses [30, 32, 42, 43]. In general, (CH$_2$OCO$_2$Li)$_2$ and Li$_2$CO$_3$ are better passivating agents than ROLi and ROCO$_2$Li because they are less soluble in the solvents. These studies were in close agreement with another study which showed that EC reduction products are insoluble and hence more passivating [21]. Further, on addition of reactive additives the reaction pathways change depending on the nature of the additive [21]. Aurbach’s group reported enhanced Li$_2$CO$_3$ content in the SEI and hence improved battery performance by using CO$_2$ as additive [34, 36]. The effect of additives in electrolyte has been reviewed by Zhang [88].

Rather more complicated chemistry occurs during the reduction of salts. The correlation of the nature of salt with the composition of SEI was studied by Aurbach et al. [89]. The system gets more complex in the presence of HF, which appears in the electrolytes containing fluorinated salts like LiAsF$_6$, LiPF$_6$, etc. Aurbach et al. stated that Li$_2$CO$_3$ in the SEI can disappear by reaction with HF in the electrolytes containing LiPF$_6$ and LiBF$_4$ [34, 36]. Effect of additional HF on SEI was studied on LiPF$_6$ in EC:DMC electrolyte by Sato et al. [90]. The main consequence of HF in the electrolyte is the precipitation of LiF, which forms an integral inorganic part of the SEI [23]. In order to predict the solvent reduction products and the overpotential they required for their formation; Peled et al. [40] calculated rate constants of reactions between solvated electrons with salts and solvents of electrolyte. They correlated these rate constants to the potential at which the corresponding SEI component would form. The main conclusion of this study was that materials having low rate constant need a higher overpotential for formation and thus form at more negative potentials, while those that have high rate constant are formed at more positive potential. This study illustrates the profound effect of kinetics on the SEI formation. Good precursors or additives can enhance electrolyte reduction kinetics resulting in a faster SEI formation.

3.3.4. Other factors

In addition to the chemical factors affecting SEI, the electrochemical conditions also play a significant role. Mode of cycling [91], mode of polarization (galvanostatic, potentiostatic cycling, or potential sweeps, etc) [31, 71], and overpotential [40] are a few to mention.
Temperature during cycling, SEI formation, and battery storage is also critical because it has a direct consequence on the reaction kinetics [92].

### 3.4. Characterization of SEI

Analyzing pristine SEI is a tedious task. Some of the fundamental facts which make the SEI analysis challenging are summarized in this section. SEI is a very thin layer adhering to the active material surface. It is almost impossible to demarcate the boundary between the end of the SEI and beginning of the electrolyte. So, it is always tricky to justify what thickness of the surface layer on carbon one wishes to analyze. Peeling off the SEI from carbon surface too is difficult and almost impossible to be performed precisely. In the methods which measure the SEI along with the electrolyte or after washing with solvents of the electrolyte, there is always an uncertainty as to which component actually belongs to the SEI and which ones are from the electrolyte or is a side–product of the separation procedure? Moreover the functional groups and chemical composition of the solvents and SEI components are very similar, thus differentiating between the two is always difficult. It is unlikely that the SEI preserves its pristine nature after steps of separation, washing, and drying. There are many possibilities of SEI components undergoing modification and degradation during these procedures. Most of the components of SEI are highly sensitive to contamination, air, and humidity. ROCO₂Li and ROLi may convert to Li₂CO₃ by reacting with CO₂ [37]. ROCO₂Li reacts with water to form Li₂CO₃, CO₂, and ROH [58]. Other alkyl lithium carbonates react with water to form LiOH or Li₂CO₃ [93]. Li reacts with O₂ to form Li₂O, Li₂O₂, and LiO₂. All of these are strong nucleophiles and react further with organic solvents and semicarbonates to form carbonates and alkoxides [93].

For **ex situ** analysis a transfer or encapsulating mechanism is required*, which allows the sample to be transported from the glove box (inert atmosphere) to the analysis chamber of any analytical machine without exposure to air and humidity. For machines which operate under ultra high vacuum or high vacuum like XPS, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) these devices are even more difficult to design. Orisini et al. designed a movable airlock [94] for recording live SEM images of dendrites formation on lithium [95]. Tarascon’s group used similar transfer techniques for studying SEI via other techniques like FTIR and TEM [96].

*Note: During the course of this work, we too developed a transfer chamber for SEM analysis of the air-sensitive and cycled samples. It will be described in details in chapter 5.
A large variety of techniques have been used for analyzing SEI ranging from spectroscopy to microscopy to diffraction and thermo analysis. Since SEI is a surface phenomenon the surface analysis techniques like XPS, AES, AFM, SIMS, TOF-SIMS, STM (all abbreviations listed below) are most frequently used. SEM and TEM are used for imaging the surface film. Vibration spectroscopies like FTIR, IRAS, Raman, and XANES provide valuable surface information regarding the chemical functional groups. EIS is used to study the evolution of the interphase resistance. Diffraction techniques like XRD are used for determining the ordering and structure of SEI. Thermo analytical techniques like DSC, ARC, and TPD are used to study various reactions like SEI formation and degradation. And finally the techniques like NMR and AAS give bulk information of SEI components. These techniques along with corresponding citations are listed below.

- AES (Auger Electron Spectroscopy): [38, 51]
- AFM (Atomic Force Microscopy): [21, 97, 98, 99, 100]
- STM (Scanning Tunneling Microscopy): [104, 105]
- SPM (Scanning Probe Microscopy): [106]
- SEM (Scanning Electron Microscopy): [38, 107]
- TEM (Transition Electron Microscopy): [96, 108]
- IRAS (Infrared Absorption Spectroscopy): [51]
- Raman Spectroscopy: [92, 109]
- XANES (X-ray Absorption Near Edge Structure): [102, 110, 111]
In the following section the analyses of the SEI by FTIR and XPS will be compiled. These two techniques are not only highly surface sensitive but are also complementary to each other. Information from these two techniques put together provides a good picture of the SEI. The other reason for confining this study to FTIR and XPS is that these are amongst the most widely used techniques for the SEI analysis. These have been used by numerous research groups and abundant FTIR and XPS data exists in the literature about SEI and its various components. Thus, it will be useful to compile this data into one table which is easier to compare, interpret, and comprehend. This will also constructively define facts like relative error between different studies on similar material and general trends. These data sets will be used as reference for comparing and analyzing experimental data throughout this work. Background of FTIR and XPS techniques will be described in chapter 7.

3.4.1. FTIR and XPS data

Tables 3.2 and 3.3 list literature data on the FTIR and XPS analysis of the various components of the SEI respectively. Since many organic components are present in the SEI, deconvolution and analysis of the C 1s, O 1s, Li 1s, and F 1s spectra are crucial for comprehending the information. The deconvoluted binding energies of these elements in different chemical environments are compiled in table 3.4.
**Table 3.2. FTIR data of the SEI components as reported in the literature**

<table>
<thead>
<tr>
<th>Component</th>
<th>Functional group</th>
<th>Vibration wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_2\text{OCO}_2\text{Li})_2)</td>
<td>C=O asym st</td>
<td>1634 [34], 1650 [21], 1654 [37]</td>
</tr>
<tr>
<td></td>
<td>CH₂ bend</td>
<td>1396 [34], 1400-1450 [21, 37]</td>
</tr>
<tr>
<td></td>
<td>C=O sym st</td>
<td>1300 [34], 1301 [37], 1320-1290 [21]</td>
</tr>
<tr>
<td></td>
<td>C-O st</td>
<td>1050 [34], 1100-1070 [21], 1083 [37]</td>
</tr>
<tr>
<td></td>
<td>OCO₂ bend</td>
<td>822 [37], 840-820 [21]</td>
</tr>
<tr>
<td>ROCO₂Li</td>
<td>C-H</td>
<td>2950-2820 [50], 2930-2850 [21]</td>
</tr>
<tr>
<td></td>
<td>C=O asym st</td>
<td>1610 [31], 1650 [21, 31, 93], 1668 [37], 1685 [51], 1680-1640 [50]</td>
</tr>
<tr>
<td></td>
<td>CH₂ bend</td>
<td>1450-1400 [21, 50]</td>
</tr>
<tr>
<td></td>
<td>C=O sym st</td>
<td>1300 [31], 1350 [51], 1350-1300 [50], 350-1320 [21, 93]</td>
</tr>
<tr>
<td></td>
<td>C-O st</td>
<td>1060-1020 [26], 1090 [31], 1100 [50], 1115 and 1044 [51], 1100-1050 [93], 1100-1080 [21]</td>
</tr>
<tr>
<td></td>
<td>CO₃²⁻ bend</td>
<td>820 [50, 93], 855 [51], 840-80 [21]</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>C-O st</td>
<td>1400 [43], 1470-1450 [93], 1450 and 1500 [37], 1510-1450 [31], 1520-1480 [21], 1520-1500 [93], 1542-1455 [51]</td>
</tr>
<tr>
<td></td>
<td>CO₃²⁻ bend</td>
<td>875 [21], 876 [51], 879 [37], 890-870 [31]</td>
</tr>
<tr>
<td>ROLi</td>
<td>C-H st</td>
<td>2963 [31], 2900-2700 [93]</td>
</tr>
<tr>
<td></td>
<td>C-O st</td>
<td>1000 [31], 1050 [126], 1080 [31], 1100-1000 [93]</td>
</tr>
<tr>
<td></td>
<td>Li-O st</td>
<td>600-500 [93]</td>
</tr>
<tr>
<td>Li₂O</td>
<td>Li-O st</td>
<td>600 [31, 93]</td>
</tr>
<tr>
<td>Compound</td>
<td>Mode</td>
<td>Wavenumber Range</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>------------------</td>
</tr>
<tr>
<td>RCOOLi</td>
<td>$\text{C=O}$ asym st</td>
<td>1500-1700 [43]</td>
</tr>
<tr>
<td>LiOH</td>
<td>O-H st</td>
<td>3670 [43], 3675 [93], 3660-3675 [51]</td>
</tr>
<tr>
<td>Li$_2$C$_2$O$_4$</td>
<td>$\text{C=O}$ st</td>
<td>1640 [43]</td>
</tr>
<tr>
<td>HCOOLi</td>
<td>$\text{C=O}$ st</td>
<td>1606 [34], 1620 [127]</td>
</tr>
<tr>
<td></td>
<td>COO$^-$ bend</td>
<td>1380, 790 [127] [34]</td>
</tr>
<tr>
<td>PVDF</td>
<td>C-F st</td>
<td>1200 [31]</td>
</tr>
</tbody>
</table>
Table 3.3. XPS data of the SEI components as reported in the literature

<table>
<thead>
<tr>
<th>Binding energy (eV)</th>
<th>C 1s</th>
<th>O 1s</th>
<th>F 1s</th>
<th>Li 1s</th>
<th>B 1s</th>
<th>P 2p</th>
<th>Cl 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEI component</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiF</td>
<td></td>
<td></td>
<td>685.9 [128], 686 [29, 53], 685-686 [21], 686.2 [52, 129], 686.4 [40], 686-686.5 [30]</td>
<td>56 [128, 130], 56.4 [52], 56.5 [29], 56.2-56.6 [30]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li₂O</td>
<td>528.3 [53], 527.6 [51], 528.7 [52, 129, 131], 528-529 [23]</td>
<td>53 [51], 53.7 [52, 53, 131], 54 [23]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>290 [29, 51], 290.1 [128], 290.5 [52], 289.8-290.2 [129], 291.5 [30, 132]</td>
<td>531.5 [51], 531-532 [23], 532 [29], 532.5 [52], 532.7 [128], 533.5-534 [30]</td>
<td>55.3 [51], 55.5 [23, 29, 128, 131], 56.5 [30]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiBF₄</td>
<td></td>
<td>688.2 [29], 688.5-689 [30], 57 [30], 58 [29]</td>
<td>196.3 [29], 196.5 [30]</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Species</td>
<td>Peaks (ppm)</td>
<td>Assignments</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>------------------</td>
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<td></td>
</tr>
<tr>
<td>ROCO₂Li</td>
<td>287.6 [132], 289 [52], 289-290 [30, 130], 288-292 [62]</td>
<td>55 [52]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiOH</td>
<td>531.5 [51], 531.9 [52, 133], 532 [131]</td>
<td>55.5 [131], 55.3 [51, 52]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiCl</td>
<td>198.4 [51], 199 [40, 128], 200 [21]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVDF</td>
<td>290.5 [132]</td>
<td>688 [21]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEO</td>
<td>286.5 [29] [30]</td>
<td>533 [29]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other polymeric species</td>
<td>284.8 [52], 285.5-286.5 [30]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li₂C₂</td>
<td>282.4 [131], 282.5 [128], 283 [130]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>52.3 [128, 131]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C sp²</td>
<td>284.2 [132], 284.3 [29], 284.4 [52], 285 [29, 52, 131]</td>
<td></td>
<td></td>
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<td></td>
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</tbody>
</table>
Table 3.4: Deconvolution of the C 1s, O 1s, Li 1s, and F 1s spectra of SEI as reported in the literature

<table>
<thead>
<tr>
<th>C 1s photoelectron peak position (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>282.5 [52]</td>
<td>Li₂C₂</td>
</tr>
<tr>
<td>283.7 [52], 284 [32], 284.3 [30], 284.4 [21, 33, 124, 133], 284.8 [30], 285 [53]</td>
<td>C-H, sp² carbon</td>
</tr>
<tr>
<td>285.5 [129], 286 [128], 286.1 [134], 287 [130]</td>
<td>C-OH</td>
</tr>
<tr>
<td>285.5 [30, 52, 130]</td>
<td>Polymers in SEI</td>
</tr>
<tr>
<td>286.5 [33, 48]</td>
<td>(-CH₂CH₂O⁻)ₙ</td>
</tr>
<tr>
<td>285 [128], 285.5 [129], 286 [23, 53], 286.5 [30, 32, 129]</td>
<td>C-O-C</td>
</tr>
<tr>
<td>287-288 [30], 287 [51], 286-287 [129]</td>
<td>Ether carbon in various environment</td>
</tr>
<tr>
<td>287 [128], 287.3 [134]</td>
<td>C=O</td>
</tr>
<tr>
<td>287.6 [132], 289-290 [30], 289.1 [134]</td>
<td>C-(OR)(CO₂Li) or COOR</td>
</tr>
<tr>
<td>288-291 [32], 290 [129], 290.6 [51, 134]</td>
<td>RO-CO₂Li (alkyl lithium carbonates)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>O 1s photoelectron peak position (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>532.4 [133], 533.8 [51], 534.5 [30]</td>
<td>RO-CO₂Li (various carbonates)</td>
</tr>
<tr>
<td>532.5 [129], 533 [30, 128, 133], 534 [128, 133]</td>
<td>C-O-C or C-O-H</td>
</tr>
<tr>
<td>531 [128, 133]</td>
<td>C=O</td>
</tr>
<tr>
<td>530.8 [128]</td>
<td>C-O-Li</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Li 1s photoelectron peak position (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>54 [23]</td>
<td>Li-O</td>
</tr>
<tr>
<td>55.5 [23]</td>
<td>Li-CO₃</td>
</tr>
<tr>
<td>55 [128]</td>
<td>Li-O-C</td>
</tr>
</tbody>
</table>
### Table

<table>
<thead>
<tr>
<th>$F, 1s$ photoelectron peak position (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>688.8 [129]</td>
<td>P-F</td>
</tr>
<tr>
<td>685-686.4 [129], 684.8 [135]</td>
<td>Li-F</td>
</tr>
<tr>
<td>683.5 [135]</td>
<td>Na-F</td>
</tr>
</tbody>
</table>

### 3.5. Features of an ideal SEI

A good SEI on negative electrode is a prerequisite for good performance of a Li-ion battery. Studying, analyzing, and understanding the SEI has underlined the significance of the many aspects related to it. It is evident that there are many interdependent and correlated factors influencing the SEI and many interdependent and correlated consequences of SEI on battery performance. On one hand, factors affecting SEI properties are type of carbon material, pretreatment of carbon material, electrolyte composition, and electrochemical and physical conditions. On the other hand, the battery performance parameters affected by the SEI are ICL, self discharge, cyclability, rate capability, and safety. Amongst the various techniques used to analyze the SEI, FTIR and XPS have proved to be very useful. For a better perception of the goal of this work, properties desirable in an efficient SEI are summarized.

An ideal SEI should have minimum electronic and maximum Li-ion conductivity. SEI formation kinetics should be fast, allowing it to form completely before the onset of Li-ion intercalation. In other words, SEI formation potential should be more positive than Li-ion intercalation potential. An ideal SEI should have uniform morphology and composition. It should contain stable and insoluble passivating agents like Li$_2$CO$_3$ rather than metastable and poorly passivating ones like ROLi and ROCO$_2$Li [31]. A good SEI should be a compact layer adhering well to the carbon. It should be elastic [48] and flexible [136] to accommodate non-uniform electrochemical behavior and active material breathing.

All the facts and data compiled in this chapter shall serve as a reference for the forthcoming experimental work related to synthesis of surface modified carbons for tuned SEI properties.
Chapter 4. Surface modifications of carbon materials

From chapter 3 it can be inferred that SEI has been extensively studied due to its critical impact on the ICL, self-discharge, cyclability, rate capability, and safety of the battery [137]. But most of the literature on SEI is focused on the analysis of the composition and characteristics of the SEI [137]. In spite of the underlined importance of the SEI, there is a dearth of methods of controlling the SEI characteristics by elegant chemistry. Due to a significant effect of the surface properties of graphite on SEI formation [76, 77, 78, 79, 138], researchers have mostly employed surface pretreatment of the graphite like chemical [81, 82], electrochemical [85], and thermal [139] for improved performance. There have been relatively few reports on modification of the surface with a defined control over the surface chemistry and reactivity for ameliorating SEI formation and characteristics. One such report is on formation of artificial SEI by electropainting and vacuum-insertion techniques [140]. But none of the reports explicitly offer a route to resolve the two main drawbacks of the natural SEI.

4.1. Limitation of the natural SEI

- The charge consumed for electrolyte reduction during the first lithiation is “lost” irreversibly and cannot be retrieved in the consecutive cycles. This charge is called the irreversible charge “loss” (shown in the electrochemical curve in figure 4.1) is one of the major issues to be solved. It is calculated as follows:

\[
ICL = \frac{(\text{charge of lithiation} - \text{charge of delithiation})}{\text{charge of lithiation}} \times 100\%
\]

ICL ranges from 8 % (for graphite of \(d_{90}=44 \mu m\)) to 22 % (for graphite of \(d_{90}=6 \mu m\)). This issue will be more apparent for the bigger batteries for applications in EVs, where the amount of the electrolyte reduction will be larger. Another perception of this problem is that the even though the capacity loss is only 5-20 % in the first cycle, this percentage of capacity is lost for every consecutive cycle, and hence the total loss after 1000 cycles would be rather grave. In addition, there are other consequences of the consumption of the electrolyte. “Loss” of Li-ions from electrolyte and positive electrode material can lead to lower conductivity of electrolyte and under capacitive cell respectively.

- The second issue related with SEI is that it is a totally natural phenomenon with no definite external control. Thus the SEI in most cases is inhomogeneous and
brittle, rather than thin homogenous uniform layer as one would desire. Moreover, the SEI components are not totally stable during cycling. There are reports that some SEI components depending on their chemical stability may dissolve or evolve during cycling. Thus, further electrolyte degradation during later cycles cannot be eliminated. A thick SEI is also not ideal, as the SEI beyond a certain thickness accounts for additional dead mass, which lowers the specific energy of the battery.

- Another critical issue is that the natural SEI is not able to avert solvent co-intercalation of PC in crystalline graphite. This results in exfoliation of graphite, where the graphene sheets open up and endless irreversible decomposition of the electrolyte occurs on the freshly exposed area. PC based electrolytes are very important for low temperature performance of a battery [141] as they freeze at -49 ºC, compared to +37 ºC for EC. PC also has higher conductivity than EC. Most methods used in the literature to improve performance of graphite in PC are by using additives [20, 142, 143], or by making composites [143, 144]. However, more effective methods have to be developed for applications in EVs, where it is mandatory to have good low temperature performance of the battery.

![Graph of ICL vs. Specific Charge](image.png)

Figure 4.1. ICL due to SEI formation occurring during first cycle of SFG6 graphite vs. Li metal in 1 M LiPF₆ in EC:DMC.

In order to curtail these major drawbacks of natural SEI, we wish to prepare by chemical means an artificial SEI. The concept is that we introduce in the battery, instead of pristine graphite, graphite particles whose surface has been modified with an organic layer, which
has properties of an SEI. This pre-formed SEI on graphite should be wettable by electrolyte, allow Li-ion intercalation, and would not allow electrolyte degradation and hence avoid ICL. The concept of an artificial SEI is diagrammatically shown in figure 4.2. The properties desired from the artificial SEI are that it should have minimum electronic conductivity and maximum ionic conductivity.

4.2. Advantages of artificial SEI over natural SEI

- An artificial SEI would be able to avoid solvent co-intercalation and hence exfoliation of graphite in PC based electrolyte. This would greatly enhance the low temperature performance of the battery.

- The organic precoating would prevent the reaction of the active material surface with the electrolyte and hence enhance the safety of the battery.

- An artificial SEI, which is a redox inactive layer, is expected to be thin, homogeneous, and stable. This would limit the dead mass on the active material surface and ameliorate the specific energy of the battery.

- An artificial SEI, by the virtue of its electrolyte reduction hindrance will suppress the ICL and hence result in improved energy efficiency.

The goal of this work is to develop novel surface modification methods as first steps towards synthesis of an artificial SEI. The target is to obtain surface modified carbons (shown in figure 4.3) which have the following properties. Modified material should

![Figure 4.2. Concept of artificial SEI as compared to real SEI.](image)

### 4.2. Advantages of artificial SEI over natural SEI

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- An artificial SEI, by the virtue of its electrolyte reduction hindrance will suppress the ICL and hence result in improved energy efficiency.
comprise of a covalently bonded layer on its surface which would stay bonded to negative electrode material throughout cycling. This is necessary in order to localize the desired effect of the surface modification on the negative electrode material. The surface layer should also be homogenous, uniform, and as thin as possible (without compromising on the mechanical stability of the film), so that the redox inactive mass (of the layer) in the material is minimal. The surface layer should have a controlled morphology and reactivity towards carbonate based non-aqueous electrolytes. The coating should coat the prismatic planes or hold the graphene sheets together in order to limit PC solvent molecules to co-intercalate, and make it possible to cycle graphite in PC based electrolyte. And finally it should result in decreased charge consumption for SEI formation (ICL) and its defined surface properties would be inflicted in the SEI properties.

![Carbon surface](carbon_surface.png)

**Figure 4.3. Diagram of the intended target material.**

### 4.3. Course of research

To prepare these materials, the pool of knowledge available in literature on surface modified materials was used. Surface modified materials are widely researched for applications in sensors [145, 146] and electroanalysis [147, 148]. Nature and applications of modified electrodes is very diverse. Substrate materials can be semi-conductors [149], metals [150, 151], carbons [152, 153, 154, 155], silica [156], etc. Immobilized species can be organic [157], inorganic [158, 159], polymers, or enzymes [160, 161]. Properties of electrodes (such as wettability, adsorption, capacitance, catalytic behaviour, kinetics, interface phenomena, etc.) can be tuned by imparting it specific functionality via surface modifications. Amongst all these studies, the most widely used method of surface modification is covalent immobilization of organic molecules by grafting technique. The methodology is to create a covalent bond between an organic moiety and the substrate surface either by using an electrochemical impulse or by an electroless method. Precursors which can be grafted oxidatively are alcohols [162, 163, 164, 165], amines [166, 167], carboxylates/acetates [168], etc. And the precursors for reductive grafting are diazonium salts [169], iodonium salts [170, 171, 172, 173, 174, 175], and sulfonium salts [176].
During the course of this work, we have performed electrochemical grafting of model alcohol, diazonium salt, and iodonium salt (results elaborated in chapter 8). Alcohol grafting posed some practical limitations like lack of suitable current collector and need of the parent alcohol to be in liquid state. The iodonium grafting method was costly and resulted in poor yield. Thus, we selected diazonium grafting for further studies and final applications for modification of graphite powders (results reported in chapter 13). Beginning with electrochemical diazonium salt grafting, the scope was extended to other chemical methods of grafting, which did not require an electrochemical potential. Various methods of grafting were compared (results shown in chapter 11). Non-electrochemical methods would be of an advantage in the long term as they eliminate a step of external energy consumption. At the lab scale this might be minimal, but would be significant on scale up.

It was shown that the surface morphology of graphite could be tuned by grafting diazonium salts via various routes. But, the diazonium salt selected for this study contained a carboxylic acid group (due to stabilizing –I effect of the carboxylic group on diazonium salt). This was expected to result in higher charge consumption for reduction of surface groups. Thus, it was mandatory to introduce a second step of treatment to the modified material to tune the reactivity of the grafted layer towards the non-aqueous electrolyte and against reduction at very low negative potentials. For this purpose various electrochemical as well as chemical methods were used to modify the terminal functional group of the grafted sample.

Various treatments and modifications were performed on model electrodes (reported in chapter 9) and model carbonate modified carbons were synthesized (reported in chapter 10). For the modification of graphite powders, it was decided to use chemical reducing agents to have the terminal functional group of the grafted layers in reduced and lithiated state (reported in chapter 13). This was expected to exhibit decreased charge consumption during cycling for reduction of surface groups. Modified graphites were also tested in a PC based electrolyte, in order to study if the grafting could prevent solvent co-intercalation and exfoliation of graphite.

In a nutshell, all the grafted samples showed lower charge consumption for SEI formation but also hindered Li-ion intercalation, due to thick grafted layer. Hence, we revisited surface modification via another approach. The second approach was to modify the surface groups already existing on the surface of graphite by chemical treatment (results
reported in chapter 14). This would result in tuned reactivity of the inherent surface groups. Many chemical methods were investigated to enhance the existing number of surface groups and tuning their reactivity thereafter (results reported in chapter 15).

In the following section II, experimental methods including materials, methods, and analytical tools employed throughout this work will be detailed. Section III contains the chapters corresponding to the results from each set of experiments. The concluding section IV will highlight the main achievements of this work and chalk out the outlook to carry forward this research.
SECTION II

EXPERIMENTAL METHODS
Chapter 5. Materials

This chapter will list various materials used throughout this work, including the active materials, electrolytes, and other chemicals used for various processes.

5.1. Active materials

Carbons are the most widely used negative electrode materials for Li-ion batteries [177]. Li metal intercalation into graphite was first shown by Herold [178]. Since then graphite intercalated compounds and stage structures are widely studied [179, 180]. Carbon materials employed as negative electrode material for Li-ion batteries can be divided into two main categories. The first ones are hard carbons [181], which are synthesized by solid phase pyrolysis and are amorphous. They are of particular importance because they can store more than 1 Li per 6 carbon atoms; they have wide synthetic range, exhibit good cyclability, and are less susceptible to exfoliation. However, due to their poor electrochemical properties including Li insertion via solid solution and large hysteresis they are lagging behind in the market. The leaders of the negative material market at the moment are the soft carbons, which are highly crystalline graphites synthesized by gas or liquid phase pyrolysis. They have manifold advantages like they are cheap, abundant, non-toxic, sustainable, and electronically conductive. Electrochemically too crystalline graphite is suitable because it undergoes Li-ion intercalation at well-defined potential, possesses very negative redox potential (E≈ 0.1 V vs. Li⁺/Li), and undergoes minimal active material breathing (10.3 %). At ambient temperature and pressure, crystalline graphite’s store 1 Li per 6 C atoms in its structure. The redox reaction of graphite as negative electrode is: C₆ + Li⁺ + e⁻ ↔ LiC₆. For this work standard commercially available synthetic soft graphite was used.

For this work mainly two carbon materials were used. Firstly, a model electrode was used for development of surface modification methods and characterization of the modified materials. Then, selected methods of modification were applied to commercial graphite powder material for testing in Li cells. These materials are detailed in section 5.1.1 and 5.1.2 respectively.

5.1.1. Glassy carbon

Graphite powders are complex systems having moderate specific surface area (~20 m²/g), grain boundaries, surface groups, structure imperfections, etc. Hence, it is rather difficult to
characterize its surface (or thin surface layers) by common analytical techniques like XPS and FTIR. Thus for preliminary experiments of method development and characterization a model electrode was a must. Glassy carbon (GC) was chosen as model electrode for graphite due to the following reasons:

- it is chemically similar to graphite (sp$^2$).
- the infrared signals obtained from SEI on graphite and GC are similar [182].
- it is convenient to pre-treat/clean.
- its surface is flat, smooth, and reflecting; ideal for XPS and FTIR analysis.
- it serves as conducting free standing electrode for electrochemical experiments.
- it is used as substrate and modified electrode for innumerable applications.

Thus, GC will be used to develop surface modification techniques and analysis of the modified samples by XPS.

Glassy carbon discs were purchased from HTW, Switzerland. It is a SIGRADUR-G disc with dimensions 15x1 mm. XPS measurements on as received GC disc showed only 1.8 % atomic oxygen impurities and very sharp C 1s peak at 284.4 eV. Pre-treatments with H$_2$O$_2$ and KMnO$_4$ resulted in increased surface oxygen to 4.6 % and 12.3 % respectively. Hence, it was decided to use the discs as received without any pre-treatments.

The GC discs were used as free-standing electrode for electrochemical grafting and tests, no further electrode preparation was required. Figure 5.1.a shows a picture of the GC disc used.

![a. Optical picture of glassy carbon disc used; b. SEM image of SFG6 graphite powder used.](image)
5.1.2. Graphite

Graphite powders used throughout this work are commercially available standard SFG6 graphite powder from TIMCAL® Switzerland. A low magnification SEM image of SFG6 powder is shown in figure 5.1.b. The specifications of SFG6 graphite (as given by TIMCAL) are:

- particle size $d_{90}$: 6.5 µm
- particle shape: strong anisometric flakes, needled
- crystallite height $L_c$: $>100$ nm
- specific surface area: 17 m$^2$/g

SFG6 graphite was chosen over other standard graphite viz. SFG44, because the ICL of SFG6 (21 %) is higher than that of SFG44 (8 %). This is attributed to the smaller particle size of the former which results in higher specific surface area, and hence larger electrolyte degradation. Changes or improvements in terms of ICL will be more apparent for SFG6 graphite, with higher ICL. It was also studied in our group that SFG6 exfoliates in electrolytes containing more than 85 % PC [183]. So this material would also be good for studying exfoliation.

5.2. Electrolytes

There were two main categories of electrochemical experiments done. The first one is related to grafting, this includes electrochemical and chemical graftings, cyclic voltammetry (CV) of grafted GC in aqueous medium containing $Fe^{2+}/Fe^{3+}$ ions, and CV of grafted GC in blank electrolyte. Electrolytes used for this set of experiments were acetonitrile based non-aqueous, or aqueous. The second category is that of carbonate based non-aqueous electrolytes which were used for testing the performance of grafted materials vs. Li metal. Different electrolytes used for various electrochemical experiments are listed in table 5.1.
Table 5.1. General electrolytes used for various electrochemical experiments

<table>
<thead>
<tr>
<th>#</th>
<th>Purpose</th>
<th>Solvent</th>
<th>Supporting salt (1 M)</th>
<th>Other salts</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Oxidative grafting of alcohols</td>
<td>Parent alcohol</td>
<td>LiClO₄</td>
<td>-</td>
<td>Parent alcohol has to be in liquid state</td>
</tr>
<tr>
<td>2</td>
<td>Reductive grafting of diazonium salts</td>
<td>CH₃CN (&gt;99 %, Aldrich)</td>
<td>(C₂H₅)₄NBF₄ (electrolyte grade, Aldrich)</td>
<td>Diazonium salt (5 mM)</td>
<td>Diazonium salt was self-synthesized</td>
</tr>
<tr>
<td>3</td>
<td>Reductive grafting of iodonium salts</td>
<td>CH₃CN (&gt;99 %, Aldrich)</td>
<td>(C₂H₅)₄NBF₄ (electrolyte grade, Aldrich)</td>
<td>Iodonium salt (5 mM)</td>
<td>Iodonium salt was self-synthesized</td>
</tr>
<tr>
<td>4</td>
<td>Electrochemistry of grafted GC</td>
<td>CH₃CN (&gt;99 %, Aldrich)</td>
<td>(C₂H₅)₄NBF₄ (electrolyte grade, Aldrich)</td>
<td>-</td>
<td>For CV of GC grafted with p-nitro benzene</td>
</tr>
<tr>
<td>5</td>
<td>Electrochemical characterization of grafted GC</td>
<td>H₂O</td>
<td>KCl</td>
<td>5 mM/ 5 mM K₃Fe(CN)₆/ K₄Fe(CN)₆</td>
<td>To study charge transfer</td>
</tr>
<tr>
<td>6</td>
<td>Cycling, CV, and EIS of graphite electrodes vs. Li metal</td>
<td>EC:DMC (1:1) w:w</td>
<td>LiPF₆</td>
<td>H₂O&lt;20 ppm</td>
<td>Standard electrolyte from Ferro®</td>
</tr>
<tr>
<td>7</td>
<td>Studying exfoliation of graphite</td>
<td>EC:PC (15:85) w:w</td>
<td>LiPF₆</td>
<td>H₂O&lt;20 ppm</td>
<td></td>
</tr>
</tbody>
</table>
5.3. Chemicals

Other reagents used for various chemical processes like synthesis of diazonium and iodonium salts, functional group transformations, chemical graftings, treatments of graphite surfaces, additives, and chemical reduction of grafted layers will be listed in the corresponding chapters in section III. All the standard chemicals were pure reagent grade purchased from Sigma Aldrich. They were used without further purification, unless mentioned otherwise. The products which were self-synthesized are also mentioned along with the method of synthesis in the corresponding sections. Crude compounds were usually characterized by FTIR-ATR mode.
Chapter 6. Cells

Various cells used for different electrochemical and other experiments are listed in this section. All the cells detailed in this chapter were developed for specific experiments and measurements related to this work. All these cells (except the cell for EIS) were designed and built by Mr. Hermann Kaiser in our group at Paul Scherrer Institut.

6.1. Electrochemical grafting of GC

A new three-electrode cell (shown in figure 6.1) was developed for electrochemical grafting and electrochemical characterization of grafted GC samples. Advantages of this cell over a conventional cylindrical jar cell with dipping electrodes are listed below:

- It allows complete immersion of GC electrode surface into the electrolyte. Thus, well-defined area undergoes electrochemistry.

- There is no need for crocodile clips to contact the electrodes, this minimizes metallic contamination.

- Cell body made from polyaryletheretherketone (PEEK) makes the cell very stable in a wide voltage window.

- It is possible to seal the cell hermetically inside the glove box.

- It is possible to use various counter and reference electrodes like Pt, Ag wires or GC rods, without modification of the cell.

- The working electrode and the counter electrode are parallel to each other, thus ensuring uniform current density distribution and hence uniform coating/grafting.

- Very small quantity of electrolyte ~10 mL is required.

- The GC samples can be mounted as received in the cell, with minimum touching, thereby reducing further contamination. This is important for XPS analysis of GC samples.

Various components of the cell are labeled in figure 6.1. For mounting the cell, first the counter electrode and reference electrode wires were plugged into the cylindrical slots through rubber stoppers. Then ~8 mL electrolyte was filled into the cell in inverted position. The GC disc was carefully enclosed between the Ti current collector and the O-ring on the
lid of the cell. This lid assembly was then tightly fixed on the inverted cell, avoiding electrolyte flow out. Assembled cell was inverted for experiments, so that the electrolyte wets the GC disc completely.

*Fig 6.1. The new three-electrode cell for electrochemical grafting and characterization of GC.*

Electrochemical experiments using this cell were performed on an external standalone Astrol system, equipped with an additional potentiostat and function generator. Astrol is described in details in chapter 7.3.

**6.2. Electrochemical grafting of graphite**

Another cell similar to the one above was built for grafting graphite electrode. This cell is a modified version of the cell shown in figure 6.1. The GC working electrode was replaced by a larger area Ti current collector plate. On this plate SFG6 graphite slurry (with styrene-butadiene rubber (SBR) binder and hexane solvent) was casted and dried. This cell also has a bigger electrolyte compartment. The cell assembly and measuring conditions were the same as those for the cell described in section 6.1.
6.3. Standard cell for cycling

For electrochemical cycling, standard two-electrode cells using Li metal as counter as well as reference electrode were used. The cell design and components are shown in figure 6.2.a.

**Fig 6.2.a.** Standard two-electrode cell for electrochemical testing vs. Li metal; b. schematic diagram of the electroactive part of the cell.

Electrode preparation: All working electrodes were prepared inside the glove box to avoid changes in the chemical composition of air sensitive samples on exposure to air. For consistency and better comparability of the results this procedure for working electrode preparation was used for all graphite powder samples. To further minimize the possible effect of binder and solvent on the chemical nature of the grafted layer, chemically inert binder SBR and inert solvent hexane was used in slurry formulation (10:90 SBR:graphite w:w). Slurry was applied onto Ti current collector stubs and dried inside the glove box. Electrode loading was normally in range 5-10 mg/cm².

Cell assembly: The bottom cylindrical container was fixed into the insulated metal base. Then the prepared working electrode discs were put in, followed by glass fiber separator. The separator was soaked with ~500 µL electrolyte. Then the counter cum reference electrode Li metal ribbon was stuck onto the metallic cylinder and inserted into the
cylindrical cavity of the bottom container. The cell was hermetically sealed after inserting the insulating ring. The electroactive part within the standard cell is shown in figure 6.2.b.

Glove box: An Ar filled glove box was used for electrode preparation, cell assembly, and storage and handling of air sensitive samples and chemicals. The O₂ content was maintained <0.6 ppm, and H₂O content <3 ppm inside the glove box in normal conditions (~25 ºC).

Measuring conditions: Electrochemical cycling tests were done galvanostatically at C/10 rate in 1 M LiPF₆ in 1:1 (w/w) EC: DMC in potential range 0.01 mV and 1.0 V vs. Li⁺/Li. For SEI formation and Li-ion intercalation characterizations, CV of SFG6 electrodes vs. Li metal was done at a scan rate of 0.01 mV/s in the potential window between 0.01 mV and 1.0 V vs. Li⁺/Li in the aforementioned electrolyte. To study the effect of surface modification on the exfoliation of graphite galvanostatic cycling at C/37 rate in 1 M LiPF₆ in 15:85 (w/w) EC: PC in potential range 0.01 mV and 1.0 V vs. Li⁺/Li was performed. An earlier study in our group showed that EC:PC mixtures containing 85 % or more of PC by weight results in exfoliation of SFG6 graphite [183]. Thus, 15:85 (w/w) EC: PC composition was selected for this study. All electrochemical experiments were conducted at 25 ºC (± 1 ºC).

6.4. Cell for electrochemical impedance measurements

A three-electrode cell (Toyota cell design) was used for electrochemical impedance measurements. It is necessary to employ a three-electrode cell rather than a standard two-electrode cell for these measurements so that precise potential of the working electrode can be measured with the help of a reference electrode. Some of the key features of this cell are:

- Being a three-electrode cell it allows measuring potential of the working electrode with the help of the reference electrode. There is negligible current flow between the counter electrode and reference electrode and hence the potential of the reference electrode does not alter.

- Since the same cell is used for all measurements, the resistance from the redox inactive components of the cell is always the same. Hence, reproducible and comparable EIS results can be obtained.
• Composite electrodes or powder materials can be used in the working electrode compartment, this gives experimental flexibility.

The cell design and components are shown in figure 6.3.

![Figure 6.3](image)

**Fig 6.3. Toyota three-electrode cell for EIS measurements.**

Prior electrode preparation was not needed as powder samples (~5 mg) were used for measurements. For cell assembly first the reference electrode part was prepared with a small piece of Li. Then the metallic container containing the active material powder was placed above it (separated by Celgard separator). Then two glass fiber separators soaked with electrolyte (~750 µL) were placed and finally counter electrode which was Li metal stuck on a metallic stub was placed. The cell was sealed hermetically inside the glove box.

Instrumental specifications of the potentiostat, measuring conditions, and operating and evaluating software’s will be described in the corresponding results and discussion chapter 15.

### 6.5. Transfer chamber for SEM

SEM analysis of surface morphology of air sensitive samples and SEI on cycled samples is a very significant part of this research. Hence, in order to avoid alterations in the surface layer or SEI properties by reaction with air and moisture we developed a special air tight chamber for sample transportation. This chamber enables the transport of the samples from Ar atmosphere of glove box (where they are synthesized, and/or washed after cell
disassembly) to vacuum chamber of SEM instrument without any contact with air or moisture. The design of this transfer chamber is shown in figure 6.4.

![Cross-section of the transfer chamber for SEM measurements.](image)

**Fig 6.4. Cross-section of the transfer chamber for SEM measurements.**

The samples were stuck onto the metallic base plate of the device (transfer chamber), with the help of standard carbon double sided adhesive discs. The samples were electrodes or powders, the total height of the sample along with the tape was <5 mm. The lid part was then placed on top and sealed by creating vacuum (pressure <5 mbar) in the void of the chamber (through a valve). After assembly in the glove box, it was transported to the SEM instrument. The sealed chamber was placed on the standard sample holder, and inserted in the fast entry air lock (FEAL). After vacuum was created in the FEAL, the chamber could be opened by the screw rod, and the normal procedure for entering the sample holder from FEAL to measurement chamber was followed as per the macro of SEM operating software. No additional modifications were required. Other details of the SEM instruments and measuring conditions will be described in chapter 7.4.
Chapter 7. Analytical techniques

In this chapter various analytical instruments used for analysis of modified and cycled samples will be detailed. These instruments are standard instruments normally used for material analysis. They are all present within PSI premises. For each instrument, a short introduction to the technique, followed by instrument specifications and measuring conditions will be listed.

7.1. X-Ray Photoelectron Spectroscopy (XPS)

7.1.1. Background

XPS, also known as electron spectroscopy for chemical analysis (ESCA) is based on the photoelectric effect. The general working principle of XPS is shown in figure 7.1.

![Figure 7.1. Principle of XPS.](image)

During an XPS measurement high energy X-ray photons (Al Kα = 1486.6 eV, Mg Kα = 1253.6 eV) are incident on the sample. Core electrons are emitted as photoelectrons from matter as a consequence of their absorption of energy from electromagnetic radiation. Energy of the emitted electron is described as per Einstein's explanation of the photoelectric effect [184]. From the kinetic energy of the outgoing photoelectron, its binding energy can be calculated using equation 7.1:

\[ BE = hν - KE - Φ \]  

\[ BE = hν - KE - Φ \]  

Where, \( BE \) = binding energy
$hv =$ energy of the incident X-rays

$KE =$ kinetic energy of the ejected photoelectron

$\Phi =$ work function of the instrument

The ejected electrons are captured by the analyzer and sent to the detector. Various photoelectrons are differentiated on the basis of the kinetic energy with which they reach the analyzer. Kinetic energy of the photoelectron is proportional to the energy of the level from which it is ejected. Ultra high vacuum in the measurement chamber is mandatory for analyzing the ejected electrons, to avoid energy losses by collisions with other gas molecules in their trajectory. XPS is a semi-quantitative technique, which allows analysis of all elements (except H and He) present in atomic concentration $> 0.1 \%$ in the outermost 10 nm of the surface [185]. Chemical shifts in the binding energies give information about the chemical environment of the atom. Thus for example, C-C, C-O, C=O can be differentiated from within the C 1s signal. The resolution of XPS is $\sim 0.1 \text{ eV}$. The penetration depth is $\sim 50 \text{ Å}$ [33]. Non-destructive elemental depth profile is normally done with angle resolved XPS ( $\sim 10 \text{ nm}$) and destructive elemental depth profile is done by Ar$^+$ sputtering (several hundred nm).

Energy of the initial state of the atoms (initial state effects) is affected by the following chemical bonding parameters.

- hybridization (C in graphite or diamond)
- chemical bonds and local environment
- covalent electronegativity difference between the atoms (C-F or C-O)
- ionic bonding (example Cl in NaCl or KCl)
- formal oxidation state (Fe in FeO or Fe$_2$O$_3$)

Initial state effects give important chemical information and can be studied by XPS. High resolution spectra of various elements can be deconvoluted and quantified. The reference binding energies of the components of high resolution spectra can be obtained from literature. For this work, the dataset is already compiled in tables in chapter 3.

General features observed in the XPS spectra (survey or high resolution) are:
• photoemission peaks
• degenerate peaks (due to spin-orbit coupling)
• X-ray satellite peaks
• shake-up satellites
• photon-induced auger lines
• inelastic scattering background
• valence band features
• multiplet splitting
• plasmon loss peaks

Each of these features provide useful information about the sample in question. For this work mainly the photoemission peaks were used for analysis. The other effects like X-ray satellite peaks and multiplet splitting are important for analysis of samples containing transition metal atoms like Ni or Fe. The inelastic scattering background is useful for sample containing multi-component layers. The pros and cons of analysis of SEI by XPS are listed in table 7.1.

Table 7.1. Pros and cons of using XPS for analyzing SEI

<table>
<thead>
<tr>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highly sensitive.</td>
<td>Charging of non-conducting samples.</td>
</tr>
<tr>
<td>Quantitative and qualitative elemental analysis possible.</td>
<td>Quantification of C containing groups on C substrates is difficult.</td>
</tr>
<tr>
<td>Depth profiling of SEI possible (angle resolved XPS or Ar⁺ sputtering).</td>
<td>Influence of ultra high vacuum on organic samples should be checked.</td>
</tr>
<tr>
<td>Unambiguous quantification possible.</td>
<td>Sample contamination should be minimal.</td>
</tr>
<tr>
<td>Detection of contaminants is possible.</td>
<td></td>
</tr>
<tr>
<td>XPS data of many materials exists in literature.</td>
<td></td>
</tr>
</tbody>
</table>
7.1.2. Instrument and measuring conditions

XPS analyses of the GC samples were performed with ESCALAB 220iXL (Thermo Scientific, USA, formerly V.G. Scientific) instrument using Al Kα (1486.6 eV) radiation. A monosource with large area XL mode was used. The beam spot diameter is ~500 µm. The operating software was Advantage 4.43, and CEM map by CEM detector toolkit software version 654321 was used for adjusting the sample height (focusing) by optimizing the electrons received by the channeltrons. In addition a manually movable X-Y stage was used along with close circuit camera to locate spots for measurements.

Apart from washing in acetonitrile and drying in the glove box, no further sample preparation was performed prior to XPS measurements, unless mentioned otherwise. The samples were clipped onto sample holder, with minimum contaminations (clean gloves, tongs etc). They were first inserted into the FEAL, where the pressure goes down until $10^{-6}$-$10^{-7}$ mbar. Then they were taken into the transfer chamber where the pressure decreases to $10^{-9}$ mbar. And finally they are taken into the measurement chamber where the pressure is maintained at $10^{-9}$-$10^{-10}$ mbar.

Survey spectrum was recorded from 0-1100 eV with pass energy 50 eV. After identification of the elements present from the survey spectrum, high resolution spectra of each individual element were made. Each high resolution spectra was recorded in the binding energy range where the most probable photoelectron peak appears. The pass energy for high resolution spectra acquisition was 20 eV. The number of spectra recorded per measurement varied generally from 5-10. Data analysis including deconvolution and quantification was done using CasaXPS software version 2.3.15.

7.2. Fourier transform infrared spectroscopy (FTIR)

7.2.1. Background

FTIR spectroscopy is a very versatile tool for analysis of the chemical nature of substances. Infrared beams of wavelength in the range 100 µm to 1 µm interact with the material during the experiment. A part of the incident beam is absorbed by the molecules for transitions from ground vibration state to higher vibration state. Frequency of the absorption is characteristic of the vibration involved. It intern depends on the bond strengths and the polarity of the molecule. Hence, various peaks in the FTIR absorption spectrum can be assigned to specific bonds vibrating in different modes (stretching,
bending, symmetric, or asymmetric). FTIR is particularly important to decipher functional groups of the molecules in question. Reaction progress or completion can also be monitored by FTIR. Tables listing characteristic vibrations for different functional groups can be found in many textbooks [186]. There are uncountable publications reporting FTIR spectra of SEI on Li, SEI on graphite, and of synthesized components of SEI. For this work they are compiled in table 3.2. High vacuum conditions are not mandatory for FTIR spectroscopy, thus it is comparatively cheaper than XPS. It is possible to use infrared spectroscopy in other modes like attenuated total reflectance (ATR), photo acoustic infrared, diffused reflectance infrared, subtractively normalized interfacial Fourier transform infrared (SNIFTIR) [187], transmission infrared, near normal incidence reflectance, grazing incidence reflectance, double modulation infrared [51], and reflection absorption infrared.

Pros and cons of FTIR spectroscopy for analysis of SEI or SEI like surface layers are listed in table 7.2.

Table 7.2. Pros and cons of FTIR spectroscopy

<table>
<thead>
<tr>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>It is a surface sensitive technique.</td>
<td>SEI is too thin to produce strong signals.</td>
</tr>
<tr>
<td>Characteristic vibrations of different functional groups are known.</td>
<td>SEI composition is inhomogeneous, inorganic components on edges and organic on basal planes.</td>
</tr>
<tr>
<td>Plausible SEI components have been characterized by FTIR in literature.</td>
<td>Too many overlapping vibrations due to similarities between electrolyte and SEI.</td>
</tr>
<tr>
<td>ATR, reflective, and in situ cell modes are available.</td>
<td>It is difficult to perform FTIR measurements without exposing the sample to air.</td>
</tr>
</tbody>
</table>

7.2.2. Instrument and measuring conditions

FTIR Spectra were recorded with Perkin-Elmer system 2000 equipped with mid infrared triglycine sulphate detector (range 15600-200 cm⁻¹). This FTIR instrument was used in ATR or reflective modes. GOLDEN GATE diamond ATR sample holder from Portmann Instruments AG was used for analysis of crude samples and powder samples. Reflective mode was used for analysis of modified GC samples, and in situ SNIFTIR analysis of SEI formation. The operating software was Spectrum version 5.3.1.
Before recording spectra the sample chamber was purged with N2 for 5 minutes. This minimizes noise in the spectra rising from CO2 and H2O absorptions. Experimental condition used were range = 4000-600 cm\(^{-1}\), resolution = 4 cm\(^{-1}\), 30 spectra/measurement. Measuring conditions for in situ experiments will be mentioned in the corresponding chapter in the results and discussion section.

7.3. Potentiostat for electrochemical measurements

7.3.1. Background

For all the electrochemical systems, the most fundamental measuring unit is a potentiostat/galvanostat. It is electronic equipment used for controlling three-electrode cells in electrochemical experiments. It enables one to apply potential, or current in various protocols to the three-electrode (or two-electrode) cell, and record the potential, current or other outputs. Normally a potential difference is applied between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode.

7.3.2. Instrument and measuring conditions

For all the electrochemical measurements (except EIS) a multichannel galvano/potentiostat system from Astrol Electronic AG was used. A BatSMALL type module was used, which has current resolution ~150 nA for measuring range of ±5 mA; and voltage resolution of ~300 µV for measuring range of ±10 V. Generally for cycling tests the current was calculated from the mass of active material for C/10 rate. C/10 rate means current is so calculated that there is one full charge/dischare in 10 hours (for graphite that corresponds to 1 Li per C\textsubscript{6} in 10 hours). This was in the current range 0.1-0.5 mA. The operating software is Computer Controlled Celldata Capture 1.3 (by Synthesis AG). Data was analysed by MSExcel 2003 and Origin 7.5 software's.

7.4. Scanning electron microscopy (SEM)

7.4.1. Background

SEM is used to obtain high-resolution images (from 10x to 100,000x magnification) for studying morphology and texture of materials. The working of a SEM is that a field emission gun emits a beam of electrons which is focused on the specimen with the help of an arrangement of many magnetic lenses and scanning coils. Electron beam-sample
interactions lead to various outgoing radiations including secondary electrons, backscattered electrons, diffracted backscattered electrons, photons, visible light, and heat [188]. As for XPS, high vacuum is required inside the sample chamber (~$10^{-5}$-$10^{-6}$ mbar) to minimize loss of information by scattering of electrons due to collisions of electron with other gas molecules. Secondary electrons and backscattered electrons are the ones used for image generation. Secondary electrons are emitted from the topmost 100 Å layer of the sample; these are most valuable for imaging the morphology and topography. The backscattered electrons are emitted from 1-2 μm depth of the sample and are useful for visualizing contrasts in composition. The working principle of SEM is shown diagrammatically in figure 7.2.

![Diagram of SEM Working Principle](image)

**Figure 7.2. Diagrammatic representation of the working principle of SEM.**

While measuring SEM, the following points have to be considered:

- Only solid samples or samples which can withstand high vacuum can be analyzed.
- Stability of the sample in high vacuum conditions must be checked.
In case of non-conducting or poorly earthed samples there can be charge accumulation on the sample, which can lead to distorted images.

Charged aggregates or ionic clusters may also lead to distorted images.

### 7.4.2. Instrument and measuring conditions

Ultra 55 Field Emission SEM (from Carl Zeiss SMT AG) was used to visualize the surface morphology of various samples. Pictures were taken using In Lens detector (which collects secondary electrons) at 3 keV accelerating voltage. The operating software was SmartSEM® V05.04. The transfer chamber described in figure 6.4 was used for transferring the electrochemically cycled samples from the glove box to the SEM measurement chamber without exposure to air. All modified samples were measured as powders on a typical adhesive double sided carbon tape. Cycled samples were washed with DMC after 50 electrochemical cycles (cycling conditions will be mentioned in the corresponding results section) and dried inside the glove box for post mortem SEM analysis. A part of the electrode was then transferred from the Ti current collector stub to carbon tape for analysis.

### 7.5. Electrochemical Impedance Spectroscopy (EIS)

#### 7.5.1. Background

Electrochemical impedance in a general sense is a vector quantity describing the relationship between a potential wave and a current wave, when an electrochemical system is perturbed by an alternating current or potential. Impedance extends the concept of resistance to alternating current. In EIS, the response of current (or potential) is measured when a sinusoidal perturbation of potential (or current) is applied at different frequencies. Perturbation has to be limited to small amplitude in order to ensure linear (or pseudo-linear) relationship between the current and potential wave. The frequency dependent proportionality between the potential signal and the current response results in the impedance data, which is normally presented in form of a Nyquist plot ($-Z_{\text{im}}$ vs. $Z_{\text{real}}$) or a bode plot (magnitude vs. frequency and phase vs. frequency). An electrochemical system can be assumed to be a network of various resistive, inductive, and capacitive components. For interpreting the spectra normally an equivalent circuit containing different electrical components is designed. If the equivalent circuit model fits the experimental
spectrum then each electrical component in the equivalent circuit is ascribed to physical processes which might be present in the system.

Normally either two-electrode or three-electrode cells can be used for EIS measurements. Two-electrode cells measure the total polarization of the cell (which would be a sum of all the resistive components present); and are hence normally used to study bulk or average phenomenon like electrolyte resistance, total resistance of the cell, etc. This kind of measurements can be carried out in our standard cells used for cycling (described in figure 6.2). For measuring reaction resistances of oxide materials, using two-electrode cells would be possible, as the time constants of the reaction resistance of the Li metal and the positive material is normally well separated. But for graphites, the separation between time constants is minimal, thus using three-electrode cell is mandatory. Normally a three-electrode setup is more helpful because it allows precise measurement of the potential of the working electrode. Potential of the working electrode is precisely measured with respect to a reference electrode. Ideally the reference electrode should be so placed that it minimizes the resistive contribution of the electrolyte. The current is applied between the working and counter electrode, and hence the reference electrode should be placed such that it does not perturb the current flow between the working and counter electrodes. The three-electrode cell used for this work is described in chapter 6.4, figure 6.3.

With EIS, processes such as electronic/ionic conduction in electrodes and electrolytes, interfacial charging (on surface or double layer), charge transfer, and mass transfer processes can be qualitatively determined [189], if the processes have different time constants. For example, charge transfer typically has intermediate time constant whereas diffusion limitation typically has a low time constant.

EIS is widely used in the field of batteries [190] and fuel cells [191] to study formation and properties of passive films on electrode surfaces, to estimate state of charge, to determine reaction rates, to measure conductivity of electrolytes etc.

7.5.2. Instrument and measuring conditions

EIS measurements were performed using the electrochemical cell which is described in chapter 6.4, figure 6.3. VMP3 multipotentiostat-galvanostat (from BioLogic Science Instruments) was used for recording EIS spectra. It offers frequency range 10 µHz to 1 MHz. Operating software was EC-LAB 9.98.
The electrochemical cell was initially relaxed for 1 hour, after that a potential perturbation of ±5 mV was applied at the measuring point (OCV or at specific potential during cycling). The frequency range was 100 kHz to 100 mHz.

7.6. Raman Spectroscopy

7.6.1. Background

Raman spectroscopy is based on scattering of light on interaction with matter [192]. Elastic collisions of incident light $h\nu_o$ with matter results in Rayleigh scattering. Inelastic collisions involve exchange of energy between the photon and molecule. As a consequence of inelastic collisions the molecule can gain or lose $\Delta E$ amount of energy as per quantum laws. $\Delta E$ represents change in vibrational or rotational energy of the molecule. Inelastically scattered light is called Raman scattering, and it comprises of two line called Stokes line (scattered lines having lower energy than incident $=h\nu_o-\Delta E$) as a result of absorption of energy by the molecule; and anti-Stokes line (scattered lines having higher energy than incident $=h\nu_o+\Delta E$) as a result of loss of energy by the molecule. However, only molecular vibrations or rotation that result in change in a component of molecular polarizibility are Raman active [192]. For molecules which have a centre of symmetry, the rule of mutual exclusion applies [192]. This rule states that Raman active vibrations are infra-red inactive and vice versa [192].

Raman spectroscopy is widely used for structural characterization of various materials. Disorder-induced Raman bands of graphite have been a subject of study for many decades, and are discussed in details by Reich and Thomsen [193]. They explain the origin of various bands based on structural vibrations. Hence, Raman spectroscopy serves as useful tool to analyze surface structural disorder of graphitic materials. This is useful for studying exfoliation of graphite in PC based electrolyte [194], and SEI formation [195].

7.6.2. Instrument and measuring conditions

Raman spectra were acquired on a Horiba-Jobin Yvon Labram HR800 system equipped with a Helium-Neon laser (wavelength= 632.8 nm). Raman spectra were recorded in spectral range 1100-1900 cm$^{-1}$, under confocal conditions, employing an X50 objective, with spatial resolution of 2-3 $\mu m^3$. The operating conditions were D1 intensity filter, 600 grating, 60 s/scan, and 2 scans/measurement. The operating software was LabSpec version 5.45.09.
SECTION III

RESULTS AND DISCUSSION
Chapter 8. Electrochemical grafting

8.1. Motivation

The first step towards forging an artificial SEI is to develop methods for covalently binding organic moiety to the surface of the electrode material. For this purpose vast know how available in the field of chemically modified carbons [196, 197] was used. The most widely used method of covalent immobilization of moieties onto electrode surfaces is electrochemical grafting of organic precursors. Electrochemical grafting can either be done reductively, where a negative potential is applied to the working electrode (whose surface is to be modified) or oxidatively, where a positive potential is applied to the working electrode. Organic precursors which can be used for oxidative electrochemical grafting are diagrammatically shown on the left side of the figure 8.1, whereas the ones which can be reductively grafted are shown on the right side of the figure 8.1.

![Diagram of various methods of modifying carbon surfaces.](image)

Fig 8.1. Various methods of modifying carbon surfaces. The molecules having functional groups written in red (left) are grafted onto carbon by oxidative means; and the ones having functional groups written in blue (right) are grafted by reductive routes.

For method development and surface characterization by XPS, GC will be used as model electrode for graphite. To compare oxidative grafting vs. reductive grafting methods; oxidative grafting of alcohols, and reductive grafting of iodonium salt and diazonium salt was performed. The grafting mechanisms of these methods are shown in figure 8.2. During alcohol grafting the proton of the alcohol is removed, and the resulting radical attached to the substrate surface. During diazonium salt grafting the diazonium reduces, \( \text{N}_2 \) is released as gas, and the remaining part of the molecule attaches to the surface. During iodonium grafting, part of the iodonium salt attached to a more electron withdrawing group forms the radical and is eventually grafted onto the surface of the material; whereas the part containing more electron donating group is removed as its iodo-product [170].
For method development, and unambiguous analysis by XPS model compounds containing a heteroatom were chosen for grafting.

\[
\begin{align*}
\text{a.} & \quad \text{alcohol grafting:} \quad \text{C}_2\text{H}_5\text{OH} + \text{C}_2\text{H}_5\text{Cl} \xrightarrow{-e, -H^+} \text{C}_2\text{H}_5\text{Cl} + \text{C}_2\text{H}_5\text{OH} \\
\text{b.} & \quad \text{diazonium salt grafting:} \quad \text{C}_6\text{H}_4\text{NO}_2^+ + e^- \rightarrow \text{C}_6\text{H}_4\text{NO}_2 \\
\text{c.} & \quad \text{iodonium salt grafting:} \quad \text{C}_6\text{H}_5\text{I} + \text{C}_2\text{H}_5\text{Cl} \xrightarrow{e^-} \text{C}_6\text{H}_5\text{Cl} + \text{C}_2\text{H}_5\text{I} 
\end{align*}
\]

Figure 8.2. Mechanism of covalent attachment of organic moieties during electrochemical grafting. a. alcohol grafting; b. diazonium salt grafting; c. iodonium salt grafting.

8.2. Experimental

All the electrochemical experiments in this chapter were carried out in the cell described in chapter 6.1, figure 6.1.

Alcohol grafting of 3-chloropropanol was done in an electrolyte containing parent alcohol as solvent and 0.1 M LiClO₄ as supporting salt. Grafting CV (5 scans) were run from 0.0 V to 2.2 V vs. Ag wire at a scan rate of 5 mV/s.

For diazonium grafting of \( p \)-nitrobenzene diazonium tetrafluoro borate salt (PNBD), the electrolyte was 0.1 M tetraethylammonium tetrafluoroborate (TEAB) in CH₃CN (stored over molecular sieves 4 Å, H₂O< 50 ppm, analyzed by Karl Fischer titration), containing 5 mM diazonium salt. Grafting CV was scanned from -1.6 V to 0.5 V vs. Ag wire (5 scans).

Literature describes the synthesis of iodonium salts from iodosobenzene. Hence first iodosobenzene was synthesized by base hydrolysis of iodosobenzene diacetate [198]. Then the iodonium salt 5-chloro-1-pentyne(phenyl)iodonium tetrafluoroborate (CPI) was synthesized from iodosobenzene and 5-chloro1-pentyne [199]. All the crude products were characterized by FTIR. For grafting, the electrolyte was 0.1 M TEAB in CH₃CN, containing
5 mM CPI. Grafting CV was scanned from -1.5 V to 0.3 V vs. Ag wire (5 scans) at a rate of 5 mV/s.

All the grafted samples were ultrasonically washed in acetone before XPS and CV, so that any weakly adsorbed or loosely bound moieties are removed from the surface and only the covalently bonded ones remain.

8.3. Results and discussion

Grafting CVs of the aforementioned model compounds on GC are shown in figure 8.3. An irreversible peak is observed in the first scan of all the grafting CVs (starting at ~ +1.2 V vs. Ag wire for oxidative grafting, starting at ~ -1.2 V vs. Ag wire for diazonium grafting, and starting at ~ -0.5 V vs. Ag wire for iodonium grafting). These irreversible peaks correspond to the current consumption for grafting of the organic precursors. In all the cases the maximum peak current appears in the first scan, after which there is minimal grafting current in the consecutive cycles. This proves that grafting is an electrochemically irreversible process, which is almost complete in the first scan.

Figure 8.3. a. CV of alcohol grafting on GC electrode; b. CV of diazonium salt grafting on GC electrode; c. CV of iodonium salt grafting on GC electrode.
To further study the electrochemical properties of the modified surfaces, CVs of the modified GC electrodes were performed in 5 mM $K_3Fe(CN)_6 + 5$ mM $K_4Fe(CN)_6$ in 1 M KCl aqueous solution. CVs of pristine and modified GC electrodes are shown in Fig. 8.4. Pristine GC is a good electronic conductor and hence gives a characteristic voltammogram of $Fe^{2+}/Fe^{3+}$ redox system. However for grafted GC samples (after the covalent immobilization step) the charge transfer peaks of the redox couple are diminished. This proves that the surface of grafted GC electrodes is coated with a layer which diminishes electron transfer. We assume that grafted species hinder the approaching $Fe(CN)_6^{4-}$ or $Fe(CN)_6^{3-}$ ions from undergoing charge transfer.

![Graph showing CV of pristine GC and various grafted GC in $K_3Fe(CN)_6 + K_4Fe(CN)_6$ aqueous solution.](image)

*Figure 8.4. CV of pristine GC and various grafted GC in $K_3Fe(CN)_6 + K_4Fe(CN)_6$ aqueous solution.*

To further verify that the grafting step resulted in covalent immobilization of the organic species containing heteroatom, XPS analysis of grafted GC was carried out. N 1s high resolution spectrum for diazonium grafted GC and Cl 2p high resolution spectra of alcohol grafted and iodonium grafted GC samples are compared with those of pristine GC in figure 8.5. As compared to the pristine GC (with absence of Cl signal), there was clear Cl 2p signal for the alcohol grafted and iodonium grafted GC, shown in figure 8.5.a and 8.5.c respectively. To confirm that the origin of the Cl signal is indeed from covalently grafted layer and not from adsorbed species, another GC sample was electrochemically cycled in 1 M NaCl solution and compared with that of the grafted samples. The Cl content found in the former (0.03 % of Cl compared to total carbon content of GC electrode) was found to be much less than that in the latter (0.17 % of Cl compared to total carbon content for alcohol grafted GC electrode, and 0.10 % of Cl compared to total carbon content for
iodonium grafted GC electrode). By deconvolution of the peaks in the high resolution spectra, the chemical composition of the grafted GC samples and the quantity of the grafted layer (containing the heteroatom) was quantified. The results are summarized in table 8.1. The functional group analysis has been done by using references from table 3.4.

Table 8.1. Qualitative and quantitative XPS analyses of pristine GC and grafted GC surfaces. The binding energies reported are for the deconvoluted component of the signal which is assigned to the corresponding functional group. \( y = \) atomic percentage of the deconvoluted component of the functional group/ total atomic percentage of carbon.

<table>
<thead>
<tr>
<th>Structure of GC electrode</th>
<th>Binding energy (eV) of terminal group</th>
<th>Functional group assignment</th>
<th>Quantitative analysis ( (y) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>284.3 (C 1s)</td>
<td>-CH\textsubscript{2}</td>
<td>0.77</td>
</tr>
<tr>
<td>O\textsubscript{2}Cl</td>
<td>200.0 (Cl 2p\textsubscript{3/2})</td>
<td>-Cl</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>201.6 (Cl 2p\textsubscript{1/2})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>407.8 (N 1s)</td>
<td>-NO\textsubscript{2}</td>
<td>0.11</td>
</tr>
<tr>
<td>Cl\textsubscript{2}</td>
<td>200.1 (2p\textsubscript{3/2})</td>
<td>-Cl</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>201.7 (2p\textsubscript{1/2})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In figure 8.5.b N 1s spectra of diazonium grafted sample, shows clearly two kinds of N species, which are attributed to the -NO\textsubscript{2} group (407.8 eV) and semi-reduced N groups (402.0 eV) specie [200]. This peak at 402 eV is also reported by other studies in literature [200, 201, 202, 203, 204, 205, 206, 207, 208], and is ascribed to partially reduced NO\textsubscript{2} species. We verified this experimentally, by performing a CV of the diazonium grafted GC sample in a blank electrolyte (0.1 M TEAB in CH\textsubscript{3}CN). The grafted p-benzenenitro moiety showed reduction peaks, originating from reversible four electron transfer [208], ranging from -1.3 V to -1.5 V vs. Ag wire (CV shown in figure 8.6). This potential window overlaps with that of the grafting window (0.0 V to -1.7 V vs. Ag wire, grafting peak maxima at 1.32 V vs. Ag wire). From analysis of the XPS data, this peak is assigned to NHOH chemical composition. Hence, it can be inferred that partial reduction of the grafted nitro group takes place during consecutive grafting CV scans.
Grafting of the diazonium salt was also confirmed by reflective mode FTIR (spectrum shown in figure 8.7). Strong vibrations of -NO₂ stretching (1513, 1341 cm⁻¹) were visible in the GC sample grafted with PNBD. Absence of NΞN (2306 cm⁻¹) vibration supports the mechanism of grafting illustrated in figure 8.2.b. However, the signal to background ratio of the spectrum was poor, because very thin grafted layer results in low absorption. Similar characterization could not be made on the other grafted samples due to poor reflectivity of samples, and poor signal strength.

![Figure 8.5.a. Baseline normalized XPS Cl 2p spectra of pristine GC and alcohol grafted GC; b. baseline normalized XPS N 1s spectra of pristine GC and diazonium grafted GC; c. baseline normalized XPS Cl 2p spectra of pristine GC and iodonium grafted GC.](image-url)
Figure 8.6. CV of p-benzenenitro grafted GC in 0.1 M TEAB in CH₃CN.

Figure 8.7. Reflective mode FTIR spectrum of p-benzenenitro grafted GC.

It was seen in figure 8.4 that the electron transfer process across the grafted layer on the GC electrodes was highly depressed. However, for application of the grafting technique to graphite for Li-ion battery, we need the grafted material to allow Li-ion transport (for good cyclability). In order to verify that the grafting would not completely block Li-ion transport (which is critical for good cycling), we grafted GC with ethylene oxide oligomer, namely tri(ethylene glycol) monomethyl ether. It has been shown in literature that Ca²⁺ [209] and Ba²⁺ ions [164] act as ionophore and assist in charge transfer across grafted ether molecules. Hence, as a proof of concept the electrochemical response of the ether grafted GC in an electrolyte containing alkali earth metal ion Ba²⁺ was checked. This system resembles the electrochemical environment inside a Li-ion battery, and could be considered as its aqueous analogue. Hence, it can give an early insight about the
electrochemistry of carbon electrode modified with small organic molecules in an electrolyte containing alkali or alkali earth metal ions. The structure of the ether molecule is shown in figure 8.8.

![Figure 8.8. Structure of tri(ethylene glycol) monomethyl ether](image)

Since, this molecule is an alcohol and liquid at room temperature, we choose oxidative grafting of alcohol for grafting it. The ether grafted GC sample showed similar electrochemistry as that of the other grafted samples in Fe$^{2+}$/Fe$^{3+}$ aqueous solution (figure 8.4), which was complete suppression of charge transfer (shown in the red curve in figure 8.9). However, the electrochemical activity of this sample was revived when Ba$^{2+}$ ions were added to the electrolyte (5 mM K$_3$Fe(CN)$_6$ + 5 mM K$_4$Fe(CN)$_6$ in 1 M KCl + 4 mM BaCl$_2$ aqueous solution). The redeemed electrochemical response (shown in the blue curve in figure 8.9) is attributed to the ionophore effect of the Ba$^{2+}$ ions [164]. This experiment proves that grafting does not make the material electrochemically inert, and it is possible to have ion transport across the grafted layers owing to the ionophore effect.

![Figure 8.9. Comparison of CV of pristine GC, and ether grafted GC in 5 mM K$_3$Fe(CN)$_6$ + 5 mM K$_4$Fe(CN)$_6$ in 1 M KCl with CV of ether grafted GC in 5 mM K$_3$Fe(CN)$_6$ + 5 mM K$_4$Fe(CN)$_6$+ 4 mM BaCl$_2$ in 1 M KCl aqueous solution.](image)

8.4. Conclusions

We have established electrochemical grafting as the first step towards surface modification of carbon electrodes for Li-ion batteries. By XPS analysis the grafting step was shown to result in covalent immobilization of various model compounds. The electrochemistry of the
grafted samples was studied in a Fe$^{2+}$/Fe$^{3+}$ aqueous system and it was shown that the
grafted GC samples drastically hindered the electrochemical charge transfer. The
complete electrochemical isolation of the material by grafting can however be prevented
by ionophore effect, which is expected to occur in electrolytes containing alkali or alkali
earth metal ions [164].

On comparing the different methods of electrochemical grafting, we infer that oxidative
grafting of alcohols is not a suitable method for application to materials for in Li-ion
batteries. The reasons include, firstly very positive potentials employed during oxidative
grafting, which render the conventional current collectors of negative electrode of Li battery
unsuitable. Secondly, the local environment of graphite inside a Li battery is highly
reducing; hence the stability of a film obtained by oxidation at very positive potentials is
doubtful.

Iodonium grafting method will also be ruled out for further research in this work because of
lower grafting yield (compared with diazonium, as shown in XPS analysis results in table
8.1), tedious organic synthesis involved, high cost of the reagents, and large quantity of
byproducts. Another synthetic limitation of iodonium grafting is that the electron
withdrawing part of the iodonium salt attaches to the substrate surface, which makes
further modification of the grafted moiety challenging.

Diazonium salt grafting offers good grafting yield (as shown in XPS analysis results in
table 8.1) and is one of the most promising methods for further research. There is
abundant literature available on diazonium salt grafting as this method is the most widely
studied and applied method for surface modification. We can design various diazonium
salts and vary their chemical nature with synthetic organic chemistry. The only limitation of
this method is the chemical instability of diazonium salts. However there exists literature
about non-electrochemical methods of grafting diazonium salts (in situ methods) with
which this limitation can be surpassed (these results will be reported in chapter 11).

In the following chapter, we will further modify the functional groups of the layers tethered
on the carbon surface by various methods.
Chapter 9. Functionalization of grafted material

9.1. Motivation

After the step of covalent immobilization of organic moieties on the electrode surface, it is rarely the case that one obtains the desired functionality, due to limited choice of the precursors. For example, diazonium salts of electron donating groups are not stable; hence normally the surface functional groups obtained by diazonium grafting are electron withdrawing like -NO₂ or -COOH. But for battery application one requires surface modified with electron donating groups like -CH₂OH, ideally in reduced and lithiated forms. It is thus necessary to introduce a second step of transforming the terminal functional group of the immobilized moiety. After the grafting step which can be done by either oxidative or reductive grafting, we can transform/reduce the grafted moiety by either of the two methods. The first method is electrochemical reduction, where external power source would be used (by applying negative potentials to the working electrode). The second method of choice could be chemical (by using reducing agents). For the chemical route wettability, reagent diffusion, interfacial reactivity, etc. are the critical factors. However, with the electrochemical route the critical issues are the conductivity of the grafted layer, stability of the bonds in the potential window, suitable solvent, etc. By using the electrochemical route we assist the reduction by providing abundant electrons from an external potentiostat to the surface, i.e. the site of reduction, hence the grafting yield is expected to be high. With the chemical route the advantage is that there are innumerous chemical synthesis and transformation routes available in literature [210] which can be employed. However it should be noted that the reaction mechanisms may be different for molecules attached to a solid substrate than for molecules in the bulk. One route or the other may be advantageous for a specific modification. The steps of surface modification with the possible pathways are summarized in the flowchart in figure 9.1.

To optimize the method of concatenating the grafting step with the functional group transformation step we carried out a series of experiments using different functional group transformation methods on various grafted model GC electrodes [211]. Understanding which method of functional group transformation is more suitable for which grafted specie is important for selecting optimal methods for preparing materials with tailored surface reactivity. Tuning the terminal functional group of the grafted layer is of utmost importance, as it determines the reactivity of the grafted layer towards the electrolyte and hence the electrochemical properties of the surface modified material.
In this chapter we will study various method of reducing the terminal functional groups of GC samples grafted with model compounds namely, 1,3-propanediol, PNBD, and \( p \)-carboxylic benzene diazonium (PCBD). The diol is grafted via oxidative grafting, whereas the diazonium salts are grafted reductively. The chemical composition of the resulting grafted samples are GC-O-(CH\(_2\))\(_2\)-COOH, GC-C\(_6\)H\(_4\)-COOH, and GC-C\(_6\)H\(_4\)-NO\(_2\). Each of these grafted samples will be reduced by both electrochemical and chemical methods. We prepared with a proper combination of the two consecutive steps (grafting and functional group transformation) three model surface modified electrodes with required functionality. GC-O-(CH\(_2\))\(_3\)-OCO\(_2\)Li was prepared by electrochemical oxidative grafting of
1,3-propanediol followed by chemical transformation, GC-C₆H₄-CH₂OH was prepared by electrochemical reductive grafting of PCBD followed by chemical as well as electrochemical reduction, and the GC-C₆H₄-NHOH was prepared by electrochemical reductive grafting of PNBD followed by electrochemical reduction. Which grafted species are likely to prefer one or the other method of functionality transformation is discussed.

**9.2. Experimental**

Covalent Immobilization: Grafting of the alcohol and diazonium salt precursors on GC was done as described in the chapter 8.2. Different grafting electrolyte, grafting potential window, and the structures of the precursor and the grafted moiety are illustrated in figure 9.2. Pristine GC sample is labelled A, alcohol grafted GC is labelled B, PNBD grafted GC is labelled C, and PCBD grafted GC sample is labelled D.

![Grafting Scheme](image)

**Figure 9.2.a. Scheme of grafting of 1,3-propanediol; b. scheme of grafting of PNBD; c. scheme of grafting of PCBD.**
Figure 9.3.a. Chemical transformation of the alcohol grafted GC (B) to carbonate containing GC (E); b. electrochemical reduction of the alcohol grafted GC (B); c. chemical reduction of the PNBD grafted GC (C); d. electrochemical reduction of the PNBD grafted GC (C) to phenyl hydroxylamine containing GC (H); e. chemical reduction of the PCBD grafted GC (D) to benzyl alcohol containing GC (I); f. electrochemical reduction of the PCBD grafted GC (D) to benzyl alcohol containing GC (J).
Functional group transformation: Electrochemical and chemical methods used to transform the terminal functional groups of the grafted samples B, C, D are shown in scheme in figure 9.3. Sample B was chemically reduced by stirring in a solution of acetonitrile with excess of LiH overnight in an inert atmosphere. Without exposing the resulting alkoxide to air, CO₂ was bubbled through the solution for 4-5 hours (figure 9.3.a); the resulting sample is labeled E. Sample B was reduced electrochemically by CV in 0.1 M TEAB in CH₃CN from 0.0 V to -3.0 V (figure 9.3.b). Cycled sample was sonicated in acetone; the resulting sample is labeled F. For the chemical reduction sample C, it was reduced with Zn, CaCl₂ [212] in aqueous ethanol under reflux for 2 hours (figure 9.3.c). The resulting sample was sonicated in acetone and labeled G. For the electrochemical reduction, sample C was cycled in 0.1 M TEAB in CH₃CN from 0.0 V to -2.0 V at 5 mV/s for 10 cycles (figure 9.3.d). The resulting sample was sonicated in acetone and labeled H. For the chemical reduction of sample D, it was stirred in 1 M BH₃ in THF overnight under Ar atmosphere (figure 9.3.e). It was then sonicated in CH₃CN. The resulting sample was labeled I. For electrochemical reduction of sample D, it was cycled in 0.1 M TEAB in CH₃CN from 0.0 V to -3.0 V at 5 mV/s for 10 cycles (figure 9.3.f). It was then sonicated in acetone. The resulting sample was labeled J. All the steps of functionality modification were monitored by XPS.

9.3. Results and discussion

Each of the grafted samples B, C and D was subjected to chemical and electrochemical methods of end functional group reduction. These experiments and results are summarized in table 9.1. The XPS results are shown in figure 9.4, 9.5, and 9.6. All the XPS spectra have been normalized with respect to intensity of the peak with highest counts per second. We observe that the alcohol grafted sample can be reduced to lithium alkoxide (evidenced in the further transformation to lithium alkyl carbonate) via chemical method. The evolution of the C 1s spectra of the pristine GC surface after the grafting and the chemical treatment is shown in figure 9.4.a. The signals at higher binding energies in the grafted sample B are attributed to the –C-O-C- (286.5 eV) and C=O (of –COOH) (289.1 eV) carbons. Due to the very positive potential applied during grafting CV, the alcohol group (-CH₂OH) at the unattached end of the precursor diol molecule is oxidized to –COOH group [213]. After the treatment however it is seen that the C 1s signal attributed to C=O is diminished and a signal at lower binding energy (-CH₂O-) appears. Another signal appears at high binding energy at 291.2 eV, this is attributed to the carbonate carbon (-CO₃Li). Lithium alkoxides are common precursors for lithium alkyl carbonate synthesis [58, 124], hence observation of the carbonate signal on the sample after
exposure to CO$_2$ can be worked back to be an evidence of the existence of lithium alkoxide (ROLi) after the LiH reduction step. But B (alcohol grafted GC) could not be reduced electrochemically. This is evident from the XPS C 1s spectrum of sample F shown in figure 9.4.b. This may be attributed to the hindered transference of electrons through the saturated alkyl chain during the electrochemical reduction of the grafted sample B. The electrons supplied by the external potentiostat could not reach the -COOH end group, due to the absence of a conduction pathway for electrons such as a delocalized $\pi$-cloud (or a conjugated system) in the grafted layer. On the other hand, the chemical reduction is feasible because the alkyl chain can be wetted by the reagents to undergo reaction on the surface. Additionally, reaction of B with 1-octyl amine did not result in formation of amide. This was confirmed by XPS analysis, as insignificant amount of N (2 atomic %) was detected on the surface of GC sample B after reaction with 1-octylamine. Similarly, reaction of B with 4-bromobutyril chloride did not result in the formation of ester. This was confirmed by extremely low amount of Br (0.1 atomic % by XPS analysis) present on surface of GC sample B after reaction with 4-bromobutyril chloride. This may be attributed to two reasons, firstly there is a possibility that the grafted sample has ring closures (cyclization), which are not re-opened by these reagents, but are re-opened by aggressive LiH. Second explanation could be that the mechanisms of these condensation reactions are difficult to realize on a supported molecule.

The PNBD grafted sample C could not be reduced by chemical method using Zn, CaCl$_2$ (procedure described in figure 9.3.c, XPS spectra shown in figure 9.5.a, and results summarized in table 9.1). From the XPS spectrum of sample G, it is observed that there is no significant decrease in the intensity of the peak corresponding to NO$_2$. This illustrates hindered reactivity of the surface groups towards the reagents. Since this reaction requires reflux conditions, it may also be that the heat transfer is not homogeneous when the molecule is attached to a substrate as compared to when it is a bulk pot synthesis. However, the grafted -NO$_2$ group could be relatively easily reduced by electrochemical method. As per the four electron reduction -NO$_2$ is reduced to -NHOH [214], confirmed by CV in figure 8.6. This is evident in the XPS spectra of the samples illustrated in figure 9.5.b. Sample C has two main N 1s peaks, the one at high binding energy of 407.8 eV is assigned to NO$_2$ whereas the one at 401.9 eV is assigned to reduced nitrogen species. This peak at lower binding energy has been observed for grafted NO$_2$ diazonium salts by many research groups and has been attributed to the reduced –NO$_2$ species [200, 201, 202, 203, 204, 205, 206, 207]. In the previous chapter, we have proved that this peak originates from –NHOH species which are formed during reductive diazonium grafting.
After the electrochemical reduction step the peak at higher binding energy (-NO₂) is almost completely depressed at the expense of the N 1s peak at lower binding energy attributed to NHOH. Even the oxygen content of that sample decreases from 16 atomic % (at 534.8 eV) to 11 atomic % (at 533.4 eV) after reduction. Decrease of the surface oxygen content and shift of the O 1s peak towards lower binding energy prove reduction of the -NO₂ group to -NHOH.

PCBD grafted sample D was chemically reduced by borane (procedure described in figure 9.3.e, results summarized in table 9.1), the XPS results of the surface modification are shown in figure 9.6.a. The grafted sample D shows C 1s peak at 289.4 eV which is attributed to carboxylic acid (–COOH). After the chemical reduction step sample I shows complete absence of peak at 289.4 eV with a concomitant decrease in the quantity of the oxygen on the sample. This proves that the carbonyl carbon has been reduced. However there still remains a shoulder on the C 1s spectrum of the sample I which is attributed to the C-O carbons of the reduced species. PCBD grafted sample D was also reduced electrochemically (procedure described in figure 9.3.f, results summarized in table 9.1). The XPS results are shown in figure 9.6.b. The signal at 289.4 eV attributed to -COOH is completely depressed after reduction (sample J), with a concomitant decrease of quantity of oxygen. The shape of the C 1s spectra of sample I and sample J is not completely identical, due to different mechanisms operational during different reduction procedures, which result is slightly different surface chemical composition. The apparent differences in the shape of the C 1s spectra of sample D in figure 9.6.a and figure 9.6.b are due to the normalization performed on results which had different maximum intensity during individual XPS measurement. There could also be slight variation in the different grafted samples of the same kind due to slight variation in the grafting time.

Thus from the results of the electrochemical reduction of the diazonium grafted samples (C and D) it is observed that the grafted samples which have a conjugated system between the surface and the terminal functional group can be reduced by electrochemical means. This is attributed to the fact that the electrons can transport via the π-electron cloud from the bulk electrode through the organic grafted layer to the terminal group. The conjugated system of the benzene ring serves as a convenient pathway for the electrons to travel during electrochemical reduction to reach the terminal functional group. This observation can be used to electrochemically reduce surfaces grafted with aryl moieties. This is especially a useful pathway to reduce the species which are otherwise difficult to reduce at ambient temperature like –NO₂. Even for the PCBD grafted sample
which is reducible by chemical means, the electrochemical method is a good alternative as it avoids the use of expensive and toxic chemicals like borane.

Table 9.1. Summary of the experiments, outcome, and results of the chemical and electrochemical functional group transformations of the grafted samples B, C, and D.

<table>
<thead>
<tr>
<th>Grafted sample</th>
<th>Functional group transformation</th>
<th>Outcome (y/n)</th>
<th>XPS results</th>
<th>Modified sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>Chemical</td>
<td>y</td>
<td>Fig 9.4.a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Electrochemical</td>
<td>n</td>
<td>Fig 9.4.b</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Chemical</td>
<td>n</td>
<td>Fig 9.5.a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Electrochemical</td>
<td>y</td>
<td>Fig 9.5.b</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Chemical</td>
<td>y</td>
<td>Fig 9.6.a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Electrochemical</td>
<td>y</td>
<td>Fig 9.6.b</td>
<td></td>
</tr>
</tbody>
</table>
Figure 9.4.a. XPS C 1s high resolution spectra of pristine GC (A) (■), alcohol grafted GC (B) (●), and chemically modified B containing carbonate (E) (▲); b. XPS C 1s high resolution spectra of pristine GC (A) (■), alcohol grafted GC (B) (●), and electrochemically modified B (F) (▲).

Figure 9.5.a. XPS N 1s high resolution spectra of pristine GC (A) (■), PNBD grafted GC (C) (●), and C after chemical reduction (G) (▲); b. XPS N 1s high resolution spectra of pristine GC (A) (■), PNBD grafted GC (C) (●), and electrochemically reduced C containing phenyl hydroxylamine (H) (▲).
9.4. Conclusions

Model GC electrodes grafted by two methods (oxidative grafting and reductive grafting) were used to develop optimal methods for transformation of their terminal functional groups. Two methods of terminal group transformation namely, electrochemical and chemical method were tested on the grafted samples and three model GC samples having tuned reactivity were prepared. GC electrode with covalently attached lithium alkyl carbonate (-O(CH₂)₃OCO₂Li) surface layer was prepared by electrochemical oxidative grafting of alcohol followed by chemical transformation steps. Phenyl hydroxylamine (-C₆H₄NHOH) modified GC was prepared by electrochemical reductive grafting followed by electrochemical reduction. This material would have potential applications in the field of protein absorption [155] and composite formation [215]. Benzyl alcohol (-C₆H₄CH₂OH) modified GC was prepared by electrochemical reductive grafting followed by both chemical as well as electrochemical reduction. The methodology of using a second step of transformation on grafted electrodes to obtain desired functional groups can be extended in many dimensions and would be used in the upcoming chapters. If the grafted moiety contains a conjugated system then its electrochemical reduction is feasible. This is because the electrons can transport through the delocalized π-cloud to the terminal
functional group to be reduced. However, electrochemical reduction of a saturated grafted moiety is difficult due to unavailability of electron conduction pathway across the layer. Thus, it can be concluded that electrochemical reduction is a feasible method to reduce surfaces grafted by aryl species; whereas chemical method is more suitable when the grafted species is alkyl or saturated. In short, we developed an approach that can be used to modify the surface of carbon materials for various applications.

In the following chapters we will extend this to obtain carbonate modified surfaces and thereafter to modify graphite powder surfaces.
Chapter 10. Carbonate modified glassy carbon

10.1. Motivation

The methods developed for concatenating an electrochemical grafting step of covalent immobilization and a functional group transformation step to obtain tailor made surfaces will now be used for synthesis of an artificial SEI. As it was inferred from the bibliographic study in chapter 3, the natural SEI formed in a typical Li-ion battery comprises predominantly of various organic and inorganic electrolyte degradation products. Conventionally organic carbonates are the solvent of choice over ethers, which undergo solvent co-intercalation into graphite; or esters, which do not form an effective SEI. Amongst the various organic carbonates EC is the most commonly used one because of its high dielectric constant, selective Li\(^+\) solvation, good oxidative stability (5.3 V vs. Li\(^+\)/Li\(^-\)), and adhesive SEI formation. DMC or PC is usually added to reduce the viscosity of the electrolyte, and to extrapolate its liquid state to lower temperatures respectively [216]. Hence, typical components of the SEI are one or two electron reduction products of EC, DMC, or PC. Li\(_2\)CO\(_3\) is one of the major components of a real SEI, but it will not be used as a component for the synthesis of artificial SEI. The primary reason for this is that this compound is inorganic and the bonds are ionic in nature. Hence, immobilizing this specie on the surface would not be possible by covalent bonding. Even if Li\(_2\)CO\(_3\) is somehow incorporated into the negative electrode (as it has been done by few researchers [217, 218, 219]); it would partially dissolve in the electrolyte and flow away from the negative electrode into the bulk electrolyte or even to the positive side during cycling. Coating graphite particles with Li\(_2\)CO\(_3\) also runs the risk of isolating of the active material particles due to the poor electronic conductivity of Li\(_2\)CO\(_3\). Hence, for our research we have selected covalent immobilization of alkyl/aryl carbonates on the surface of the negative electrode material. By doing so we ensure that the effect of the components of the artificial SEI are localized on the negative active material (where it is actually needed), without having any possible adverse effect on the positive electrode material. Owing to the localized effect of the artificial SEI, the mass of this layer required can be minimized. This gives our method an edge over others like using film forming additives [88] in the electrolyte in terms of specific energy of the battery. The covalent nature of the bonding of an artificial SEI will also ensure that the layer remains attached to the carbon surface throughout cycling, and hence result in good cycling stability. Thus in this chapter we will report preparation by various synthetic routes GC model electrodes modified with organic
carbonates. Some of the selected procedures will also be applied to graphite material to test the electrochemical performance of the modified material in a Li cell.

In this chapter we report the synthesis of an alkyl carbonate, GC immobilized with alkyl carbonate, and GC immobilized with aryl carbonate; and the characterization of these materials and some of their graphite analogues by XPS and electrochemistry. All the modified GC samples are labelled alphabetically at different stages of surface treatment. This is a new series of labels and is independent of labelling used in the previous chapters.

### 10.2. Experimental

#### 10.2.1. Synthesis of lithium alkyl carbonates

Lithium alkyl carbonates are usually prepared from corresponding alcohol precursors [58, 124]. Hence, before commencing synthesis of carbonates on grafted organic moieties, we synthesized lithium ethyl carbonate from ethanol, using pot synthesis as per scheme in figure 10.1. Pure product with characteristic FTIR vibrations (722 cm⁻¹, 865 cm⁻¹, 1081 cm⁻¹, 1316 cm⁻¹, 1372 cm⁻¹, 1417 cm⁻¹) was obtained in 85 % yield. This demonstrates that carbonates can be successfully synthesized from alcohol precursors by converting them to lithium alkoxide followed by CO₂ bubbling. This product will serve as reference product with which C 1s XPS spectra of carbonate modified GCs will be compared.

![Scheme of synthesis of lithium ethyl carbonate from ethanol](image)

Figure 10.1. Scheme of synthesis of lithium ethyl carbonate from ethanol.

#### 10.2.2. Immobilizing lithium alkyl carbonate on GC and graphite

Combining the knowledge of alcohol grafting reported in the previous chapters, and synthesis of carbonate beginning from alcohols, the scheme shown in figure 10.2 for obtaining covalently bonded alkyl carbonate on carbon surface was developed.
Figure 10.2. Scheme for immobilization of lithium alkyl carbonates on GC.

Since the free –OH end of the diol oxidizes to -COOH during oxidative grafting [213], a reduction step is required to obtain an alkoxide (-CH$_2$OLi), which is a precursor for the carbonate synthesis. GC will be modified using this synthesis scheme and analyzed by XPS. Then same procedure was performed on graphite powder, and it was tested electrochemically by cycling vs. Li metal in a standard electrochemical test cell to study the effect on ICL.

The grafting procedure for oxidative grafting of 1,3-propanediol was the same as reported in figure 9.2.a. The GC grafted with the diol was then stirred in a solution of acetonitrile with excess of LiH overnight in an inert atmosphere. This reduces the carboxylic acid group into Li alkoxide (air sensitive). For conversion of lithium alkoxide attached to GC surface into carbonate, CO$_2$ was bubbled through the solution containing the GC, for 4-5 hours without exposing the resulting alkoxide to air. CO$_2$ was generated in a separate apparatus using NaHCO$_3$ and H$_2$SO$_4$ and transported to the main reaction flask by a pipe attached to a capillary tube. After the whole procedure the GC sample was washed ultrasonically in acetonitrile.

Unavailability of a suitable current collector that would withstand both oxidative potentials during grafting alcohol (+2.5 V vs. SHE) and reductive potential in Li battery (-3.0 V vs. SHE) was the hindrance to apply this technique to graphite powder. As an ad hoc solution to the problem, leads of a clutch pencil (HB 0.5 mm) were tested as freestanding graphite electrode. Standard test cells using Li metal as counter and reference electrode in 1 M LiPF$_6$ in 1:1 EC:DMC electrolyte were made with pristine pencil lead electrode and with the
treated ones. These cells were cycled at C/50 rate, and compared with respect to ICL and specific charge.

10.2.3. Immobilizing lithium aryl carbonate on GC and graphite

Due to inherent limitations of alcohol grafting it is desirable to replace oxidative grafting of diol with reductive grafting of diazonium. This would facilitate the transfer of the modification technique from GC to graphite. A similar scheme as before for immobilizing lithium aryl carbonate to GC beginning with diazonium salt reduction was developed. It is illustrated in figure 10.3.

![Scheme of immobilization of carbonates on GC via diazonium grafting.](image)

Grafting of the diazonium salt PCBD was carried out as per the procedure described in figure 9.2.c. Reduction with LiH and CO₂ bubbling were done in the similar manner as described in section 10.2.2. The resulting GC samples were analyzed with XPS.

This method of reduction using LiH was successful for grafted alkyl carboxylic acid (10.2.2). However, LiH was not strong enough to reduce the aryl carboxylic acid obtained after grafting of PCBD (XPS results shown in section 10.3.2). This is attributed to the delocalization of the aromatic electrons over –COOH group, which decreases the electrophilicity of the carbonyl carbon.

Other limitations of employing LiH was its limited solubility and hence reactivity in CH₃CN. LiH in CH₃CN is also not very stable due to the possibility of proton abstraction of CH₃CN by LiH. A critical limitation of reduction by LiH is that the by-product of this reaction is...
mainly Li$_2$CO$_3$. Li$_2$CO$_3$ being a solid will be difficult to separate from graphite powders, when this method would be applied to grafted graphite powder.

Hence, an alternative reducing agent selected to overcome the challenges faced by LiH was BH$_3$ (in THF). Advantages of using BH$_3$ for carboxylic acid reduction based on literature [220, 221] are listed below:

- BH$_3$ is selective for reduction of sterically hindered carboxylic acids (this would be useful for treating grafted groups which are also sterically hindered by the substrate).
- BH$_3$ reduction is a compromise between very strong reducing agents like lithium aluminum hydride (pyrophoric) and lithium triethylborohydride (non-selective, aggressive reaction), and mild reducing agents like lithium aminoborohydrides and sodium borohydride (do not reduce acids).
- BH$_3$ is a liquid reagent, thus wets (and hence reacts with) the grafted groups.
- The byproducts of the reduction are usually soluble boro–compounds which can be easily removed by washing with common solvents.

After reduction with BH$_3$, the carbonyl groups reduce to protonated alcohols. However, for conversion to carbonates the precursor required is Li alkoxide. Therefore, to convert alcohols to their corresponding Li alkoxides the samples were treated with n-butyl lithium (BuLi). The scheme for synthesis of immobilized lithium aryl/alkyl carbonate using BH$_3$ is shown in figure 10.4.

![Figure 10.4. Scheme of conversion of grafted benzoic acid to monocarbonate by chemical reduction.](image-url)

Figure 10.4. Scheme of conversion of grafted benzoic acid to monocarbonate by chemical reduction.
The methods and procedure for the electrochemical grafting were the same as before. The grafted GC samples were stirred in 1 M BH₃ in THF overnight under Ar atmosphere. This was followed by washing with CH₃CN. Then the samples were stirred in 1.6 M BuLi in hexane fraction overnight. Finally the samples were washed well with CH₃CN.

The results of reduction of grafted benzoic acid reported in figure 9.6 revealed that both electrochemical as well as chemical method reduce the –COOH to -CH₂OH. Hence, these samples were used to prepare carbonates by exchanging proton with Li, followed by CO₂ exposure as per the schemes in figure 10.4 and figure 10.5.

\[
\begin{align*}
\text{E} & \quad \text{COOH} \quad -3.0 \text{ V vs. Ag wire} \quad 1 \text{ M Et₄NBF₄ in CH₃CN} \\
\text{M} & \quad \text{CH₂CO₂Li} \quad \text{CO₂ (air)} \quad \text{K} \quad \text{CH₂OH} \\
& \quad \text{1.6 M C₄H₉Li in hexane} \\
& \quad \text{L} \quad \text{CH₂OLi}
\end{align*}
\]

Figure 10.5. Scheme of conversion of grafted benzoic acid to monocarbonate by electrochemical reduction.

10.3. Results and discussion

10.3.1. Characterization of lithium alkyl carbonate immobilized GC and graphite

Figure 10.6.a. shows the XPS C 1s spectra of pristine GC (A), 1,3-propanediol grafted GC (B), and GC sample after all the steps of treatment (D). The C=O signal from the –COOH group of sample B is evident in the spectrum shown in blue. After CO₂ bubbling step the C=O signal diminishes at the expense of the C-O signal, and concomitantly there is a new peak at ~290 eV, which corresponds to the –CO₃Li group. To verify that this signal at high binding energy does correspond to the carbonate group the XPS spectrum of this sample was compared with that of as synthesized compound lithium ethyl carbonate (figure 10.6.b). The carbonate peak of the compound (after charge compensation) matches that
of the grafted sample, hence confirming formation of carbonate group on the modified sample $D$.

![Normalized XPS C 1s spectra of pristine GC (A); GC grafted with 1,3-propanediol (B), and GC after all the 3 steps of treatment (D); b. comparison of XPS C 1s spectra of GC sample D and ethyl lithium carbonate compound.](image)

Table 10.1 lists the results of the detailed XPS analysis of samples $A$, $B$, and $D$ along with the binding energy of the peaks, their deconvoluted components, and their assignment to different functional groups.

After establishing that lithium alkyl carbonate is immobilized on GC surface, this procedure was applied to a model graphite free standing electrode (lead of pencil), to check the electrochemical performance of the modified material. The results of the first electrochemical cycle are shown in table 10.2. It should be noted that a slow discharge/charge rate is used (C/50) because these are not powder electrodes and Li$^+$ diffusion in the solid state material is a slow process. This also justifies why we do not obtain 100 % theoretical specific charge of graphite.
Table 10.1. Binding energy peaks, relative atomic concentrations, and functional group assignments of XPS C 1s and O 1s spectra of pristine, 1,3-propanediol grafted GC, and GC after all the three steps of treatment.

<table>
<thead>
<tr>
<th></th>
<th>Pristine GC (A)</th>
<th>GC grafted with 1,3-propanediol (B)</th>
<th>GC after complete treatment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>peak position (eV)</td>
<td>284.4</td>
<td>284.5</td>
<td>285.1</td>
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<tr>
<td>total atomic %</td>
<td>97</td>
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<td>52.7</td>
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</tr>
<tr>
<td></td>
<td>289.1</td>
<td>23.5</td>
<td>290.0</td>
</tr>
<tr>
<td></td>
<td>COOH</td>
<td></td>
<td>CO₃Li</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.0</td>
<td>1.8</td>
<td>532.4</td>
</tr>
<tr>
<td></td>
<td>C-O (GC)</td>
<td>17.9</td>
<td>C=O</td>
</tr>
<tr>
<td></td>
<td>533.7</td>
<td>10.7</td>
<td>C-O</td>
</tr>
</tbody>
</table>

Table 10.2. Comparison of pristine and treated free standing graphite electrodes cycling vs. Li counter electrode in 1 M LiPF₆ in 1:1 EC:DMC electrolyte at C/50 rate. 100 % is theoretical specific charge of graphite = 372 mAh/g.

<table>
<thead>
<tr>
<th></th>
<th>Pristine</th>
<th>Modified</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st cycle</td>
<td>2nd cycle</td>
</tr>
<tr>
<td>Lithiation/ Delithiation (L/D)</td>
<td>L D</td>
<td>L D</td>
</tr>
<tr>
<td>% of theoretical specific charge</td>
<td>62 %</td>
<td>62 %</td>
</tr>
<tr>
<td>Charge lost in one cycle (L-D)</td>
<td>16 %</td>
<td>1 %</td>
</tr>
</tbody>
</table>
The results of this part are summarized below:

- Graphite modified with lithium alkyl carbonate did not show substantial decrease in the ICL.

- Since, this route of modification involves oxidative grafting, the know problems of high oxidizing potential and lack of suitable current collector exist, which makes application of this procedure to graphite powder electrodes tedious.

- Thus for the future work, we switch from oxidative grafting of alcohol to reductive grafting of diazonium salt.

10.3.2. Characterization of lithium aryl carbonate immobilized GC

GC immobilized with lithium aryl carbonate was synthesized starting from reductive grafting of diazonium salt as per scheme in figure 10.3. XPS C 1s spectra of pristine GC (A), PCBD grafted GC (E), and carbonate modified GC (G) are shown in figure 10.7.

Table 10.3 lists the binding energy of the peaks, their deconvoluted components, and their assignment to different surface functional groups.

Figure 10.7. Normalized XPS C 1s spectra of pristine GC (A) (■); GC grafted with PCBD (E) (●), and GC with carbonate (G) (▲).
Table 10.3. Deconvoluted XPS C 1s and O 1s spectra of pristine GC (A), GC grafted with PCBD (E), and GC with carbonate (G) ($C_b = C_{benzene}$).

<table>
<thead>
<tr>
<th></th>
<th>Pristine GC (A)</th>
<th>GC grafted with PCBD (E)</th>
<th>GC modified with carbonate (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>peak position (eV)</td>
<td>atomic% group</td>
<td>peak position (eV)</td>
</tr>
<tr>
<td>C 1s</td>
<td>284.4</td>
<td>97 C-C $sp^2$ (GC)</td>
<td>284.5</td>
</tr>
<tr>
<td></td>
<td>285.3</td>
<td>27.9 $C_b$-COOH</td>
<td>287.0</td>
</tr>
<tr>
<td></td>
<td>286.5</td>
<td>12.9 C-COOH</td>
<td>289.0</td>
</tr>
<tr>
<td></td>
<td>289.2</td>
<td>7.6 COOH</td>
<td>290.6</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.0</td>
<td>1.8 C-O (GC)</td>
<td>532.4</td>
</tr>
<tr>
<td></td>
<td>534.0</td>
<td>5.3 C-O</td>
<td></td>
</tr>
</tbody>
</table>
10.3.3. Reduction with BH₃ and BuLi of pristine SFG6 graphite

The modified synthesis scheme for preparing carbons with lithium aryl carbonate modified using BH₃ reagent for reduction is shown in figure 10.4. To obtain a blank reference, a pristine GC disc was treated with BH₃, then with BuLi, and finally exposed to air for conversion to carbonate. XPS analysis of this series of surface modification of pristine GC is shown in figure 10.8. Unexpectedly, the C 1s spectrum of the final sample showed a large peak corresponding to carbonate functional group. To confirm that this carbonate group was actually tightly bonded to the surface of the carbon and not a loosely bond impurity the sample was washed ultrasonically in water and reanalyzed by XPS. The washing did not result in decrease in the carbonate signal in the C 1s spectrum.

![Figure 10.8. XPS C 1s spectra of pristine GC, GC treated with BH₃, BH₃ treated GC treated with BuLi, BH₃ and BuLi treated GC exposed to air.](image)

Since, this method had resulted in carbonate formation on the surface without a grafting step, this method was applied to SFG6 powder graphite and the charge consumption for SEI formation was studied. The beginning part of the first lithiation curve of treated SFG6 graphite vs. that of pristine SFG6 is shown in figure 10.9. The treated SFG6 shows slightly lesser charge consumption for SEI formation compared to pristine; the shape of the curve is also different, indicating an effect of the surface modification on the electrochemical properties. This result encourages research towards surface modification for further improvement of the electrochemical properties. It also opens new doors to other method of surface modification, where the surface groups existing on graphite could directly be functionalized. This method will be revisited and the results are reported in chapters 14-15.
10.3.4. Comparison of electrochemical and chemical methods of reduction for carbonate formation

It was shown in chapter 9 that electrochemical as well as chemical methods of reduction could be used for converting carboxylic acid group to aryl alcohol. Hence, samples reduced by both methods were further converted into carbonates as per schemes in figure 10.4 and figure 10.5 respectively. The evolution of the terminal functional group of the grafted moiety at every consecutive step of treatment was monitored by XPS and is reported in figure 10.10. The C 1s signals corresponding to carboxylic carbon is at 289 eV in the PCBD grafted sample E. The carbonate signal appears at higher binding energy (~291.5 eV) after the final modification step (sample J for chemical reduction and sample M for electrochemical reduction). It is clearly evident from the intensities of the carbonate signals that the electrochemical method of reduction leads to better carbonate formation. Since, the electrochemical method involves cycling up to -3.0 V vs. Ag wire (≈ 0.18 V vs. Li⁷/Li) during the electrochemical reduction step, we can be sure that the chemical bonds in the grafted layer are stable in the potential window of graphite intercalation (from 0.25 V until 0.1 V vs. Li⁷/Li). Thus, the grafted layer is expected to be stable during cycling of graphite vs. Li in a standard cell. Hence, this method is selected to be applied to SFG6 graphite.

Figure 10.9. SEI formation part of the first lithiation curve of pristine SFG6 electrode and treated SFG6 (with BH₃, BuLi, and air) electrode in 1 M LiPF₆ in EC:DMC at C/10 discharge rate.
10.4. Conclusions

Various model carbon electrodes modified with carbonate functional group were prepared to imitate the real SEI. The steps used to prepare the aforementioned surface modified carbons were alcohol and diazonium salt grafting followed by functional group transformation using LiH, and BH₃ and BuLi reagents. Lithium ethyl carbonate compound was synthesized from corresponding alcohol to master the chemistry of carbonate synthesis. This compound was also used as reference for XPS analysis of modified carbons.

Figure 10.10. Normalized XPS C 1s spectra of GC samples after ever step of surface modification procedure; a. chemical method of carboxylic reduction followed by carbonate formation; b. electrochemical method of carboxylic reduction followed by carbonate formation.
Lithium alkyl carbonate was immobilized on GC and graphite electrodes. The synthetic scheme successfully resulted in carbonate formation, which was proved by XPS. However, the corresponding graphite electrodes did not show a substantial decrease in the ICL. The practical limitations of the synthesis scheme also posed some challenges. Firstly the inherent limitations of alcohol grafting, rendered the use of conventional current collectors unfeasible. Secondly LiH reagent used was poorly soluble in the solvent, and results in Li₂CO₃ precipitate byproduct after the CO₂ bubbling step (which is difficult to separate from graphite powder). Hence, overall the application of this method to SFG6 powder graphite was not practical.

Therefore, lithium aryl carbonate beginning with diazonium grafting (instead of alcohol grafting) and BH₃ reagent (instead of LiH) was synthesized on GC surface. Alongside, it was found that SFG6 treated with BH₃ and BuLi also results in improved electrochemical behavior in the SEI formation potential window. This result encourages modification of the existing surface groups on graphite for future work.

Two routes of immobilizing lithium aryl carbonate on GC were investigated, namely diazonium grafting of PCBD followed by chemical reduction with BH₃ and BuLi; and diazonium grafting of PCBD followed by electrochemical reduction. Both routes had a common last step of conversion to carbonate. From a comparative XPS analysis it was found that the route with electrochemical reduction results in better carbonate formation. Hence, this method is selected for further research and application to SFG6 graphite powder. These results will be reported in chapter 12.

So far we have established that our method of surface modification using grafting as the initial step results in improved electrochemical performance in the potential window of SEI formation. Hence, now we shall develop other non-electrochemical methods of grafting and compare with electrochemical grafting in order to select the most suitable method for application to graphite powders.
Chapter 11. Comparison of various methods of grafting

11.1. Motivation

Until now we have developed electrochemical method of grafting. This method of grafting has an advantage of high grafting yield and well defined surface chemistry. However, this step consumes external source of energy for the electrochemical pre-treatment. Hence, from a futuristic point of view it may not be viable to spend additional energy for obtaining a material which is targeted for lowering the energy consumption. This irony contradicts the goal of this work. In addition some practical limitations are foreseen with respect to using this method for grafting graphite powders, and eventual upscaling. Some of these issues are discussed below:

- For performing electrochemical grafting of graphite, it should be in form of an electrode, either free standing or doctor bladed. This requires a binder to be incorporated into the electrode formulation. The effect of the presence of the binder during grafting is uncertain. The binder may also dissolve in the solvent of the grafting bath, and result in loss of graphite powder material during grafting. In addition, after the grafting, when the electrode is to be washed and retrieved as powder, for consecutive chemical treatments; it becomes tedious to remove the binder completely. The amount of binder remaining behind in the material is also difficult to estimate. This then results in further uncertainty when electrodes of the material are prepared after the chemical step and for calculation of the specific charge of the material during cycling in Li cell.

- Electrochemical grafting of graphite will be quite different from that of GC in terms of current density distribution. During electrochemical grafting of GC, the current density distribution is rather uniform throughout the surface, as the substrate is a flat disc with smooth surface. Hence, in this case we obtain total surface coverage, which is evidenced in complete depression of Fe$^{2+}$/Fe$^{3+}$ voltametric redox activity, when the modified GC is used as working electrode. However, this kind of homogeneous surface coverage is difficult to achieve while performing electrochemical grafting of composite electrode comprising of powder graphite with relatively higher specific surface area (17 m$^2$/g). In this case, unlike the grafting CV of GC, the peak current attributed to grafting does not decrease drastically but rather continues to be large for many consecutive scans.
Another limitation, is that the ammonium supporting salt used in the grafting bath, is a source of contamination, and it may be not be completely removed after the washing procedures. If some amount of this salt remains in the material, it may result in alleviated side reactions with the chemical reagents in the functional group transformation step. Left over ammonium salt impurity may also have adverse effect on the electrochemical performance of the final material.

Finally, due to the driving force at the interface, the efficiency of electrochemical grafting is quite high. However, in the worst case, it may result in a very thick layer covering the surface of the graphite completely. This may result in isolation of the particles, and hence “loss” of active material for electrochemical cycling. If the layer is too thick it may also retard Li\(^+\) intercalation kinetics and result in high resistance in the electrode. If the layer is too thick, it acts as additional redox inactive dead mass in the battery, which could lower the overall specific charge of the material. These properties may result in poor cyclability and rate capability of the material.

Hence, before proceeding with modification of graphite powders, we develop and compare electrochemical method of grafting with other non-electrochemical methods. The other methods of grafting reported in the literature include in situ methods. In situ method of grafting was developed by Bélanger et al. and they have reported many studies using this technique of grafting [202, 203, 222]. The methodology differs in the precursor used for grafting and the driving force for the covalent immobilization. For in situ methods an amine which is a precursor of a diazonium salt is used in presence of a diazotizing agent in a suitable medium. The synthesis and decomposition of the diazonium salt occurs simultaneously in a bulk solution (or suspension), which contains the graphite particles to be modified. The key difference is that the diazonium salt degrades spontaneously in a short time interval after its synthesis in the same solution. Owing to this process, a relatively homogeneous grafting can be expected as powder samples can be grafted under constant stirring. Washing away of the byproducts and reagents can also be simply done by decanting or filtration. We have used for this work in situ grafting of PCBD. In situ grafting can be carried out in both aqueous [214] as well as non-aqueous [200] media. Hence, we have used both methods for a broader comparison. If both methods give good results, the aqueous method will be more feasible for scale up due to economic reasons. Another method of grafting that we have chosen for comparison is called spontaneous grafting. In this method we will use an isolated diazonium salt in a non-aqueous medium along with the particles to be grafted. This method is not reported in the literature yet. It is
done to compare the chemical decomposition of diazonium salt generated in situ to one which is isolated and added individually to the grafting bath. Various methods of grafting, which were developed and compared are diagrammatically shown in figure 11.1. In this chapter, we will report the grafting procedures and XPS analysis of grafted GC samples.

![Diagram of various methods for grafting GC and graphite powder surfaces.](image)

**Figure 11.1. Various methods applied for grafting GC and graphite powder surfaces.**

11.2. Experimental

The routes employed for surface modification of carbon surfaces are schematically shown in figure 11.2. Method a, b, c, and d refer to electrochemical grafting, in situ non-aqueous grafting, in situ aqueous grafting, and spontaneous grafting respectively. The diazonium salt used was PCBD. This salt was chosen due to relative stability of the diazonium salt and because carbonyl groups are the ones most commonly present on the graphite surface. It is also feasible to transform carboxylic acid groups by various chemical methods to alkoxides or carbonates, as shown in chapter 10. PCBD was synthesized from p-amino benzoic acid as per the route described in literature [223]. FTIR spectrum of the product (PCBD) as compared to the precursor (p-amino benzoic acid) showed the loss of NH$_2$ ($3458, 3360$ cm$^{-1}$) and appearance of N≡N$^+$ ($2304$ cm$^{-1}$) and BF$_4^-$ ($1037$ cm$^{-1}$) vibrations. Model electrode GC was grafted and analyzed by XPS.
5 mM PCBD + 1 M Et4NBF4 in CH₃CN

Figure 11.2. Scheme of a. electrochemical grafting; b. in situ non-aqueous grafting; c. in situ aqueous grafting; and d. spontaneous grafting.

**Electrochemical grafting:** For electrochemical grafting of GC, CV was run from -2.0 V to 0.5 V vs. Ag wire at a scan rate of 5 mV/s. The grafting bath was 0.1 M (C₂H₅)₄NBF₄ in CH₃CN, H₂O<50 ppm, containing 5 mM PCBD.

**In situ grafting (non-aqueous):** 2.9 millimoles p-amino benzoic acid was stirred in 50 mL CH₃CN. To this GC disc was added. Then, 6.2 millimoles tert-butyl nitrite was added drop wise under constant and vigorous stirring. The mixture was stirred for two hours. The powder was filtered and washed well with CH₃CN. The whole procedure was performed in the absence of O₂ and moisture.

**In situ grafting (aqueous):** GC disc was chemically grafted by p-amino benzoic acid following the synthesis described by Martin et al. [224].

**Spontaneous grafting:** Isolated PCBD was dissolved in CH₃CN. To this GC disc was added. The mixture was stirred for two hours. The powder was filtered and washed well with CH₃CN. The whole procedure was performed in the absence of O₂ and moisture.
All GC samples were washed with CH₃CN and analyzed by XPS.

11.3. Results and discussion

For quantitative comparison of the chemical composition of the grafted layers, GC was used as model for graphite powder. Comparative XPS measurements on grafted GC sample and grafted graphite powder sample showed that the signals from the grafted layer were more predominant in GC sample (results shown in figure 11.3). Chemical information from XPS of grafted GC samples can be translated and correlated with properties of grafted graphite's.

Figure 11.3. XPS C 1s spectra of a. pristine GC and PCBD grafted GC; b. pristine SFG6 electrode and PCBD grafted SFG6 electrode.

GC samples were grafted by electrochemical grafting, in situ aqueous grafting, in situ non-aqueous grafting, and spontaneous grafting techniques as per the schemes shown in figure 11.2. C 1s XPS spectra recorded for pristine GC and grafted GC samples are shown in figure 11.4. XPS C 1s spectra of all the grafted GC samples show a new peak (at binding energy ~289.1 eV) as compared to pristine GC, it is attributed to the carbon of the carboxylic acid group [134, 211]. This is direct evidence that the grafting of diazonium salt PCBD has occurred in all the four cases. However, the loading of the grafted layer is not the same for all samples. In order to quantify the content of carboxylic acid groups in the surface layer each C 1s spectrum was deconvoluted with 4-5 peaks and quantified. This quantification is shown in table 11.1.
Figure 11.4. XPS C 1s spectra of pristine GC, GC grafted by electrochemical grafting, in situ non-aqueous grafting, in situ aqueous grafting, and spontaneous grafting.

In the surface layer of electrochemically grafted, in situ non-aqueous grafted, in situ aqueous grafted, and spontaneous grafted GC samples 7.3 %, 6.8 %, 5.6 %, and 4.8 % of the carbon was that of carboxylic acid group respectively (percentage= C of -COOH/ total C content). The error range for this calculation is ±0.2 %. The order of extent of grafting is hard to perceive from the C 1s envelope shown in figure 11.3, but note that our calculations also take into account different full width at half maxima of -COOH components in various spectra. The reason of different shapes of the -COOH components is believed to be the different local chemical environment of the -COOH group, which results from different side reactions occurring during different grafting procedures. Thus, loading of the grafting decreases in the order electrochemical > in situ non-aqueous > in situ aqueous > spontaneous. This trend is in line with our expectation. During electrochemical grafting many radicals are generated on carbon surface due to the electrochemical potential applied, which propel diazonium salt disintegration and hence the grafting efficiency is highest. During in situ grafting in non-aqueous medium, the salt is formed from the precursor amine and is decomposed on the carbon surface within a very short time frame in the same bath, thus the grafting yield is good. These results are consistent with the literature reports that show that electrochemical grafting results in higher loading than in situ method [225]. Lower grafting yield for the in situ aqueous method can be attributed to the lower stability and higher self-degradation rate of diazonium salt in aqueous media as compared to non-aqueous. And finally the
spontaneous grafting has lowest yield; this could be due to the stability of the isolated salt in dissolved state, which is less vulnerable to disintegrate on the surface of carbon.

Table 11.1. XPS quantification of GC samples grafted by various methods

<table>
<thead>
<tr>
<th>Grafting technique used</th>
<th>C 1s component peak binding energy (eV)</th>
<th>Functional group</th>
<th>-COOH /Σ C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine GC</td>
<td>284.5 C-C (sp²)</td>
<td></td>
<td>0.97</td>
</tr>
<tr>
<td><strong>electrochemical</strong></td>
<td>285.0 C-C (sp²)</td>
<td></td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>286.6 C-O</td>
<td></td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td><strong>289.2 COOH</strong></td>
<td></td>
<td><strong>0.07</strong></td>
</tr>
<tr>
<td></td>
<td>291.2 π→π*</td>
<td></td>
<td>0.04</td>
</tr>
<tr>
<td><strong>in situ non-aqueous</strong></td>
<td>284.5 C-C (sp²)</td>
<td></td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>285.6 C-O</td>
<td></td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>286.8 C_b-COOH</td>
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<tr>
<td></td>
<td><strong>289.4 COOH</strong></td>
<td></td>
<td><strong>0.068</strong></td>
</tr>
<tr>
<td></td>
<td>290.5 π→π*</td>
<td></td>
<td>0.065</td>
</tr>
<tr>
<td><strong>in situ aqueous</strong></td>
<td>284.4 C-C (sp²)</td>
<td></td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>285.3 C-O</td>
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<td>0.35</td>
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<td></td>
<td>286.9 C_b-COOH</td>
<td></td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td><strong>289.0 COOH</strong></td>
<td></td>
<td><strong>0.056</strong></td>
</tr>
<tr>
<td></td>
<td>290.9 π→π*</td>
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<td>0.046</td>
</tr>
<tr>
<td><strong>spontaneous</strong></td>
<td>284.4 C-C (sp²)</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>285.4 C-O</td>
<td></td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>286.8 C_b-COOH</td>
<td></td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td><strong>289.3 COOH</strong></td>
<td></td>
<td><strong>0.048</strong></td>
</tr>
<tr>
<td></td>
<td>290.7 π→π*</td>
<td></td>
<td>0.07</td>
</tr>
</tbody>
</table>
11.4. Conclusions

Three non-electrochemical methods of grafting were developed and applied to GC model electrodes. The chemical composition and layer loading of GCs modified by different methods was quantified by XPS and compared with each other. Loading of the grafting was found to decrease in the order electrochemical > *in situ* non-aqueous > *in situ* aqueous > spontaneous. Chemical information from XPS on GC can be assumed to hold true for graphite powder, and will later be combined with the morphological analysis of grafted graphite samples.

The next chapter reports grafting of SFG6 graphite by the four grafting methods developed in this chapter. Grafted SFG6 material will be studied electrochemically in standard Li cells.
Chapter 12. Grafting graphite powders

12.1. Motivation

In spite of the importance of SEI, there is a dearth of methods for controlling SEI characteristics by elegant chemistry. Due to a significant effect of surface properties of graphite on SEI formation [76, 77, 78, 79, 138], researchers have mostly employed surface pretreatment of graphite like chemical [81, 82], electrochemical [85], and thermal [139] for improved electrochemical performance. There have been relatively few reports on modification of the surface with a defined control over the surface chemistry and reactivity for ameliorating SEI formation and characteristics. One such report is on formation of artificial SEI by electropainting and vacuum-insertion techniques [140]. There are only a few publications on employing grafting for Li–ion battery applications, like those from Pan et al. [83, 84, 226, 227] and Martin et al. [224]. However, the main focus of these studies is to use grafting for improving cyclability of silicon based negative materials.

We will report in this chapter grafting of diazonium salts on graphite powders, and study its effect on SEI formation, Li-ion intercalation, and suppressing exfoliation of graphite in PC based electrolyte. Electrochemical grafting [169], in situ grafting [224], and spontaneous grafting will be performed on micrometer size graphite powder. XPS study on GC (reported in chapter 11) will be correlated with the morphological study of grafted graphite by SEM to get combined chemical and morphological information of grafted carbons. For morphological analysis graphite electrodes (which will be then tested electrochemically vs. Li) were used because GC is a brittle disc having smooth geometric surface which cannot be used as model for graphite surface, which is a micrometric powder, having high surface area, edge planes, basal planes, grain boundaries, defects, crevices etc. The morphological differences between various grafted graphites may give indirect supporting evidence to the extent of layer loading. We will show how surface morphology (along with layer loading) of the grafted layer depends on the method of grafting. Consequence of grafting on electrochemical properties like SEI formation and Li-ion intercalation will be reported. The evolution of the grafted layer is studied after 50 electrochemical cycles in 1 M LiPF$_6$ in EC: DMC (1:1). Grafted graphites are also tested in 1 M LiPF$_6$ in EC:PC (15:85 w/w), to study if grafted graphite materials could cycle without exfoliation in a PC based electrolyte.
12.2. Experimental

For electrochemical grafting of SFG6 graphite; the working electrode was prepared by casting a slurry of SFG6 graphite with SBR binder (90:10 w/w) in hexane on a Ti current collector, and drying at 80 °C under vacuum for a few hours. The rest of the grafting procedure was the same as reported in previous chapters. However, for porous composite electrode made from SFG6 graphite powder, grafting CV was run for 5 cycles, to ensure complete grafting. For in situ non-aqueous grafting, in situ aqueous grafting, and spontaneous grafting, the procedures were also the same as reported in chapter 10.2.1. Except that 400 mg SFG6 graphite powder was used instead of one GC disc. Instrument and condition used for Raman spectroscopy are as detailed in section 7.6.2.

Thermo gravimetry analysis (TGA): TGA experiments were conducted with PerkinElmer TGA4000 instrument. The temperature profile was an isothermal step at 50 °C for 1 min, followed by scan at 20 °C/min from 50 °C to 800 °C, under flow of N₂ gas at 20 mL/min. The weight loss was calculated by a step and derivation function. The operating/analysis software was Pyris 6.

12.3. Results and discussion

12.3.1. TGA

From TGA analysis of various grafted graphites (curves shown in figure 12.1), it was found that the electrochemically grafted sample showed a loss of 4.7 % of the mass at 434 °C. The in situ non-aqueous and in situ aqueous grafted samples showed loss of 12.2 % at 191 °C, and 0.6 % at 293.5 °C respectively. These results are in agreement with literature, where it is shown that the mass losses between 300-500 °C are due to loss of covalently attached organic groups [228]. The spontaneously grafted sample did not show any significant mass loss in the scanned temperature range. This is attributed to small quantity of the surface layer, whose mass loss percentage is below the detection limit of the TGA instrument. The mass losses of various grafted graphite samples follow the same trend as that found by XPS analysis of GC samples. Electrochemically grafted sample does not follow the expected trend. The low mass loss of this sample might be attributed to presence of binder in the material with which the grafted material may have bonded, but the exact reason is unclear. The differences between the offset temperatures of mass loss of various samples could be due to the different local chemical environments existing in different samples due to different side reaction, which occur during different methods of
grafting. Thus, TGA analysis proves that grafting results in covalently attached moieties and the percentage of mass of the surface layer ranges up to tens of percents.

![TGA curves of SFG6 pristine, and SFG6 grafted by various methods.](image)

**Figure 12.1.** TGA curves of SFG6 pristine, and SFG6 grafted by various methods.

### 12.3.2. SEM

Different grafting methods result in distinctly different surface morphology of the layers. This is clearly visible from the SEM images shown in figure 12.2.a-e of pristine SFG6, SFG6 after electrochemical, *in situ* non-aqueous, *in situ* aqueous, and spontaneous grafting respectively. Figure 12.2.a shows smooth and bare basal planes of the pristine SFG6 particles. The prismatic planes of this sample are also clearly visible (it is through these edges that Li-ion intercalation occurs in ideal graphite). In the electrochemically grafted sample shown in figure 12.2.b, one can see holes of very small size uniformly present throughout the grafted layer which covers basal planes. We believe these holes have been created due to N₂ gas evolution during electrochemical reduction of diazonium salt. As the loading of this sample is expected to be high (from XPS analysis of the corresponding grafted GC samples), the layer could be dense, and N₂ gas bubbles might have created these holes in order to escape through the grafted layer. Figure 12.2.c shows that the *in situ* non–aqueous grafted sample has threads of coating randomly covering the particles, including both prismatic as well as basal planes. This thread-like morphology of the grafted layer is attributed to the fact that the diazonium salt was synthesized *in situ*, disintegrated, and grafted on graphite particles during constant stirring. There could be dynamic synthesis, dissolution, and grafting occurring in the system simultaneously.
Figure 12.2. SEM images of a. pristine; b. electrochemically grafted; c. in situ non-aqueous grafted; d. in situ aqueous grafted; and e. spontaneously grafted SFG6 graphite powders. They are compared with the cycled a’. pristine; b’. electrochemically grafted; c’. in situ non-aqueous grafted; d’. in situ aqueous grafted; and e’. spontaneously grafted SFG6 graphite powders.
However, this thread-like morphology is absent in the *in situ* aqueous grafted sample shown in figure 12.2.d. The morphology of the grafted layer in this sample is rather uniform and rough. The absence of threads and uniform morphology could be due to higher solubility and faster disintegration of diazonium salt in aqueous medium. More pronounced features of this grafted layer could not be observed by SEM probably due to lower layer loading (as expected from XPS quantification of GC samples shown in chapter 11). Finally, on the spontaneously grafted sample shown in figure 12.2.e, one observes a rather thin film, which is also broken in several places; this could be due to its fragility. However, the broken areas are of visual aid to see the thin grafted layer in this case. The surface morphology of cycled samples shown in figure 12.2.a’-e’ will be discussed in section 12.3.4.

12.3.3. Electrochemical characterization

CVs of the pristine SFG6 electrode and those of the various grafted powder samples are compared in figure 12.3. The current has been normalized with respect to the mass of the active material used. In figure 12.3.a we see a zoom into the SEI formation step which normally occurs around 0.8 V vs. Li⁺/Li. The negative peak at this potential is associated with electrochemical reduction of the electrolyte. It is seen from figure 12.3.a that SEI formation peak current follows the order electrochemically grafted < *in situ* non-aqueous grafted < *in situ* aqueous grafted < spontaneous grafted < pristine. This is in direct agreement with the extent of loading quantified for model GC electrodes by XPS in chapter 11, and indirectly visible in the morphological analysis by SEM shown in section 12.3.2. Hence, it implies that higher the loading of the grafted layer, lesser is the current in the SEI formation/electrolyte degradation potential window. This logical trend is in accordance with our expectation. Electrochemically grafted and *in situ* non-aqueous grafted samples are the ones having highest loading of the grafted layer, and thus have greater effect on the SEI formation peak. For certain grafting, the peak currents are depressed to such an extent that the potentials of the peak maxima are difficult to identify. The reason for this may be that charge transfer from carbon to the electrolyte is hindered due to the presence of the grafted layer. The flat nature of CV in this potential region could imply hindered charge transfer, which would result in lower electrolyte degradation and/or slower kinetics. For the *in situ* aqueous grafted sample the suppression of the peak current is lower but still visible. And for the spontaneously grafted sample the peak suppression is minimally visible perhaps due to thin and broken nature of the grafted layer (as shown in figure 12.2.e). However, the peak potential is shifted by ~10 mV towards negative, which points to
expected attenuation in charge transfer kinetics caused by the grafted layer, even though the grafted layer is rather thin. The shift in peak potential observed for the *in situ* aqueous grafted and spontaneously grafted sample is difficult to evaluate (figure 12.3.a).

![Graph](image)

**Figure 12.3.** CV of the pristine, electrochemically grafted, *in situ* non-aqueous grafted, *in situ* aqueous grafted, and spontaneously grafted SFG6 graphite powders in 1 M LiPF₆ in EC:DMC electrolyte vs. Li metal at 0.01 mV/s. a. SEI formation potential region; b. Li-ion intercalation and deintercalation potential region.

Figure 12.3.b shows the CV of pristine and grafted samples in the Li-ion intercalation/deintercalation potential range. The three main reduction peaks in the CV of pristine SFG6 at 0.18 V, 0.08 V, and 0.04 V are attributed to transitions stage 1’→4, stage 3→stage 2, and stage 2→stage 1 respectively as per literature [12, 229]. During intercalation of lithium in pristine graphite these phase transitions are very sharp and thus clearly visible as peaks in the CV. However, in case of all the grafted samples these three peaks are depressed and distorted significantly, implying altered Li-ion intercalation kinetics. The trend of extent of distortion seems to follow the same order as that of the loading of grafted layer (established by XPS on GC samples in chapter 11). In all the grafted samples it appears
that the Li-ion intercalation is slowed down and thus phase transitions are not clearly seen at particular potentials (at scan rate 0.01 mV/s). The intercalation rather looks like a smooth envelope spread over potential window 0.2 V-0.0 V.

Figure 12.4. First and second cycle of CV in 1 M LiPF$_6$ in EC:DMC electrolyte vs. Li metal at 0.01 mV/s of a. pristine SFG6 electrode; b. electrode of electrochemically grafted SFG6; c. electrode of in situ non-aqueous grafted SFG6; d. electrode of in situ aqueous grafted SFG6; e. electrode of spontaneously grafted SFG6.
The peaks of various phase transitions reappear in the second cycle of the CV for electrochemically grafted, \textit{in situ} non-aqueous grafted, \textit{in situ} aqueous grafted, and spontaneously grafted samples (shown in figure 12.4.b, 12.4.c, 12.4.d, and 12.4.e respectively).

For the electrochemically grafted sample it appears as if the peak of stage $1'\rightarrow 4$ is shifted to more negative potential (indicating that there is a higher overpotential for this process) and has become broader. This increased overpotential is attributed to hindered charge transfer across the resistive grafted layer. Similar features are harder to be noticed visually for other grafted samples, probably due to their lower loading as compared to that of the electrochemically grafted one. The de-intercalation part of the CV is also altered for the grafted samples. The two main Li-ion de-intercalation peaks are shifted to more positive potentials (that implies higher overpotentials). The extent of this shift is again consistent with extent of the layer loading. Please note that in this potential window of CV, one also observes an effect of the quantity of Li-ion intercalated in the material (specific charge). This effect is discussed in details later in this section.

![Graph showing potential vs. specific charge for different samples](image)

\textit{Figure 12.5. Beginning part of the first lithiation process of pristine and various grafted SFG6 graphite powder samples, performed galvanostatically at C/10 rate in 1 M LiPF$_6$ in EC:DMC electrolyte.}

Figure 12.5 shows the beginning part of the first lithiation (reduction) process of pristine and various grafted SFG6 electrodes, performed galvanostatically at C/10 discharge rate in 1 M LiPF$_6$ in EC:DMC electrolyte. The potential region from the open circuit potential (OCP) to $\sim 0.8$ V is associated with the reduction of surface groups of graphite [230]. Since we dock carboxylic acid groups on the surface via grafting it is expected that charge consumption for reduction of the surface groups will be higher. This effect is clearly visible
in figure 12.5. Electrochemically grafted, in situ aqueous grafted, and the spontaneously grafted sample show increased charge consumption in the same order as the extent of grafting on GC samples reported in chapter 11. The quantity of extra charge consumed for reduction of the grafted carboxylic acid groups is directly proportional to the quantity of grafting and hence the number of carboxylic acid groups present per unit surface. The potential plateau at ~2.2 V vs. Li⁺/Li for the in situ non-aqueous grafted sample however does not follow this trend. The reason for this exceptional behavior is not very clear. It may be attributed to the bulk reduction of the carboxylic acid groups present at cross-points of threads of the grafting (see figure 12.2.c). We have experimentally confirmed that this plateau at ~2.2 V is indeed due to carboxylic acid reduction. Upon chemical reduction of this sample (with LiAlH₄ reagent) prior to cycling, this plateau disappears (these results will be discussed in detail in chapter 13).

Figure 12.6. The specific charge (during the charge/lithiation) vs. cycle number of pristine, electrochemically grafted, in situ non-aqueous grafted, in situ aqueous grafted, and spontaneously grafted SFG6 graphite electrodes cycled galvanostatically at C/10 rate in 1 M LiPF₆ in EC:DMC electrolyte.

Figure 12.6 shows the cyclability of various grafted samples compared to that of pristine SFG6. It is observed that the practical specific charge retrieved reversibly at C/10 rate from the electrochemically grafted and the in situ non-aqueous grafted sample is much lower than that of the other samples (cycling at slower rates was not tested). This is attributed to the strongly hindered charge transfer and consequently hindered Li-ion intercalation in these samples, due to heavy loading of the grafted layer (as expected by XPS analysis of grafted GC and SEM analysis of grafted graphite). It may also be attributed to electrical isolation of some particles due to their entire surface coverage by
passive grafting. The heavily grafted particles may be shielded from electronic conduction pathways and may thus not be available for Li-ion intercalation. However, we assume that electron transfer is not completely blocked by the grafted layer due to the presence of the conjugated aromatic ring present in it. This delocalized system could serve as electron conduction pathway, and when thin enough it should allow electrons as well as Li-ions to transfer through it [211]. Another reason for a low value of specific charge could be that we have not subtracted the mass of the redox inactive layer from the total active mass for the normalization of specific charge. The spontaneously grafted and the in situ aqueous grafted samples have similar practical specific charge as that of the pristine SFG6. This is attributed to thin grafted layer in these samples, due to which particle blocking or isolation is less prominent. This proves that if the grafted layer is thin enough, it is capable of good cycling concomitantly with lower electrolyte degradation and modified Li-ion intercalation (shown in the CV in figure 12.3). Note that the cyclability of SFG6 pristine electrode is not optimum, due to difficult electrode preparation process in the glove box, which was necessary for this work.

12.3.4. Post mortem SEM

Post mortem SEM was performed for all grafted samples after 50 electrochemical cycles in 1 M LiPF$_6$ in EC:DMC vs. Li metal. SEM image of each as prepared sample (figures 12.2.a-e) is compared with that of the corresponding cycled sample (figures 12.2.a'-e'). Pristine SFG6 shows a thick, broken, and discontinuous SEI (figure 12.2.a'). Electrochemically grafted sample shows a smooth and homogenous SEI with inherent holes of the as synthesized sample (figure 12.2.b'). The cycled in situ non-aqueous grafted sample shows that the threads of the as synthesized samples are still present but are rather thicker after cycling (figure 12.2.c'). The cycled in situ aqueous grafted sample shows that rough morphology of the as synthesized sample is retained, but the surface layer is now thicker also covering prismatic planes of the particles (figure 12.2.d'). And finally, cycled spontaneously grafted sample shows that the SEI is broken and discontinuous (figure 12.2.e'). In all these samples, the inherent nature of the surface morphology of as synthesized samples is retained after 50 electrochemical cycles. This is a strong proof of the stability of the grafted layers. This supports TGA results and proves that the grafted layers were indeed attached via strong covalent linkages to the surface of graphite particles, and did not noticeably dissolve or migrate during 50 electrochemical cycles at C/10 rate in a basic electrolyte medium. This assures that the desired effects of the grafted layer (which aim at lesser electrolyte degradation and controlled Li-ion
intercalation), are localized on the surface of negative electrode material particle. This opens the path to design materials with thin grafted surface layers, where its role will be limited to the site only where it is required. In addition, it can also be inferred that SEI formed on each of the grafted sample is adopting the inherent surface morphology of the grafted layer. This implies that we could direct the growth of SEI by providing it sites for nucleation and growth. When electrolyte undergoes degradation, the degradation products preferably deposit on the topology of the grafted layer. Hence, controlling SEI morphology by intelligent grafting appears to be possible.

12.3.5. Exfoliation in PC based electrolyte

Charging curves of pristine and in situ non-aqueous grafted graphite in PC based electrolytes are shown in figure 12.7.

![Charging curves of pristine graphite, electrochemically grafted graphite, in situ aqueous grafted graphite, and spontaneously grafted graphite; and reversible charge/discharge of in situ non-aqueous grafted graphite in 1 M LiPF₆ in EC:PC (15:85) at C/37 rate.](image)

As known, for high concentrations of PC, pristine SFG6 graphite undergoes endless charge reduction due to continuous electrolyte degradation along with exfoliation. Whereas, graphite grafted by in situ non-aqueous grafting method shows normal reversible behavior. This means that the grafted layer, which is like a network of threads across basal and edge planes (figure 12.2.c), might be exerting a strong force bundling the graphene sheets, and preventing solvent co-intercalation. The in situ aqueous grafted, spontaneous grafted, and the electrochemically grafted graphites were not able to cycle reversibly in the tested PC based electrolyte as the grafting could not suppress solvent co-intercalation. The reason for the failure of the former two samples to avert exfoliation may
be that the surface layer is not thick enough to hinder solvent co-intercalation. There are also many defects and ruptures seen on the surface layer of the spontaneously grafted graphite (figure 12.2.e), which could allow solvent molecules to co-intercalate. Due to heavy layer loading on the electrochemically grafted sample, it is expected to cycle reversibly in the PC based electrolyte, but its failure to do so. This may be ascribed to inhomogeneous grafting, which may occur because the grafting is done on electrodes casted on a current collector. Part of the electrode close to the current collector may not be undergoing complete grafting due to poor porosity of the electrode. This ungrafted part might be allowing solvent co-intercalation. Alternatively, it is possible that the holes on the grafted film serve as pores through which solvent co-intercalation occurs.

Post mortem SEM images of pristine and grafted graphite’s after 50 electrochemical cycles in PC based electrolyte are shown in figure 12.8. SEM images clearly show that the graphene sheets have been ripped apart due to solvent co-intercalation and hence exfoliation in case of pristine graphite, electrochemically grafted graphite, in situ aqueous grafted graphite, and spontaneously grafted graphite, which are shown in figures 12.8.a, 12.8.b, 12.8.d, and 12.8.e respectively. Alongside it can also be seen that the electrolyte degradation products are deposited between the exfoliated graphene sheets. This supports the mechanism of exfoliation proposed by Besenhard et al. [19], which says that exfoliation occurs due to solvent co-intercalation followed by degradation of solvent in the opened structure. On the other hand, SEM image of in situ non-aqueous grafted sample cycled in PC electrolyte (figure 12.8.c) shows no signs of exfoliation. The structure and stacking of the graphene sheets in the graphite particles are intact. This is attributed to the strands of grafting, which hold or bundle the graphene sheets, and the pressure exerted by the covalently bonded surface layer limits solvent co-intercalation. This is visually clear from figure 12.8.c, where the grafting strand stretches from the basal plane across the prismatic plane. Thus, post mortem SEM images verify the results and hypothesis reported before in this section.
12.3.6. Post mortem Raman analysis

Another tool for confirming exfoliation of graphite samples is by Raman spectroscopy. It provides information about the disorder in the near to surface structure. For graphitic samples there are two main Raman peaks called the D (1370 cm\(^{-1}\)) and G (1583 cm\(^{-1}\)) band, which are assigned to vibration signals of disordered and ordered structure. In addition there is a shoulder on the G band, called the G' band (1620 cm\(^{-1}\)) band, this is also associated to disorder in the structure [193]. It has been shown earlier that Raman spectroscopy provides evidence of exfoliation of graphite in PC based electrolytes [194].
Figure 12.9.a. Non-normalized Raman spectra of pristine SFG6 graphite and various grafted SFG6 graphites after 50 electrochemical cycles in 1 M LiPF$_6$ in EC:PC (15:85); b. Raman spectrum of SFG6 graphite grafted by in situ non-aqueous method after 50 electrochemical cycles in 1 M LiPF$_6$ in EC:PC (15:85).

In figure 12.9.a Raman spectra of uncycled pristine SFG6 graphite, and various graphite samples after cycling in 1 M LiPF$_6$ in EC:PC (15:85) are shown. Normally Raman spectra of graphite are normalized with respect to the G band; however in figure 12.9.a we rather show raw spectra recorded under nominally identical conditions because due to grafting and additional SEI formation the magnitude of the G band is decreasing. Thus in this case normalization could be misleading. From the relative intensities of the D and G band it is evident that pristine cycled, electrochemically grafted sample after cycling, *in situ* aqueous
grafted sample after cycling, and spontaneously grafted sample after cycling exhibit large disordered D and G’ band obviously as a consequence of exfoliation of graphite. This is not true for the in situ non-aqueous grafted sample, which is enlarged in figure 12.9.b. However, the signal to background ratio of this sample is rather poor. This might be due to large and inhomogeneous surface layer, which absorbs large quantity of Raman signal and also poses practical limitations in focusing the laser on the graphite crystallite. However, it is still clear that the G band of this sample has larger intensity compared to the D band, which confirms that exfoliation does not take place after this surface modification. These results are as per our expectations and confirm the results from electrochemistry and SEM.

12.4. Conclusions

We have established grafting of graphite powders for controlling its electrochemical properties in lithium-ion batteries. The samples grafted by different methods result in different surface morphology. These differences are attributed to different mechanisms of diazonium reduction occurring during these processes. The extent of loading was found to consequent in SEI formation/electrolyte degradation, first Li-ion intercalation/deintercalation kinetics, and practical reversible specific charge. Very thick layers may result in particle isolation and the practical specific charge retrieved is lowered. Whereas thin layers allow good cyclability along with tuned SEI formation and Li-ion intercalation. Surface morphology of the grafted samples is retained after fifty electrochemical cycles, which proves that the grafted layer is indeed covalently bonded. In addition, SEI may adopt the morphology of the grafted layer. The in situ non-aqueous grafting method of surface modification prevents exfoliation of graphite in PC based electrolytes, due to the bundling of the graphene sheets by the thread-like grafted layer. This was evidenced in the post mortem SEM and Raman analysis. Thus, grafting is a method which can be used to prevent exfoliation of graphites to enable their cycling in PC based electrolyte. In a nutshell, we have shown that layer loading and surface morphology can be tuned by various grafting techniques, which results in tuned SEI formation, Li-ion intercalation, and prevention of exfoliation of graphite.

In the next chapter consecutive step of tuning the functional groups of graphite samples grafted by various methods, and how the electrochemical performance is affected will be reported.
Chapter 13. Chemical reduction of grafted graphite

13.1. Motivation

We have established in our previous chapters, grafting followed by functional group transformation as a method for modifying glassy carbon surfaces with an organic moiety and then tuning its reactivity by altering the chemical nature of its terminal functional group. It was shown that the two steps can be used in conjugation to obtain desired tailor made surfaces. Here, we translate these methods of surface modification established on glassy carbon (2D sp²) to graphite powders (3D sp²). In the chapter 12 we have reported grafting of graphite powders by electrochemical grafting, \textit{in situ} non-aqueous grafting, \textit{in situ} aqueous grafting, and spontaneous grafting methods. Each grafted sample showed decrease in charge consumption in the SEI formation potential window, and modified Li-ion intercalation/ de-intercalation kinetics. However, the grafted moiety in these cases had to be \(p\)-carboxylic benzene (due to the stability of its corresponding diazonium salt). But for application in Li-ion batteries, a grafted group in oxidized state such as \(-\text{COOH}\), would result in additional charge consumption for its reduction. Hence, it is desirable to reduce the grafted \(-\text{COOH}\) functional group to the most reduced and lithiated state like \(-\text{CH}_2\text{OLi}\). These groups at the terminal of the grafted layer would not require additional charge for reduction and minimize \(\text{H}_2\) gas evolution by side reactions of the protons. Hence, the terminal functional group of already grafted graphite powders has been reduced by chemical and/or electrochemical methods. The scheme of surface modification methods employed is shown in figure 13.1. The core shaded part of the concentric diagram is the grafting step. The results of this part were reported in chapter 12. Here, the electrochemistry and morphological analysis of grafted graphite powders after chemical reduction (the outer concentric circle) are reported. Chemical reduction with lithium containing reagents was chosen to obtain terminal functional group of the grafted layer in reduced as well as lithiated state. The surface morphology of chemically reduced samples is compared with that of the parent grafted material, and analyzed after cycling in standard battery electrolyte (1 M LiPF₆ in EC: DMC (1:1)). The effect of the chemical pre-reduction is studied on electrochemical properties including charge consumption for SEI formation, SEI morphology, Li-ion intercalation/de-intercalation kinetics, cyclability, specific charge, and exfoliation of graphite in PC based electrolyte.
13.2. Experimental

The diazonium salt used was *p*-carboxylic benzene diazonium tetrafluoroborate. Grafted samples (electrochemically grafted, *in situ* non-aqueous grafted, *in situ* aqueous grafted, and spontaneously grafted sample) were prepared as described in chapter 12. Each of the chemically grafted graphite powders was further treated with 1.6 M BuLi in hexane, and 2 M LiAlH₄ in THF in separate experiments. These solutions were used as received from Sigma Aldrich. Chemically reduced samples were washed with anhydrous hexane, and dried inside the glove box. Electrochemically grafted graphite electrode was reduced electrochemically in 1 M \((\text{C}_2\text{H}_5)_4\text{NBF}_4\) in acetonitrile electrolyte using the experimental set up and conditions described in chapter 9. After electrochemical reduction graphite was scraped off, and treated with 1.6 M BuLi in hexane. The sample was washed with hexane, and dried. All the modification procedures were carried out in the glove box to avoid any reactions of the air sensitive reagents and samples with air and moisture. The resulting modified graphite’s were studied electrochemically and by SEM. Other measurement procedures and condition of electrochemical and SEM analysis (pre and post cycling) were the same as those reported in the previous chapter.
13.3. Results and discussion

13.3.1. SEM

SEM images of grafted graphite samples after chemical reduction are shown in figure 13.2. It is observed that surface morphology of each grafted sample is retained after its chemical reduction. Holes on the surface of electrochemically grafted sample shown in figure 13.2.b, are retained after its electrochemical reduction (figure 13.2.c). The thread-like morphology of the in situ non-aqueous grafted sample shown in figure 13.2.d is retained after its chemical reduction with BuLi and LiAlH₄ (shown in figures 13.2.e and 13.2.f respectively). Similarly, rough morphology of in situ aqueous grafted sample shown in figure 13.2.g is retained after its chemical reductions with BuLi and LiAlH₄ (figures 13.2.h and 13.2.i respectively). And finally, the broken nature of surface film on spontaneously grafted sample shown in figure 13.2.j is also visible after its chemical reduction with BuLi and LiAlH₄ (shown in figure 13.2.k and 13.2.l respectively). This is a direct proof that in all the cases, grafting occurs via covalent bonding and can withstand harsh chemical treatments. We also notice that each grafted surface layer became thicker after its chemical reduction. This may to be due to chemical reactions between the adjacent grafted chemical species and other side reactions of the reagent with surface groups.

Post mortem SEM images of chemically reduced samples after electrochemical cycling are shown in figure 13.3. On comparing the SEM images shown in figure 13.3 with the corresponding image of as synthesized sample shown in figure 13.2, one observes that surface morphology of surface modified samples is retained after 50 electrochemical cycles. Cycled samples shown in figure 13.3.b’ and 13.3.c’ have holes like electrochemically grafted sample shown in figure 13.2.b and thereafter electrochemically reduced sample shown in figure 13.2.c respectively. Cycled samples shown in figure 13.3.e’ and 13.3.f’ have thread-like morphology similar to samples after chemical reduction of in situ non-aqueous grafted graphite shown in figure 13.2.e and 13.2.f respectively. Cycled samples shown in figure 13.3.h’ and 13.3.i’ have a rough surface layer, like samples after chemical reduction of in situ aqueous grafted graphite shown in figure 13.2.h and 13.2.i respectively. Cycled samples shown in figure 13.3.k’ and 13.3.l’ have broken surface layer, as was the case for samples after chemical reduction of spontaneously grafted graphite shown in figure 13.2.k and 13.2.l respectively. This again emphasizes the covalent nature of the surface modification by grafting. The aggressive chemical reduction
step did not seem to weaken the bonding of the grafted layer to the graphite surface. It was observed as a general trend that reduction with BuLi results in polymer-like surface layers, and LiAlH$_4$ treatments rather result in granular layers. This is attributed to the inherent nature of the reagents, where BuLi is organic and may initiate polymerization, LiAlH$_4$ is ionic and might result in charge aggregation.

Figure 13.2. SEM images of graphites a. pristine; b. electrochemically grafted; c. after electrochemical reduction of electrochemically grafted sample; d. in situ non-aq grafted; e. after reduction by BuLi of in situ non-aq grafted; f. after reduction by LiAlH$_4$ of in situ non-aq grafted; g. in situ aq grafted; h. after reduction by BuLi of in situ aq grafted; i. after reduction by LiAlH$_4$ of in situ aq grafted; j. spontaneously grafted; k. after reduction by BuLi of spontaneously grafted; l. after reduction by LiAlH$_4$ of spontaneously grafted.
13.3.2. Cyclic Voltammetry

CVs of surface modified graphite electrodes in 1 M LiPF$_6$ in EC:DMC (50:50) at 0.01 mV/s are shown in figure 13.4. The currents have been normalized by the total mass of the active material (graphite+surface layer). Graphs in the left column show the SEI formation...
potential region of the CVs. The main peak in the negative current axis seen for pristine sample (filled circles) is associated with reduction of the electrolyte leading to SEI formation. Graphs on the right hand side column show the Li-ion intercalation/ de-intercalation potential window of the CVs. The three main peaks in this region are due to staging of Li-ions inside graphite structure [229]. It was shown in chapter 12 that grafting results in lowered charge consumption in the potential window of SEI formation and altered Li-ion intercalation/de-intercalation kinetics. Here, we compare CVs of pristine graphite (circles), with grafted graphites (squares), and with corresponding chemically reduced grafted graphite (stars and triangles). Figure 13.4.a shows the CV of electrochemically grafted sample, and thereafter electrochemically reduced sample. It is evident that the charge consumption in the potential window of SEI formation (depicted by negative peak current) is lower for the electrochemically reduced sample. This trend also holds true for in situ non-aqueous grafted (figure 13.4.c), in situ aqueous grafted (figure 13.4.e), and spontaneously grafted (figure 13.4.g) graphite samples. However, in figure 13.4.e, the grafted sample after reduction with LiAlH$_4$ shows a reversible electrochemical reaction in the SEI formation potential window. It also exhibits higher charge consumption in this potential range. The redox couple(s) involved are not understood, but increased peak current may be attributed to enhanced ionic conductivity of the surface layer due to ionic nature of LiAlH$_4$. Similar feature is observed in CV of spontaneously grafted sample reduced by LiAlH$_4$ shown in figure 13.4.g.

The envelope shape of the Li-ion intercalation/de-intercalation is also changed after the reduction step (as seen in figure 13.4.b and figure 13.4.d). From figure 13.4.d, it is clear that after every consecutive surface treatment step the amount of Li-ions intercalated into the graphite is lowered (further discussed in section 13.3.3). Li-ion intercalation/de-intercalation kinetics for the chemically reduced samples (as seen also in figure 13.4.f and 13.4.h) as compared to the grafted samples is also modified as seen from changes in overpotentials and envelope shapes, but the changes are not so drastic, and do not seem to follow a regular trend. Thus, chemical reduction of grafted graphite results in lowered charge consumption in the potential window of SEI formation (except for some samples reduced by LiAlH$_4$) and altered Li-ion intercalation/de-intercalation kinetics.
Figure 13.4. CVs of modified SFG6 graphites, left column: SEI formation potential region; right column: Li-ion intercalation/de-intercalation potential region; a,b. electrochemically grafted; c,d. in situ non-aqueous grafted; e,f. in situ aqueous grafted; g,h. spontaneously grafted.
Note: Electrochemical reduction method was selected for the electrochemically grafted graphite, because it was shown in chapter 9 that when the grafted group is aryl then electrochemical method is more feasible for reducing the end functional group of the grafted layer. But for the chemically grafted samples chemical method of reduction was chosen instead, because chemically grafted powder samples would be more homogenously reduced by chemical reagents in a pot treatment. In addition, electrochemical reduction of the chemically grafted samples in acetonitrile electrolyte might result in contamination and side reactions, which could alter the chemical nature of the grafted layer. But to compare chemical reduction with electrochemical reduction of chemically grafted graphite; we performed electrochemical reduction of the in situ non-aqueous grafted sample in carbonate electrolyte (1 M LiPF₆ in EC:DMC 1:1). Electrode of the grafted graphite was reduced until 1 V vs. Li⁺/Li (before beginning of SEI formation) in 1 M LiPF₆ in EC:DMC 1:1. It was then relaxed at zero current for 2 hours. Then the electrode was charged (lithiated) galvanostatically at C/10 rate (results shown in figure 13.5.a). Following which normal cycling at C/10 rate continued. This method of electrochemically reducing the grafted electrode until 1 V, does not offer lowering of irreversible charge loss as compared to the grafted sample which was cycled without this step. It was seen that first charge (lithiation) of the grafted sample is a sum of electrochemical reduction (until 1 V vs. Li⁺/Li), relaxation (2 hours), and continued lithiation at C/10. This implies that electrochemical reduction of grafted sample until 1 V already occurs during first charge (lithiation) of the grafted electrode, while cycling at C/10 rate. Results shown in figure 13.5.b show that this step does not offer any advantages with respect to SEI formation, practical specific charge retrieved, or cyclability (within experimental range of error). Hence, for the other chemically grafted samples, chemical method of end functional group reduction was selected.
Figure 13.5. Electrochemistry of in situ non-aqueous grafted SFG6 graphite and further reduced samples. a. initial part of the first lithiation curve; b. cyclability.

13.3.3. Galvanostatic cycling

Figure 13.6 shows the beginning region (SEI formation) of the 1st discharge profile of pristine graphite (circles), grafted graphites (squares), and chemically reduced grafted graphites (stars and triangles). The discharge profiles of the grafted graphite’s compared to the pristine graphite show additional charge consumption in the potential region from open circuit potential (OCP) to 0.8 V vs. Li⁺/Li. This is due to the additional charge required for reduction of the grafted carboxylic acid group. After chemical reduction of each grafted sample, it is observed that the charge consumption from OCP to 0.8 V decreases (in addition to that for SEI formation, which is also illustrated in section 13.3.2).
Pre-reduced samples also show lowered OCP, with respect to the grafted samples, which proves that the surface groups of the grafted sample were chemically reduced and obviously lithiated. OCP of the grafted material after reduction was lowered by ~0.9 V for electrochemically grafted graphite, by ~0.7 V (after reduction with both BuLi and LiAlH₄ reduced) for in situ non-aqueous grafted graphite, by ~1.1 V and ~0.7 V (after reduction with LiAlH₄ and BuLi respectively) for in situ aqueous grafted graphite, by ~1.2 V and ~0.6 V (after reduction with LiAlH₄ and BuLi respectively) for spontaneously grafted graphite. The error range for this data set is ±0.16 V. Thus, pre-reduction cum lithiation of the grafted surface layer directly consequents onto the SEI formation mechanism, which is depicted in the discharge profile of the first reduction of negative electrode.

Figure 13.6. SEI formation part of the 1st discharge curve of pristine SFG6 graphite, grafted graphite, and grafted graphite after chemical reductions. a. electrochemically grafted; b. in situ non-aqueous grafted; c. in situ aqueous grafted; d. spontaneously grafted.
But, chemical pre-reduction of the grafted layer also results in concomitant decrease in the practical specific charge retrieved from the graphite. This is visible in the cyclability curves shown in figure 13.7. It is evident that more heavily coated graphites (electrochemically grafted and \emph{in situ} non-aqueous grafted) show lower specific charge, than the lightly coated ones (\emph{in situ} aqueous grafted and spontaneously grafted). The second step of surface modification with aggressive chemical reagents seems to make the grafted layer thicker and more networked (seen in SEM pictures in section 13.3.1). This could be a possible reason of hindered Li-ion intercalation across the grafted layer and hence lowered practical specific charge. Another noteworthy point is that for calculation of the specific charge, we have conservatively used the total mass of the modified material (graphite + electro-inactive grafted surface layer). The specific charge would be higher if the mass of the redox inactive layer would be subtracted from the total mass for normalization. But such a number would be less relevant for practical application. The heavier coatings may however be useful for preventing exfoliation of graphite in PC based electrolytes. This is discussed in section 13.3.4.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{cyclability.png}
\caption{Cyclability of all surface modified graphites in 1 M LiPF$_6$ in EC:DMC.}
\end{figure}

Note: In order to investigate the cause of very poor cyclability of electrochemically grafted sample after electrochemical reduction, we performed Raman and XRD analysis of this sample. The Raman spectrum of the modified graphite did not show big differences compared to that of the pristine graphite. \emph{Ex situ} synchrotron XRD measurements (at MS-powder beamline X04SA at Swiss Light Source, Paul Scherrer Institut, Villigen) of pristine and grafted SFG6 powders were performed in transmission mode at 0.7085 Å with beam size of 0.5 mmX0.5 mm, where the powder samples were pressed between two self adhesive Kapton$^\text{®}$ tapes. From the XRD measurements, it was seen that that the unit cell
parameter ‘c’ does not change after the modification. The full width at half maxima (FWHM) of (002) peak was found to change slightly. It was calculated to be 0.051° for pristine SFG6, 0.061° for PCBD grafted SFG6, 0.062° for PCBD grafted SFG6 after electrochemical reduction. FWHM depends on instrumental broadening, crystallite size, and strain. Since the first factor is common, the reason for this slight evolution may be due to the latter two. However, FWHM of different peaks within one diffractogram are irregular due to anisotropy of the sample. For SFG6 pristine FWHM for (hkl) peak calculated from one diffractogram without instrumental and zero corrections are 0.051° for (002) peak, 0.108° for (101) peak, 0.065° for (004) peak, 0.067° for (112) peak, 0.134° for (116) peak, 0.045° for (109) peak. These values result in a non-linear Williamson-Hall plot [231].

FWHM*(cos Θ) vs. (sin Θ) graph. Hence distinction between size (intercept) and strain (slope) from Williamson Hall plot [231] could not be made. Due to asymmetry of the peaks (broad and sharp peaks within one diffractogram) and mixed phases {{P6\textsubscript{3}/mmc, hexagonal, a=2.460(2) Å, b=2.46 Å, c=6.704(5) Å, α=90 °, β=90 °, γ=120 °} [232] and (R-3m, rhombohedral, a=3.635 Å, b=3.635 Å, c=3.635 Å, α=39.49 °, β=39.49 °, γ=39.49 °) [233]} further analysis was tedious. Since it did not bring out vast differences, further analysis was not performed.

13.3.4. Exfoliation of graphite in PC based electrolytes

Normally, graphite undergoes exfoliation and endless charge in PC based electrolyte due to a process starting with solvent co-intercalation [19]. In figure 12.7 it was shown that graphite grafted by in situ non-aqueous grafting method does not undergo exfoliation and cycles reversibly in a PC based electrolyte. Figure 13.8 shows that in situ non-aqueous grafted graphite electrodes after reduction with BuLi and LiAlH\textsubscript{4} also cycle reversibly without undergoing exfoliation in a PC based electrolyte. It is evident that the grafted layer covalently bonded to the surface is exerting a strong force on the graphene sheets, keeping them together, and consequently preventing solvent co-intercalation, while cycling in PC based electrolyte. The covalent nature and hence the stability of the grafted layer is maintained after chemical reduction with harsh reagents, as seen in the curves (with triangles and stars) in figure 13.8. Hence, grafting and further modification of the end functional group is a way to prevent exfoliation of graphite. The in situ aqueous and spontaneous grafting methods were not able to prevent exfoliation even after the chemical reduction step. This is presumably due to broken and thin nature of the inherent grafted material, which may allow solvent co-intercalation through holes in the surface layer. The electrochemically grafted sample after electrochemical reduction and then proton
exchange with BuLi underwent partial exfoliation in a PC based electrolyte (results shown in figure 13.9).

![Graph showing electrochemistry results](image)

**Figure 13.8.** First cycle of pristine SFG6, in situ non-aq grafted, in situ non-aq grafted after reduction with BuLi, in situ non-aq grafted graphite after reduction with LiAlH4 in 1 M LiPF6 in EC:PC (15:85) at C/37 rate.

![Graph showing electrochemistry results](image)

**Figure 13.9.** First cycle of electrochemically grafted SFG6 after electrochemical reduction and then proton exchange with BuLi in 1 M LiPF6 in EC:PC (15:85) at C/37 rate.

### 13.4. Conclusions

Graphite powders were modified by a two step method, which is grafting followed by transformation of end functional group. Chemical reduction with lithiated reagents of grafted graphite was performed as the second step of functional group modification. This step modified the reactivity of the grafted material towards non-aqueous carbonate electrolytes. This was clearly depicted in the electrochemistry of SEI formation, Li-ion intercalation, and eventual exfoliation of graphite in PC based electrolyte. From the SEM
images it was inferred that the surface layer on the grafted material is covalently bonded and retains its surface morphology after reduction step. As desired, the effect of the modification was limited to, and stayed on the negative electrode material surface even after cycling (evidenced in the SEM images). It was seen that the surface morphology of the SEI formed on the modified material depends on that of the inherent grafted material. The second step of modifying the grafted samples resulted in thickening of the layers, which intern lead to decreased practical specific charge. Thus, for improved performance while retaining good specific charge and cyclability, surface modification with minimum consecutive steps should be selected. Exfoliation of graphite in PC based electrolyte could be prevented if the morphology of the grafted material is so that it binds, wraps, or brackets the graphene sheets together (to prevent solvent co-intercalation), as was the case for in situ non-aqueous grafted material. It was also found that exfoliation prevention property of the grafted material is retained after the functional group transformation step. Hence, the second step of functionality transformation of grafted graphite retains the surface morphology and exfoliation prevention property of the grafted material, while decreasing the charge consumption for SEI formation.

Following conclusions are withdrawn from the research on surface modification of graphite by grafting followed by functional group modification method.

- Surface chemistry, morphology, and reactivity of graphite towards electrolyte could be tuned using this method.
- Electrochemistry of SEI formation and SEI morphology could be controlled by the surface modification method. In general, the charge consumption in the potential window of SEI formation was lowered as a result of the modification.
- Exfoliation of graphite in PC based electrolyte due to solvent co-intercalation was averted in some cases.

However, this method involves two consecutive steps of modification, which results in thickening of the surface layer. The grafted layers were also found to be macromolecular or oligomeric rather than monolayers. These factors lead to thick redox inactive passive layers, which lower the practical specific charge retrieved per unit mass of modified graphite. Hence, in the next chapter, another method of surface modification is reported, which is expected to result in thinner surface layers.
Chapter 14. Modifying surface groups of graphite

14.1. Motivation

The main drawbacks of the grafting method for surface modification were that the thick redox inactive surface layer hampers the practical specific charge of the material and also retards the Li-ion intercalation kinetics during cycling. The inherent reasons for these drawbacks are that the method employed docks addition organic moiety on the surface, whose mass slumps the specific charge and impedes Li-ion transport. Thus the research is now diverted towards exploration of an alternative method of surface modification, where the surface groups already existing on graphite will be treated. From the results reported in section 10.3.3, it was evident that it is possible to ameliorate the electrochemical properties of graphite by chemical treatments. Literature also reports a vast diversity of surface pretreatments of graphites for improved electrochemical performance in Li-ion battery. Chemical methods of surface treatment of graphites include coating graphite with carbonates or chlorides from aqueous solutions [234, 235], coating with polymers [236, 237], chemical fluorination [238, 239], oxidation [82, 240, 241, 242], doping [243, 244, 245, 246], etching [247], treating with BuLi [81], acid treatment [248, 249, 250], and silylation [251]. Physical methods of surface treatment [252] include chemical vapour deposition (CVD) [253, 254, 255], thermal pyrolysis [256], heat treatment under gas flow [257, 258], oxygen plasma [259], vacuum evaporation [260], and chemical vapor infiltration [261]. However, the physical methods are majorly used for synthesis of high specific charge composite materials like carbon-alloy [262] or carbon-metal oxide [263]. Physical methods control the physical properties of carbons like surface area, surface structure, particle size, particle shape, etc. Whereas the chemical methods allow a more defined control in terms of surface chemistry, composition, and reactivity. Alongside, chemical methods of surface treatment are expected to result in more robust surface modification owing to the chemical bonds involved. Hence, for this work we have selected chemical methods of surface modification over physical methods.

The objective of this method of surface modification is to modify the surface groups existing on graphite by means of chemical reagents. There are two steps involved for precise control over chemical reactivity. In the first step surface groups would be activated by chemical reagents, and if the chemical nature of the surface groups is not stable after this step they will be further tuned in the next step. The results of the second step of
treatment will be reported in chapter 15. The scheme of this method is schematically shown in figure 14.1.

![Scheme of surface modification via chemical treatment of existing surface groups on carbon.](image)

Figure 14.1. Scheme of surface modification via chemical treatment of existing surface groups on carbon.

This method is inverse of grafting, since additional moieties are not docked on the surface; rather chemistry of the existing surface groups is tuned. By doing so, we wish to obtain thinner surface layers or modification. This would limit the amount of redox inactive mass on modified graphite (thereby optimizing the specific charge of the material), and allow unhindered Li-ion transport. This method is expected to result in surface layers mostly on the edge planes, as most of the surface groups, dangling bonds, unsaturated groups, and structural defects are present on the periphery of the graphene sheets in graphite particles. Hence, the resulting surface modification is expected to avert exfoliation via solvent co-intercalation.

Most of the literature reports on chemical surface modification employ oxidizing reagents. The objective of using oxidative reagents is to enhance the specific charge of graphitic carbons by creating defects and voids [82]. However, more oxidized groups should consume extra charge for undergoing reduction during first lithiation. Hence, we have rather chosen chemical reagents for reducing the surface groups into lowest oxidation state. Pre-reduced graphite is expected to show low irreversible charge loss at least in the potential range OCP until 0.8 V. Later, the reduced surface group could also serve as nucleophilic centers with which other organic molecules could be reacted. Reducing agents of varying strength were chosen starting from weak BH₃, medium BH₃—BuLi, very strong BuLi, and aggressive LiAlH₄. Graphites treated with reducing agents are studied electrochemically. To confirm the origin of the effect on electrochemistry these graphite samples are compared with those treated with various bases (NH₃, pyridine, pyrrole, and superbase Li tert-butoxide), and oxidizing agents (H₂O₂ and KMnO₄).
14.2. Experimental

Reducing agents: SFG6 graphite powder was treated with excess reagents 1 M BH₃ in THF, 1 M BH₃ in THF followed by 1.6 M BuLi in hexane, 1.6 M BuLi in hexane, and 2 M LiAlH₄ in THF, individually under inert conditions. Post treatment these powders were washed with THF, hexane, hexane, and THF respectively. The powders were dried at room temperature inside the glove box.

Bases: SFG6 graphite powder was stirred individually in excess reagents 25 % NH₃ in water, pyridine, pyrrole, and 1 M Li tert-butoxide in hexane. They were then washed in water, acetone, acetone, and anhydrous hexane respectively. NH₃ treated sample was dried overnight under vacuum at 80 °C, whereas the others were dried at room temperature inside the glove box.

Oxidizing agents: SFG6 graphite powder was stirred in excess reagents 1 M KMnO₄ in water, and 35 % H₂O₂ individually for four hours and washed copiously with water. KMnO₄ treated graphite was further reduced with BuLi and LiAlH₄ reagents. Powders were dried overnight under vacuum at 80 °C.

Electrode and cell preparation as well as the techniques and conditions for analysis were same as mentioned in the experimental methods section II. Conditions for SEM analysis prior and after cycling were also the same as in the previous chapters.

14.3. Results and discussion

14.3.1. SFG6 treated with reducing agents

The CV of SFG6 graphites reduced with various reducing agents is shown in figure 14.2.a. Figure 14.2.b shows a zoom of the CV in the potential window of SEI formation. It is evident that the electrolyte reduction peak near 0.8 V typically associated with SEI formation is drastically diminished for BuLi treated SFG6 as compared to the pristine. For the other samples too the peak was depressed but the effect was not as drastic as that with BuLi. On the contrary for the LiAlH₄ treated sample the peak current increased. This may be attributed to the ionic nature of this reagent, which might enhance the conductivity of the surface layer due to presence of charged aggregates and hence enhance charge transfer reactions. As a general trend, decrease in the peak current is found to be more for graphites reduced with stronger reducing agents (with the exception of LiAlH₄). The OCPs for pristine graphite, graphite treated with BH₃, BH₃->BuLi, BuLi, and LiAlH₄ were ~3.3 V,
~2.8 V, ~2.9 V, ~2.6 V, and ~2.1 V respectively. The OCPs of the graphite reduced with the stronger reducing agent was found to be lower vs. Li⁺/Li, and vice versa. This is in agreement with trend observed from the CVs.

From figure 14.2.b it is seen that the charge consumption in the potential window of SEI formation of BuLi treated SFG6 graphite is drastically lower compared to pristine SFG6. The ICL of this material is 33 % less than that of pristine. However, concomitantly its cyclability was poor and the practical specific charge retrieved was only 80 % of the theoretical. These results are shown in figure 14.3.a and 14.3.b respectively.

To understand the poor cyclability of BuLi treated sample, further analysis of this material by SEM, EIS, Raman spectroscopy, and XRD was done. These results are reported in chapter 15, along with methods of improving its cyclability.
Since, BuLi is known to be a strong base as well as a reducing agent; it is unclear which of these roles was responsible for the improvement in terms of ICL. Hence, in the next set of experiments graphite powders were treated with bases of varying strengths.

14.3.2. SFG6 treated with bases

SFG6 graphite was treated with bases of varying strength like pyridine (pKₐ = 5.2), NH₃ (pKₐ = 9.2), and pyrrole (pKₐ = 17.5). However, since BuLi is a superbase (pKₐ > 35), SFG6 was also treated with another superbase Li tert-butoxide. The electrochemical curves of
these materials are shown in figure 14.4. Figure 14.4.a shows the SEI formation part of the first lithiation of base treated graphite electrodes in 1 M LiPF₆ in EC:DMC electrolyte. It is seen that there is not too much effect of the treatment with the bases on the electrochemical discharge profiles. Similarly, from figure 14.4.b it is seen that the cyclability of the graphite electrode treated with bases is very similar to that of the pristine graphite and far from that of the BuLi treated one.

![Graph showing SEI formation](image1)

![Graph showing cyclability](image2)

**Figure 14.4.a.** First part of the lithiation curves of pristine graphite and graphites treated with different bases in 1 M LiPF₆ in EC:DMC electrolyte; **b.** cyclability of these graphite electrodes in the same electrolyte.

Hence, it can be concluded that it was most probably not the basic property of BuLi which was responsible for lower ICL and poor cyclability. It was indeed the role of BuLi as a reducing agent which was into play. To confirm this further we treated graphites with oxidizing agents in order to get experimental proof from the opposite extreme end.
14.3.3. SFG6 treated with oxidizing agents

GC discs and SFG6 graphite powders were treated with a mild oxidizing agent H₂O₂ and a strong one 1 M KMnO₄ in water. XPS C 1s spectra of pristine and treated GC discs are shown in figure 14.5. It is evident from the broad peaks at higher binding energy (from 285.5 eV to 287 eV) that the treatment with KMnO₄ resulted in more surface groups containing electronegative elements. From the quantitative analysis of survey spectra and other high resolution spectra it was found that the KMnO₄ treated sample contained mostly oxygen containing surface groups. The quantity of surface groups of the treated samples was found to be higher than that of the pristine sample. O/C ratio of pristine GC was 1.8 %, that of H₂O₂ treated GC was 4.6 %, and that of KMnO₄ treated sample was 12.3 %. Thus treatment with oxidizing agents’ results in enhanced surface groups and the extent of enhancement varies with the strength of the oxidizing agent.

![Graph showing XPS spectra](image)

*Figure 14.5. C 1s XPS spectra of pristine GC, GC treated with H₂O₂, and GC treated with KMnO₄.*

Thus we could use oxidizing agents to first enhance the number of surface groups, and then reduce by lithium containing reducing agents to get amplified effect of the reducing agents. For this the sample oxidized by strong oxidant KMnO₄ was reduced with strong reductants BuLi and LiAlH₄. The results of first lithiation are shown in figure 14.6.a. It is observed that after treatment with KMnO₄ there was an increase in the charge consumption for reduction of the surface groups in the potential range OCP to 0.8 V. This is in agreement with XPS results, which showed that the number of oxidized surface groups increased after this treatment. However, H₂O₂ treated SFG6 did not show any drastic changes as compared to pristine, this is attributed to only a minute increase in the
surface groups (as per XPS). After the reduction of KMnO₄ treated sample by LiAlH₄ and BuLi, it was observed that the charge consumption from OCP to 0.8 V as well as from 0.8 V until 0 V was drastically reduced. This result proves our hypothesis that the pre-reduced surface groups result in lowered charge consumption for reduction of the surface groups as well as that for electrolyte reduction during first lithiation of the material in EC:DMC electrolyte. By this two step method we were able to alleviate the effect of pre-reduction of surface groups.

Figure 14.6.a. Initial part of the first lithiation curve of pristine graphite and graphite treated with different oxidizing agents in 1 M LiPF₆ in EC:DMC electrolyte; b. cyclability of these graphite electrodes in the same electrolyte.

The surface group oxidation and reduction are also reflected in the OCPs of the treated samples. OCP for pristine, H₂O₂ treated, KMnO₄ treated, KMnO₄ treated sample reduced by LiAlH₄, and KMnO₄ treated sample reduced by BuLi were ~3.3 V, ~3.4 V, ~3.5 V,

![Graph showing initial part of the first lithiation curve](image1)

![Graph showing cyclability](image2)
\( \sim 1.7 \ \text{V} \), and \( \sim 1.2 \ \text{V} \) respectively. As expected, oxidized surface groups have higher OCP than pristine and the reduced ones have lower OCP than pristine. However, the cyclability of these samples did not show any visible improvement over that of pristine graphite electrode (figure 14.6.b). Even though the charge consumption for electrolyte degradation in the discharge profile was lower the total ICL of these samples was higher than in the pristine.

Note: High specific charge obtained by the KMnO\(_4\) treated sample (in the first few cycles) could be attributed to two reasons. Firstly, chemical etching might have created voids or cavities in the structure, where extra Li could be accommodated [82]. Secondly, the etched graphite contains more defects on which there could be extra electrolyte degradation.

Figure 14.7.a shows SEM image of the sample treated with KMnO\(_4\) and LiAlH\(_4\). This sample shows rather thin surface layer compared to the grafted samples, which were reported in chapters 12 and 13. This proves that the aim of preparing thinner surface layers by this method has been realized. From the image of this sample after 50 electrochemical cycles in 1 M LiPF\(_6\) in EC:DMC electrolyte shown in figure 14.7.b, it is seen that the SEI is binding the edges and sticks to the prismatic planes. This is attributed to the enhanced reactivity of the edge planes due the surface pretreatment with oxidizing and reducing agents.

![Figure 14.7. SEM image of a. SFG6 sample treated with KMnO\(_4\) and LiAlH\(_4\); b. same sample after 50 electrochemical cycles in 1 M LiPF\(_6\) in EC:DMC electrolyte.](image)

Note: For the other treated graphites (treated with reducing agents, bases, and oxidizing agents) the surface layers were barely visible in their SEM images. This may be due to extremely thin surface layers, which are resulted by the mere transformation of existing surface groups.
14.4. Conclusions

In order to obtain thinner surface layer, the existing surface groups of graphite were treated with various reducing agents. It was found that pre-reduced graphite electrodes give rise to lesser charge consumption in the potential window of SEI formation. Amongst the different reducing reagents used, the best results were found with treatment using BuLi. BuLi treated sample showed 33 % decreased ICL, however concomitantly it also exhibited poor cyclability. Reasons for poor cyclability will be investigated in the next chapter, along with further modification of the BuLi treated electrodes. The reason for decreased ICL by BuLi treatment could be attributed to its role as a base or as a reducing agent. In order to clarify that, we treated SFG6 graphite with some other common bases. Treatment with bases did not show any significant improvement in terms of ICL. This suggests that it was the reducing nature of BuLi that resulted in decreased ICL. To double check this hypothesis this further we treated graphites with oxidizing agents. Pre-oxidation showed increase in charge consumption for reduction of surface groups and also higher ICL. Hence, the opposing effect of treatment with oxidizing agents supports the hypothesis that reducing agents help decrease ICL. In order to amplify the effect of reduced surface groups, the oxidized samples (with enhanced surface groups compared to pristine) were reduced with reducing agents. These samples showed lower charge consumption for reduction of surface groups as well as SEI formation, but concomitantly exhibited poor cycling. SEM analysis of these sample showed that the surface modification in this case gave thinner surface layers (as per the goal) and the SEI was observed to be sticking to the edges, owing to their enhanced reactivity.

In the next chapter further analysis and synthetic methods for improving cyclability of BuLi treated graphite electrodes will be report.
Chapter 15. Tuning reactivity of modified surface groups

15.1. Motivation

In the previous chapter it was reported that SFG6 graphite treated with BuLi (SFG6BuLi) results in lower ICL, and drastically reduced charge consumption for SEI formation. However, the cyclability of this material was poor, and the specific charge retrieved was only 80% that of pristine graphite. In order to understand these favorable and adverse effects respectively, further characterization of this material is carried out. It was studied by SEM to understand visually the morphology of the surface film and that of the SEI formed over it after electrochemical cycling (in EC as well as in PC electrolyte). EIS was performed to observe the changes in electrochemical impedance due to the surface layer and its evolution during cycling. Polarization of modified electrodes during electrochemical cycling was also analyzed.

SFG6 graphite treated with BuLi was cycled in 1 M LiPF$_6$ in EC:PC (15:85) to ascertain if it could cycle reversibly in PC based electrolyte. The cycled sample was further analyzed by Raman spectroscopy and SEM for evidence of prevention of exfoliation of graphite.

One of the main possible causes for instable cycling of this material could be that the treatment with BuLi might have resulted in highly reactivity and unstable surface groups. These may be reacting with the electrolyte and undergoing continued reactions during cycling. In order to stabilize the chemical composition of the surface film, some cyclic film forming additives were used on SFG6BuLi electrodes. Use of additives is one of the most commonly employed method for improving electrochemical performance of battery materials in terms of improving SEI formation, positive electrode protection, salt stabilization, overcharge protection, fire retardation, ion solvation enhancement, Al corrosion inhibition, wetting, or viscosity dilution [88]. There are a vast variety of additives which have been reported in literature [264, 265, 266, 267, 268, 269, 270, 271]. Vinylene carbonate (VC) [75, 272], lithium bis-oxalato borate [273], and silanes [274] are a few to mention. However, for the purpose of stabilizing the reactive nucleophilic surface layer, cyclic additives with electrophilic centers were chosen. These additives are expected to undergo nucleophilic attack and open up upon reacting with SFG6BuLi to give stable chemical composition. Four classes of additives were chosen based on different chemistry. This study is also expected to elucidate at which potential various additives reduce (since there is no plateau at 0.8 V vs. Li$^+$/Li, no overlap between “standard” SEI
formation and additive reduction is expected). Additives used for this set of study along with their structures and abbreviations are illustrated in table 15.1.

**Table 15.1. Classification of additives used for further treatment of SFG6 treated with BuLi along with their structures and abbreviations.**

<table>
<thead>
<tr>
<th>#</th>
<th>Family description</th>
<th>Member 1</th>
<th>Member 2</th>
<th>Member 3</th>
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<tr>
<td>1</td>
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<td></td>
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<td><img src="O" alt="VC" /></td>
<td><img src="O" alt="PC" /></td>
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<tr>
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<td>pentacyclic rings</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
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<td><img src="O" alt="BL" /></td>
<td><img src="O" alt="CP" /></td>
</tr>
<tr>
<td>3</td>
<td>epoxides</td>
<td><img src="O" alt="PO" /></td>
<td><img src="O" alt="BO" /></td>
<td><img src="O" alt="CPB" /></td>
</tr>
<tr>
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<td>compounds containing heteroatom</td>
<td><img src="O" alt="ES" /></td>
<td><img src="O" alt="VMS" /></td>
<td><img src="O" alt="MP" /></td>
</tr>
</tbody>
</table>

The first class of additives comprises of cyclic carbonates, with varying inductive effect. This includes EC (no inductive effect), VC (-I effect, and also polymerizable olefin unit), and PC (+I effect from methyl group). These additives are expected to open up upon nucleophilic attack to form stable alkyl carbonates. VC has been extensively studied as an additive and proved to form effective SEI [275, 276, 277, 278]. The second class of additives comprises of 5-membered cyclic compounds with varying oxygen content. The strain of the pentacyclic rings is expected to propel ring opening. Varying oxygen content would compare the stability of resulting carbonate, carboxylic acid, and carbonyl functional group from ring opening of EC, butyryl lactone (BL), and cyclopentanone (CP) respectively. Lactone has been studied as an electrolyte solvent [279] and as additives [280] in the literature. The third class of additives is epoxides with varying length of side chains. Epoxides are expected to easily open up upon nucleophilic attack due to ring strain to form corresponding ethers. The varying length of side chain allows comparison in terms of inductive effect as well as degree of disorder in the surface layer. Ethers used are propylene oxide (PO) and butylene oxide (BO); they are compared with a linear halogenated alcohol chloropropanol, followed by H exchange with BuLi. This combination
of reagents is abbreviated as chloropropanol BuLi (CPB). The nucleophilic attack is expected on Cl, which would allow covalent attachment of the alkyl chain with alcohol end along with loss of LiCl. The last family of additives comprises of molecules containing heteroatoms. This includes ethylene sulfite (ES), which is widely studied electrolyte additive [281, 282, 283, 284]; vinyl methoxy siloxane (VMS), which is expected to undergo nucleophilic attack on the olefin unit; and N-methyl pyrillidinone (MP), which would result in amide formation upon ring opening.

To ensure that the second step of treating with additives does not lead to layer thickening (as was seen in chapter 13), the method of treatment with additives was different. In this case already prepared electrodes of SFG6BuLi material were treated with the additives, dried, and electrochemically cycled. This was done to avoid electronic particle isolation due to heavy surface film, which might form on the second step of surface treatment. By treating the electrodes we ensure that only the surface area of the electrodes which would be in direct contact with the electrolyte upon cycling is modified. This way the additive chemistry plays only on the surface of the modified graphite, without having an adverse effect on the positive electrode material.

**15.2. Experimental**

Electrodes of SFG6BuLi using SBR binder on Ti current collector were prepared in the usual manner. Then ~200 mL of neat additive was dropped on the prepared electrode. This procedure is schematically shown in figure 15.1. The additives were allowed to react with the electrode for ~ 10 minutes after which excess of the additive was wiped. Treated electrodes were allowed to dry inside the glove box. Additives treated electrodes were cycled in standard electrolyte at C/10 rate.

![Additive dropped](image)

*Figure 15.1. Illustration of procedure of further treating electrodes of SFG6 treated with BuLi with additives.*

Instrument and measuring conditions for SEM, EIS, and Raman analyses were the same as reported in section III.
15.3. Results and discussion

15.3.1. Analysis of SFG6 treated with BuLi

SEM images of the SFG6 treated with BuLi are shown in Figure 15.2. It is visible that graphite particles are edge decorated with a ruffle covering the prismatic planes. The basal planes on the other hand are totally bare, and no surface film is detectable. This ruffle could be a result of a physical phenomenon since it is tens of nm thick. However, the exact nature and chemical composition of this film is unknown. This kind of surface modification will be of utmost importance for averting exfoliation of graphite in PC based electrolyte, where one wishes to have a layer preventing solvent co-intercalation exclusively on edge planes. These results will be reported in section 15.3.3.

![Figure 15.2. SEM images of SFG6 treated with BuLi.](image)

To understand poor cyclability of this sample post mortem SEM was performed. SFG6 graphite after 10 electrochemical cycles (when practical specific charge becomes negligible) is shown in figure 15.3. It is evident that the particles after 10 electrochemical cycles are completely covered with a thick dense layer, which may result in particle isolation and hence in failure of the test cell. It is clear that the ruffles on the edge do not prevent SEI formation completely, even though it appears so from CV curves in figure 14.2. There is continued ICL (between 8-1.5 % until 9 cycles) occurring during consecutive cycles, which results in extra SEI formation (seen in figure 15.3).
Figure 15.3. SEM image of SFG6 treated with BuLi after 10 electrochemical cycles at C/10 in 1 M LiPF$_6$ in EC:DMC electrolyte.

Since SEM analysis showed thick surface layer on the edges poor cyclability could be attributed to impeded kinetics of Li-ion intercalation. To rule out this possibility, SFG6 treated with BuLi was cycled with different cycling protocols, using slower rates, as well as with potentiostatic step. Cycling with potentiostatic step ensures that there is complete Li-ion intercalation by keeping the electrode at a low potential until current falls to one tenth of the current at C/10. These results are shown in figure 15.4.

Figure 15.4. Cyclability of SFG6 treated with BuLi in 1 M LiPF$_6$ in EC:DMC electrolyte at different rates and cycling protocols.

If kinetics would have been the limiting factor, then cycling the electrode at low rates with potentiostatic step would have improved the cyclability of this material. However, from the cyclability curves at different rate it is clear that kinetics is not a major hindering factor for
good charge retention. Hence to assess the assumed resistance of the surface layer EIS of SFG6 treated with BuLi was performed. The evolution of the interface resistance of the sample with cycling was studied by taking electrochemical impedance spectra at different stages during cycling. EIS results for pristine and BuLi treated SFG6 graphite are shown in figure 15.5.

Figure 15.5.a. Nyquist plot at a potential of 1 V of SFG6 pristine and SFG6BuLi after 1st cycle; b. Nyquist plot at a potential of 10 mV of SFG6 pristine and SFG6BuLi during 2nd cycle; c. Nyquist plot at different potential of SFG6BuLi during 1st cycle; d. Nyquist plot at a potential of 10 mV of SFG6BuLi after 1st and 2nd cycle. The cycling and measurements are done at C/10 in 1 M LiPF₆ in EC:DMC electrolyte.
In figure 15.5.a the Nyquist plot of SFG6 pristine and SFG6BuLi are shown after 1st cycle. A very simple model is assumed where the diameter of the semicircle at high frequency (which lies on the left hand side of the Nyquist plot) is assumed to be proportional to the interface resistance. It is evident by comparing the radius of the distorted semicircles in this case that BuLi treated sample has higher interfacial resistance. The diameter of the semicircle in the Nyquist plot can be attributed to two phenomenons namely, SEI resistance and charge transfer resistance at the interface [68, 285]. Since this EIS measurement was done at 1 V, it is expected that there is quite less Li⁺ intercalation and hence negligible charge transfer reaction; thus the source of resistance is primarily SEI. From figure 15.5.b the total resistance including both charge transfer as well as that of SEI can be compared. The Nyquist plot shows that resistance at 10 mV during the second cycle of SFG6BuLi is higher than that of SFG6 pristine. This indicates that apart from the resistance of the SEI formation, that of charge transfer may also be higher in the BuLi treated sample, owing to the presence of the heavy surface film on prismatic planes. However, from figure 15.5.c it is evident that the resistance of charge transfer is decreasing as lithiation progresses during the 1st cycle. This implies that the charge transfer reaction is not blocked, but only impeded by the presence of the surface layer. And in figure 15.5.d, the Nyquist plot shows the resistance of SEI after the 1st and 2nd cycle of SFG6BuLi. It is observed that the radius of the semicircle is bigger after the second cycle, than after the first cycle. This evidence supports the hypothesis that the surface film present on SFG6BuLi is reactive and is continuously reacting with the electrolyte to form a thicker and more resistive SEI.

15.3.2. Treatment of SFG6 treated with BuLi with various additives

Electrochemical performance of SFG6BuLi electrodes treated with additives is shown in the first lithiation curves in Figure 15.6. Their cyclability in 1 M LiPF₆ in EC:DMC electrolyte is shown in Figure 15.7. In Figure 15.6.a, it is observed that when cyclic carbonate additives are added to SFG6BuLi the irreversible charge consumption around 0.8 V is further decreased. Concomitantly, addition of these additives especially EC, improves the cyclability drastically (shown in Figure 15.7). The cyclability expressed as fading of specific charge per cycle is even better in this case than that of pristine SFG6 electrode. Good cyclability of this sample is attributed to the stability of the resulting chemical composition of the surface film, which is alkyl carbonate. However, the practical specific charge remains lower than that of pristine graphite; this is inherited from the SFG6BuLi material. To ensure that the positive effect of treatment with EC (which is done at 40 °C due to high
melting point of EC) is not due to the elevated temperature used during the treatment; SFG6BuLi electrodes were also treated with PC at 40 °C. This result is labeled as SFG6BuLi PC high temperature (HT) in figure 15.6.a and figure 15.7. As it is evident from the figure increase in temperature by 15 °C does not have any significant effect on the electrochemistry of the modified material. From Figure 15.6.b, we can see that the potential of SEI formation moves to more positive potentials vs. Li⁺/Li as the oxygen content in the additive molecule decreases from EC to BL to CP. SEI formation at more positive potential would be advantageous, as it would occur well in advance of the onset of Li⁺ intercalation. But this would not be the method of choice due to poor cyclability of SFG6BuLi CP (shown in Figure 15.7). Depending on these results a hypothesis can be stated that more O containing moiety is more chemically stable, due to lowered nucleophilicity, and hence assures better electrochemical cycling (because it doesn’t undergo further chemical reactions with electrolyte during cycling).

![Graph a](image-a)

![Graph b](image-b)

![Graph c](image-c)

![Graph d](image-d)

*Figure 15.6. Part of the first lithiation profile in 1 M LiPF₆ in EC:DMC electrolyte of SFG6BuLi treated with a. EC, PC, VC, PC (HT); b. PO, BO, CPB; c. EC, BL, CP; d. MP, VMS, ES.*
From the ether based systems shown in Figure 15.6.c it is observed that the charge consumption for SEI formation is even lower than that of SFG6BuLi. But the cyclability of these materials is also worse than that of SFG6BuLi. Thus, it can be concluded that the ether based SEI would not be very effective in maintaining the cyclability of graphite in carbonate based electrolyte. This is explainable because the resulting chemical composition of the layer would be an alkoxide, which is itself nucleophilic and is susceptible to further chemical reactions with electrolyte during cycling. And in figure 15.6.d, it is seen that electrode modified with MP shows onset of SEI formation at more positive potential vs. Li⁺/Li. This electrode shows a modified lithiation curve, implying that the course of the SEI formation and Li⁺ intercalation in this electrode is quite different from that of the SFG6 pristine and SFG6BuLi. The cyclability of this material is also better compared with that of SFG6BuLi, which may be due to stability of the resulting amide functional group. Hence, N containing film forming additives resulting in stable functional groups like MP would be a promising way to go. Thus, based on this study it can be said that the additives resulting in stable chemical composition after ring opening like carbonate and amide are better SEI forming additives. The best additives found from this set of study are EC, VC, and MP. These show lower charge consumption for SEI formation along with good specific charge retention upon cycling.

![Graph showing cyclability of SFG6BuLi electrodes modified with various additives in 1 M LiPF₆ in EC:DMC electrolyte.](image-url)
The practical specific charge of all electrodes using SFG6BuLi as base material was lower than that of the pristine graphite electrode. The reason for this is that for the calculation of specific charge the mass of the redox inactive surface layer has not been taken into account. The specific charge has been calculated per gram of total active material (graphite + surface layer). To estimate the weight percentage of the layer present we washed the treated material and weighed it after removal of layer (layer removal confirmed by SEM). From this experiment the mass of the surface layer was found to be in the range 30±10 %. The amount of intercalatable carbon was also calculated back from the second cycle of this material with potentiostatic step, assuming that there was 100 % intercalation of lithium at the end of the potentiostatic step. The result of this calculation was in agreement with that of the washing and weighing experiments.

One of the most probable reasons for poor cyclability of SFG6 treated with BuLi was increase in polarization due to resistance of the film. Polarization is proportional to the difference in potential of lithiation and delithiation under constant current flow. Evolution with cycling of charge/discharge curves of SFG6 pristine, SFG6 treated with BuLi, and SFG6 treated with BuLi after EC additive are shown in figures 15.8.a, 15.8.b, and 15.8.c respectively. Shrinking of the curves to lower specific charge in figure 15.8.a showing pristine SFG6 electrode is due to loss of active material from the electrode during cycling. This is attributed to poor electrode engineering, which had to be with SBR binder inside the glove box so as to be comparable with other materials which are air sensitive. There is no obvious increase in polarization during cycling in this case as the shrinkage is only along horizontal and not vertical axis. On the contrary the curves shown in figure 15.8.b show a shift in both specific charge (horizontal) as well as potential (vertical) axes. This implies that BuLi treated SFG6 graphite material exhibits strong polarization. Continued increase in polarization with cycling is attributed to continued reactions of the highly reactive surface layer with the electrolyte and consequently thickening of resistive passive layer. However, after treating these electrodes with EC, the increase in polarization is strongly suppressed. This is shown in figure 15.8.c. The curves are shifted to a much smaller extent along the potential axis as compared to those in figure 15.8.b. This supports our argument of decreased reactivity due to stabilized chemical composition of the surface layer after treatment with the additive. The initial polarization of additives treated SFG6BuLi is similar to that of SFG6BuLi. However, upon cycling, the one treated with EC shows lesser increase in polarization, owing to lesser reactions of the chemically stable surface layer with the electrolyte for further SEI formation. Hence it can be inferred that
treating SFG6BuLi electrodes with EC results in stabilized chemical composition, which is less reactive with the electrolyte, and hence shows lowered polarization upon cycling. Calculations of polarization (average potential during the entire one lithiation step/delithiation step vs. cycle number) for EC, VC, and MP treated SFG6BuLi are shown in the graph in figure 15.9. This result also supports that the polarization of SFG6BuLi electrode is rather high and increases upon cycling as compared to pristine, and is lowered after it is treated with EC, VC, and MP additives.

Figure 15.8. Cycling curves of first 30 electrochemical cycles in 1 M LiPF₆ in EC:DMC electrolyte of a. SFG6 pristine; b. SFG6 treated with BuLi; c. SFG6 treated with BuLi after using EC additive.
Figure 15.9. Polarization (calculated as average potential of the entire lithiation/delithiation step vs. cycle number) evolution during cycling of SFG6 pristine, SFG6 treated with BuLi, SFG6BuLi treated with additives.

15.3.3. Prevention of exfoliation of SFG6 by treatment with BuLi

Since, treatment with BuLi results in exclusively edge decorated particles (shown in figure 15.2), it is expected to avert solvent co-intercalation through the prismatic planes and hence exfoliation of graphite in PC based electrolyte. The first cycle of SFG6 pristine and SFG6 treated with BuLi in 1 M LiPF$_6$ in EC:PC (15:85) electrolyte is shown in figure 15.10. Pristine SFG6 undergoes endless charge due to continuous electrolyte degradation along with exfoliation, whereas the graphite which was treated with BuLi shows normal reversible behavior, without noticeable SEI formation plateau at 0.8 V vs. Li$^+/\text{Li}$. This means that surface coating on the edges of the graphite particles (shown in figure 15.2) acts as an artificial SEI, averts exfoliation, and makes it possible to cycle SFG6BuLi efficiently in PC based electrolyte. This result is highly promising as it opens the way towards modification of highly crystalline graphites for their usage in batteries employing PC based electrolytes, for low temperature applications.
Figure 15.10. First cycle of SFG6 pristine and SFG6BuLi in 1 M LiPF$_6$ in EC:PC (15:85) electrolyte.

Since the cycling behavior of SFG6BuLi was poor in EC based electrolyte, it was possible to be the same case with cycling in PC based electrolyte. However, the results were opposite to our expectation. Cyclability of SFG6BuLi in PC based electrolyte is compared with that of SFG6 pristine, SFG6BuLi, SFG6BuLi treated with EC, and SFG6BuLi treated with PC in EC based electrolytes in figure 15.11. It is seen that fading of the specific charge SFG6BuLi in PC based electrolyte is comparable to normal cycling of SFG6 pristine in EC:DMC electrolyte (although the specific charge is lower). This implies that SFG6BuLi results in low ICL, cycles reversibly in PC based electrolyte, and shows good specific charge retention in PC based electrolyte.
Figure 15.11. Cyclability of SFG6 pristine, SFG6BuLi, SFG6BuLi treated with EC, and SFG6BuLi treated with PC in 1 M LiPF$_6$ in EC:DMC electrolyte; and that of SFG6BuLi in 1 M LiPF$_6$ in EC:PC (15:85) electrolyte.

For further evidence that SFG6BuLi does not exfoliate, SEM analysis of SFG6BuLi cycled in PC electrolyte was carried out. The electrode after 50 electrochemical cycles is shown in figure 15.12. It is evident from picture 15.12.a that the SEI formed in this case is rather homogenous and uniform. There are no obvious cracks and fractures visible in the SEI. Picture in figure 15.12.b shows that the edges of the particles are covered with a slightly thicker SEI than the basal planes. This might be the reason for prevented solvent co-intercalation. From picture in figure 15.12.c, it is seen that the nature of the SEI is polymeric/flexible and obviously not brittle. The layer appears to be elastic and looks flexible, as it stretches across the prismatic planes. This image also supports effective SEI formation along the edge planes, without visible exfoliation of graphite. Figure 15.12.d shows the edge planes of a few graphite particles. There are no signs of exfoliation and the stacking of graphene sheets is retained after electrochemical cycling.
To further prove that SFG6BuLi does not exfoliate on cycling, post mortem Raman spectroscopy measurements were performed on the SFG6BuLi electrodes after 50 cycles in 1 M LiPF$_6$ in EC:PC (15:85) electrolyte. The Raman spectra of as synthesized SFG6BuLi and that of cycled electrode are shown in figure 15.13. The spectra shown in the figure are normalized with respect to the G band, which is the highest peak in both spectra. However the signal to background ratio of the cycled sample is poorer due to additional SEI film present on the surface. The additional film results in decreased intensity of G band, absorption of the incident photons by the SEI, and poses practical limitations of focusing on such samples. The as synthesized sample shows clearly an ordered structure due to presence of a stronger G band as compared to D band. The cycled sample also shows that graphite particles have not been exfoliated as the G band is still much stronger than the D band. Had there been exfoliation, the D band (which is attributed to the disorder in the structure) would have been larger than the G band, as was the case in the spectra shown in figure 12.9.
15.4. Conclusions

SFG6 graphite treated with BuLi was found to have exclusively edge decorated particles with a ruffle on the prismatic planes. There was a heavy coating on the prismatic planes of the graphite particles, with basal planes being almost bare. The exact nature of this surface ruffle is not clear but is assumed to be highly reactive and nucleophilic in nature. After 10 cycles this material showed almost no practical specific charge. SEM proves this to be due to particle isolation (due to heavy coating of particles due to excessive SEI formation). Poor cyclability of the material was not solely due to kinetic limitations, this was proved by checking the cyclability of the material at lower cycling rates. EIS proved that the resistance of the SEI formed on the SFG6BuLi was higher than that formed on pristine SFG6. It also showed the charge transfer reaction of Li-ion intercalation was impeded but not blocked by the presence of the film. EIS also showed that the resistance of the SEI increased with every consecutive cycle, implying continued reactions of the surface film with electrolyte to form more resistive SEI.

To improve the cyclability of this material, electrodes of SFG6BuLi were treated with various cyclic additives. The additives were expected to open up upon reaction with the
highly reactive surface layer of SFG6BuLi and result in a stable chemical composition and hence good cyclability. Additives which showed improved performance in terms of charge consumption in potential window of SEI formation and specific charge retention were EC, VC, and MP. Cyclability of the electrode treated with EC as additive was even better than that of the pristine SFG6 electrode material but at lower specific charge level. Polarization curves supported our hypothesis that the poor cyclability of SFG6BuLi was due to highly reactive surface layer, which results in continued SEI formation due to excessive reactions of the layer with the electrolyte. The resistance of the interface also influences the overall kinetics. The polarization decreased after treating SFG6BuLi electrodes with EC, VC, and MP additives. This is obviously because the surface chemical composition was stabilized, which led to decreased reaction rate between the surface layer and the electrolyte.

SFG6BuLi owing to the exclusive and heavy edge coverage did not undergo solvent co-intercalation and hence exfoliation in PC based electrolyte. Even the cyclability of this material in PC electrolyte was promising. Post mortem SEM analysis showed homogeneous, uniform, and flexible SEI. The SEI was covering whole of the particles, with a thicker layer on the edges. There were no signs of exfoliation of graphite particles throughout the electrode. In addition to SEM, post mortem Raman spectroscopy also proved that there was no detectable exfoliation of graphite after 50 cycles in 1 M LiPF₆ in EC:PC (15:85) electrolyte.
SECTION IV

CONCLUSIONS AND OUTLOOK
Chapter 16. Summary and conclusions

16.1. Summary

Biggest challenges faced by the currently growing electromobility technology are that of safety and energy efficiency of Li–ion batteries used in electric vehicles. Since graphite is the most commonly used negative material in Li-ion batteries, it is vital to optimize its performance with respect to these issues. Solid electrolyte interphase formed on graphite electrode is the key component which dictates the safety and energy efficiency of the battery. SEI is formed during first electrochemical lithiation of the graphite electrode as a result of controlled degradation of the electrolyte. SEI is mandatorily required because once formed it averts further electrolyte degradation and ensures good cyclability by allowing Li-ions to transport through it. Formation of an effective SEI prior to Li-ion intercalation is also necessary to prevent solvent co-intercalation and hence exfoliation of graphite particles. This is rather critical for PC based electrolytes, which are important for low temperature applications. However, the natural SEI is formed (~ 0.8 V vs. Li+/Li) below the potential where PC solvated Li-ions begin to intercalate (~ 1.0 V vs. Li+/Li). It is hence in most cases unable to prevent exfoliation of crystalline graphites. In addition, during formation of a natural SEI, charge is irreversibly consumed for electrolyte reduction. This results in “loss” of Li-ions, charge, as well as reversible specific charge of the material; hampering the energy efficiency of the battery. In spite of its advantages the natural SEI is not ideal as it is inhomogeneous, brittle, and partially soluble. Hence, it may dissolve during cycling and pave way for further electrolyte degradation. The objective of this thesis was to form an artificial SEI on graphite particles prior to cycling to solve these issues related with the natural SEI. The goal was to develop novel surface modification methods as first steps towards an artificial SEI. Surface modified carbons with tuned morphology and reactivity towards electrolytes would ameliorate properties of SEI in terms of irreversible charge “loss”, exfoliation of graphite, and cyclability.

Electrochemical grafting was used as a method for binding organic moiety to the surface of carbons. Oxidative grafting of alcohols and reductive grafting of iodonium or diazonium salts were demonstrated as ways of achieving covalent immobilization on GC electrodes. Oxidative grafting of alcohols was not the most viable method for modifying graphite due to lack of suitable current collectors. Iodonium grafting method was also ruled out because of lower grafting yield, tedious organic synthesis involved, high cost of the reagents, and large quantity of byproducts. Diazonium salt grafting offers good grafting yield, and
synthetic flexibility hence it was selected for further modifications. After grafting the terminal functional group of the grafted layer is in oxidized state, like –COOH. But for battery application one requires reduced and lithiated surface groups like -CH$_2$OLi, to maintain low ICL. Hence, terminal functional groups of model grafted electrodes were transformed by chemical and electrochemical methods. It was found that electrochemical reduction is more suitable to reduce surfaces grafted by aryl species; whereas chemical method is viable when the grafted species is alkyl or saturated.

GC functionalized with alkyl lithium carbonate was successfully synthesized but this method could not be applied to graphite powder due to limitations of oxidative grafting, and insoluble byproducts. Therefore, aryl carbonate modification was done by electrochemical grafting of diazonium salt followed by electrochemical reduction. Since this method employs two steps of electricity consumption, this method would not have been most energy efficient. Hence, other chemical methods of grafting were developed. Aqueous and non-aqueous in situ methods were used, where an amine (precursor of a diazonium salt) is used in presence of a diazotizing agent in the grafting solution. Spontaneous grafting method used an isolated diazonium salt in a non-aqueous medium. Different grafting methods resulted in different surface morphologies of the grafted samples. Morphologies of the grafted samples were retained after fifty electrochemical cycles and that of the SEI formed also resembled morphology of as synthesized samples. Loading of the surface layer, and charge consumption for SEI formation, were found to follow the order electrochemical > in situ non-aqueous > in situ aqueous > spontaneous. The specific charge of heavily grafted graphite’s was however lower, due to large mass of the redox inactive layer. In situ non-aqueous method of grafting averted exfoliation of graphite in PC based electrolyte, due to its thread like morphology, which held graphene sheets together. As the second step of tuning functionality of the grafted layers, grafted graphite’s were chemically reduced. The surface morphology of the grafted samples was retained after the reduction step, but the layers were found to thicken. The charge consumption for SEI formation was found to decrease after this step. However, the specific charge of the material also decreased due to layer thickening.

To limit the layer thickness another method employing modification of existing surface groups of graphite was developed. Chemical pretreatment with various reducing reagents was done for reducing the surface groups into lowest oxidation state. Treatment with BuLi resulted in 33 % decrease in ICL. It was confirmed that the effect was due to the role of BuLi as reducing agent and not as a base. Pretreatment of graphite with oxidizing agents
also supported this result. It was found that treatment with reducing agent decreased the ICL whereas that with oxidizing agent increased it. Graphite treated with BuLi showed exclusively edge covered particles. The nature of the surface film is not clear but was assumed to be highly reactive. This could be the cause of poor cycling of this material. The chemical composition of this material was stabilized by treating it with cyclic additives. The best additives which improved the cyclability of this material were EC, VC, and MP. The reason for improved cyclability was decreased reactions for the surface layer with the electrolyte. Graphite treated with BuLi was also able to cycle reversibly in PC based electrolyte without undergoing exfoliation. The cyclability of this material in PC based electrolyte was comparable to that of pristine graphite in EC:DMC electrolyte.

On the whole, two methods for surface modification of carbons were developed. Both these methods resulted in decreased charge consumption for SEI formation and averted exfoliation of crystalline graphite in PC based electrolyte.

16.2. Conclusions

- Two methods of surface modification were developed for tuning electrochemical properties of graphite’s; namely grafting followed by terminal functional group transformation, and treatment of existing surface groups.

- Grafting followed by terminal functional group transformation:
  - The first step of grafting results in covalent immobilization and the second step tunes the reactivity of the surface layer towards the electrolyte.
  - Electrochemical reduction is more suitable to reduce grafted moieties which are aryl or conjugated; whereas chemical method is viable for alkyl or saturated grafted species.
  - Surface morphology of SEI, charge consumption for SEI formation, Li-ion intercalation/deintercalation kinetics, and exfoliation of graphite in PC based electrolyte can be tuned by this method of surface modification.
  - Different surface morphology can be obtained by different grafting methods. The surface morphology is retained after electrochemical cycling. Surface modification which leads to bundling or bracketing of graphene sheets
together can prevent solvent co-intercalation and hence exfoliation of graphite.

- Thickness of the surface layer increases with every consecutive step of treatment. Thus, number of steps should be minimized to obtain thin layers.

- Treatment of existing surface groups
  - Treatment of negative electrode material with reducing agents decreases the ICL whereas that with oxidizing agent increases ICL.
  - Treatment of graphite with BuLi results in 33% lowered ICL.
  - When the cyclability of a graphitic material is poor due to highly reactive surface, it can be improved by stabilizing the surface chemical composition by treating it with suitable additives. SFG6BuLi treated with EC showed better cycling stability than pristine SFG6.
  - Edge covered graphite particles do not undergo exfoliation. This proves that solvent co-intercalation is the main reason for exfoliation and that it can be averted by covering the prismatic planes of graphite particles with an artificial SEI. SFG6BuLi showed good reversible cycling in PC based electrolyte.

- Surface modification methods have proved effective for ameliorating SEI properties, and can be further extended for improving performance of materials for Li-ion batteries.
Chapter 17. Outlook

Both the surface modification methods developed during this work have a potential for being employed for other processes within Li-ion battery research arena. Some of the possible follow up research projects nucleating from this work are listed below.

- Owing to the robustness of the covalent immobilization by grafting, it can be used as an efficient method for synthesizing composite materials. One of the prime candidates for this purpose is Si-C composites. Si is a promising negative material due to its high specific charge (4200 mAh/g), and abundance. However, it is not yet broadly commercialized due to severe limitations including 400% volume expansion of Si during alloying, poor electronic conductivity of Si, and absence of good SEI formation on Si [286]. These limitations could be solved by incorporating carbon in Si electrodes [287]. Carbon would serve as a volume buffer, would serve as conduction pathways for electrons, and allow good SEI formation. Grafted graphite's could be reacted with functionalized Si nano-materials to form high specific charge negative materials. Since the potential of Li-ion intercalation in carbon (0.2 V vs. Li+/Li) and Li alloying of Si (0.4 V vs. Li+/Li) is close, the electrochemistry is not expected to impede. The covalent nature of conjunction would ensure that carbon will not detach from Si particles during volume expansion while cycling. When coupled with air or sulfur positive electrode, this system could be up to four fold better in terms of specific energy than the state of the art systems.

- On similar lines, grafting electrode materials would allow them to be coupled with binders via covalent bonds. This will ensure good and stable electrode engineering and hence long cycle life, which is vital for industrial batteries.

- Surface modification with tuned functional groups could be used to design model electrodes with particular surface functional groups. This could be used for studying the effect of each functional group on SEI formation and Li-ion intercalation. It would be an experimental set of data for comparing with similar theoretical models.

Surface modification can be performed on various solid additives used in Li-ion batteries. For example, surface modification of ceramic fillers for ether based solid polymer electrolytes, or conductive additives in electrode formulation could improve their compatibility with the electrolyte, or active material particles respectively.
Bibliography


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</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
<td></td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
<td></td>
</tr>
<tr>
<td>EQCM</td>
<td>Electrochemical quartz crystal microbalance</td>
<td></td>
</tr>
<tr>
<td>ELSA</td>
<td>Elemental line scan analysis</td>
<td></td>
</tr>
<tr>
<td>EMC</td>
<td>Ethyl methyl carbonate</td>
<td>O&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;2&lt;/sub&gt;H</td>
</tr>
<tr>
<td>ES</td>
<td>Ethylene sulfite</td>
<td>O&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;H</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron spectroscopy for chemical analysis</td>
<td></td>
</tr>
<tr>
<td>EV</td>
<td>Electric vehicle</td>
<td></td>
</tr>
<tr>
<td>FEAL</td>
<td>Fast entry air lock</td>
<td></td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
<td></td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
<td></td>
</tr>
<tr>
<td>GC</td>
<td>Glassy carbon</td>
<td></td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
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<tbody>
<tr>
<td>HT</td>
<td>High temperature</td>
</tr>
<tr>
<td>HV</td>
<td>Hybrid vehicle</td>
</tr>
<tr>
<td>IC</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>ICL</td>
<td>Irreversible charge loss</td>
</tr>
<tr>
<td>IRAS</td>
<td>Infrared absorption spectroscopy</td>
</tr>
<tr>
<td>KE</td>
<td>Kinetic energy</td>
</tr>
<tr>
<td>MP</td>
<td>N-Methyl pyridione</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>OCP</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>PCBD</td>
<td>$p$-carboxylicbenzenediazonium tetrafluoroborate</td>
</tr>
<tr>
<td>PEEK</td>
<td>Polyaryletheretherketone</td>
</tr>
<tr>
<td>PHV</td>
<td>Plug in hybrid vehicles</td>
</tr>
<tr>
<td>PNBD</td>
<td>4-Nitro benzene diazonium tetrafluoroborate</td>
</tr>
<tr>
<td>PO</td>
<td>Propylene oxide</td>
</tr>
<tr>
<td>PVDF-HFP</td>
<td>Polyvinylidene difluoride-hexafluoropropylene</td>
</tr>
<tr>
<td>SBR</td>
<td>Styrene-butadiene rubber</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SFG6BuLi</td>
<td>SFG6 graphite treated with n-butyl lithium</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>SNIFTIR</td>
<td>Subtractively normalized interfacial Fourier transform infrared</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanning probe microscopy</td>
</tr>
<tr>
<td>st</td>
<td>Stretching vibration</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscopy</td>
</tr>
<tr>
<td>sym st</td>
<td>Symmetric stretching vibration</td>
</tr>
<tr>
<td>TEAB</td>
<td>Tetraethylammonium tetrafluoroborate ((\text{C}_2\text{H}_5)_4\text{N}^+\text{BF}_4^-)</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo gravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TOF-SIMS</td>
<td>Time of flight-secondary ion mass spectroscopy</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
</tr>
<tr>
<td>VC</td>
<td>Vinylene carbonate</td>
</tr>
<tr>
<td>VMS</td>
<td>Vinyl methyl siloxane</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray diffraction</td>
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</tbody>
</table>
List of peer reviewed publications

1. P. Verma, P. Maire, P. Novák; *A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries.* Electrochimica Acta, 55 (2010) 6332-6341

2. P. Verma, P. Maire, P. Novák; *Concatenation of electrochemical grafting with chemical or electrochemical modification for preparing electrodes with specific surface functionality.* Electrochimica Acta, 56 (2011) 3555-3561

3. F. Simmen, A. Foelske-Schmitz, P. Verma, M. Horisberger, T. Lippert, P. Novák, C.W. Schneider, A. Wokaun; *Surface layer formation on Li$_{1+x}$Mn$_2$O$_{4+5}$ thin film electrodes during electrochemical cycling.* Electrochimica Acta, 56 (2011) 8539- 8544
List of oral presentations

1. **P. Verma, P. Maire, P. Novák**
   *Chemically modified carbons as negative electrodes in Li-ion batteries*
   Empa PhD Student’s Symposium 2009
   19th November, 2009
   Dübendorf, Switzerland

2. **P. Verma**
   *Novel approaches to obtain surface modified carbons for safer Li-ion batteries*
   General Energy Department Seminar
   7th April, 2011
   Paul Scherrer Institut, Switzerland

3. **P. Verma** and **P. Novák**
   *Grafting as novel approach to obtain surface modified carbons for tuning Li⁺ intercalation kinetics and SEI morphology*
   Lithium Batteries Discussion 2011
   12th June, 2011 - 17th June, 2011
   Arcachon, France
List of poster presentations

1. **P. Verma, P. Maire, P. Novák**  
   *Concatenating electrochemical grafting and reduction step to prepare modified carbon surfaces*  
   International Society of Electrochemistry Annual Meeting 2010  
   26th September, 2010 – 2nd September, 2010  
   Nice, France

2. **P. Verma, P. Maire, P. Novák**  
   *Bridging of electrochemical grafting with further modification for preparing carbons with specific surface properties*  
   Empa PhD Student’s Symposium 2010  
   7th October, 2010  
   Dübendorf, Switzerland

3. **P. Verma** and P. Novák  
   *Surface modified carbons for Li-ion batteries*  
   27th One-Day-Symposium of Electrochemistry Laboratory on “Electromobility” 2011  
   11th May, 2011  
   Paul Scherrer Institut, Switzerland
Curriculum Vitae

Ms. Pallavi Verma
Margrethenweg 9,
CH-5314 Kleindöttingen,
Switzerland
Tel: +41 76 707 8897
Email: pallavi.verma@psi.ch

25.06.1985
Indian
Single

Education

10/2008-10/2011 PhD, ETH Zürich
- “Development of materials for Li-ion batteries”
- Surface modification, electrochemical and XPS analysis
- Supervised by Prof. Petr Novák and Prof. Alexander Wokaun
- Graduated on 05/10/2011

09/2006-09/2008 Master of Science (Erasmus Mundus), University Paul Sabatier, Warsaw University, University Picardie Jules Verne
- “Materials for Energy Storage and Conversion”
- Materials science, electrochemistry, battery technology
- Topper of the batch with 16.6/20 (French system)

07/2003-07/2006 Bachelor of Science (Honours), University of Delhi
- “Chemistry”
- Inorganic, organic, physical chemistry, mathematics, physics
- Topper of the University with 1189/1350 (total of 3 years)

Work experience

10/2008-10/2011 PhD student, Paul Scherrer Institut
- Research: electrochemistry, materials science, Li-ion battery
- Project management: planning and organization of a SNF project
- Communication: writing reports, papers; presenting talks, posters
02/2008-09/2008 Master thesis, research assistant, LRCS, Amiens
-Research: synthesis and characterization of dual conductivity polymers

06/2007-07/2007 Summer internship, research trainee, CIRIMAT, Toulouse
-Research: X-ray diffraction of thin films

05/2005-06/2006 Summer internship, research trainee, University of Delhi, Delhi
-Research: study of phosphate uptake by plants

Awards and achievements

2008 Topper of the Erasmus Mundus Master course (class#3)
2006-2008 Erasmus Mundus scholarship for Master’s by European Commission
2006 Students Union Merit Medal
2006 Balaji Gold Medal for first position in University of Delhi
2003-2006 Science Meritorious Awards by University of Delhi

Language skills

English Excellent, English medium education
German Basic, learnt for two years, A2 level completed
Hindi Excellent, mother tongue, national language