In situ Raman microscopy of insertion electrodes for lithium-ion batteries and supercapacitors

Author(s):
Hardwick, Laurence James

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IN SITU RAMAN MICROSCOPY
OF INSERTION ELECTRODES FOR
LITHIUM-ION BATTERIES AND SUPERCAPACITORS

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZURICH

for the degree of
DOCTOR OF SCIENCES

Presented by
LAURENCE JAMES HARDWICK

MChem.
University of Southampton, United Kingdom
born on February 17, 1981
citizen of Britain

accepted by the recommendation of

Prof. Dr. A. Wokaun, examiner
Prof. Dr. R. Nesper, co-examiner
PD Dr. P. Novák, co-examiner

2007
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Finally I wish to thank Nina, my parents and my sister, Gemma for their love and support.
SUMMARY

The lithium-ion battery possesses the greatest energy density of all known rechargeable battery systems and has a power density close to the nickel-cadmium battery. This has allowed lithium-ion batteries to become the major power source of portable electronic devices, such as mobile phones and laptops. The lithium-ion battery generally consists of two insertion electrodes. The role of the more negative electrode is to uptake lithium-ions from the more positive lithium intercalation host during the charge step and then to release the lithium-ions in the discharge step. During discharge the lithium-ions go from a high energy state in the negative electrode to a low energy state in the positive electrode, while the electrons pass through an external circuit with a release of energy.

The major challenge of lithium-ion battery research is to develop systems with even higher power and energy densities. Improvements to the battery will not only depend on the discovery of new materials, but also advancement in the understanding of the surface and interfacial region of battery electrodes.

Investigations of electrode reactions benefit substantially when it is possible to record spectra for the electrode/solution interface, as the electrochemical response is obtained. The major difficulties are to design the experiment so that it is possible to achieve the sensitivity to record the spectroscopic response of the interfacial region and, at the same time, to discriminate the spectrum of the interface from the response of the bulk electrolyte solution. Raman spectroscopy is one such method. The use of a confocal hole and slit, in combination with an in situ Raman cell, which allows measurement at the back-side of the electrode through a small hole in the current collector, has overcome this obstacle. This has allowed the measurement of in situ Raman spectra with excellent signal to noise ratio, with minimal to no detection of the electrolyte.
The aim of this study was to broaden the knowledge of the behaviour of insertion electrodes used in lithium-ion batteries and electrode degradation processes in electrochemical double-layer capacitors (EDLCs) by characterisation with ex situ, and primarily in situ Raman microscopy. The objective for this work was therefore to monitor the course of ion insertion and its effect on the host material structure at the surface region of the electrode.

In chapter 3, an examination of ex situ Raman mapping in the recording of electrode surface variations with micrometer resolution is presented. Specifically graphitic carbons, lithium cobalt oxide (LiCoO₂) and lithium manganese oxide (LiMn₂O₄), are investigated.

Chapter 4 concentrates on in situ Raman microscopy of graphitic materials. In particular in situ Raman mapping, the D-band (1330 cm⁻¹) disappearance, local impact of La, effect of graphite particle size and rhombohedral fraction, detection of graphite exfoliation and the influence of temperature on the appearance of the stage 2 liquid phase staged compound are investigated. It was found that intercalation takes place heterogeneously with some graphitic materials. This effect could have serious implications for electrode lifetimes. Furthermore, it was found that the onset of exfoliation can be monitored by the appearance of a band at 1597 cm⁻¹ that can be related to the presence of Li(solvent)x moieties (x > 0).

Chapter 5 presents in situ Raman microscopy of nano silicon, titanium dioxide anatase (TiO₂), LiCoO₂ and LiMn₂O₄. The first lithiation Raman spectra of nano silicon showed a decrease in intensity of the main band at 520 cm⁻¹. In situ Raman spectra of TiO₂ showed the biphasic transition from tetragonal TiO₂ to orthorhombic LiₓTiO₂. In fact, this phase transition is seen to depend on the crystallite size. Spectra showing the first de-lithiation of LiCoO₂ and LiMn₂O₄ concur with known literature.

Finally in chapter 6, the question of ion intercalation in graphite-like domains of activated carbons, is explored. The electrochemical double-layer capacitor (EDLC) is another developing electrochemical energy storage system. Even though EDLCs possess low energy densities, advantages over current batteries include a much greater electrode stability and device cycle life performance, since the charge storage is based on double-layer charging rather than faradaic reactions. In situ Raman microscopy indicates that not only double-layer charging occurs, but also insertion reactions.


In Kapitel 3 wird die ortsaufgelöste ex situ Raman-Mikroskopie für das Mapping von Inhomogenitäten von Elektroden vorgestellt, wobei Graphite, Lithium-Kobaltoxid (LiCoO₂) und Lithium-Manganoxid (LiMn₂O₄) mit einer Auflösung von wenigen μm untersucht wurden.

Kapitel 4 befasst sich mit der in situ Raman-Mikroskopie von graphitischen Materialien. Die Schwerpunkte dieses Kapitels sind das in situ Raman-Mapping, das Verschwinden der D-Bande bei 1330 cm⁻¹, der lokale Einfluss von L₉, der Einfluss der Partikelgröße und des rhomboedrischen Anteils, Detektion der Graphit-Exfoliation und der Einfluss der Temperatur auf die Existenz der sogenannten Flüssigphasen-Verbindung mit Stufe 2. Insbesondere wurde festgestellt, dass die Interkalation von Ionen in einigen graphitischen Materialien ausgeprägt heterogen auftreten kann. Diese Tatsache könnte schwerwiegende Folgen für die Lebensdauer der Elektrode haben. Weiterhin wurde festgestellt, dass das Eintreten der Exfoliation zur Erscheinung einer Bande bei 1597 cm⁻¹ führt, was auf die Gegenwart von Li(Solvent)ₓ Spezies (x > 0) zurückgeführt werden kann.

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# LIST OF SYMBOLS, FUNDAMENTAL CONSTANTS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_i$</td>
<td>activity of species $i$</td>
<td>mol dm$^{-3}$</td>
</tr>
<tr>
<td>C-rate</td>
<td>rate of charge</td>
<td>Ah</td>
</tr>
<tr>
<td>$C$</td>
<td>capacitance</td>
<td>F m$^{-2}$</td>
</tr>
<tr>
<td>$c_i$</td>
<td>concentration of species $i$</td>
<td>mol dm$^{-3}$</td>
</tr>
<tr>
<td>$E'$</td>
<td>standard electrode potential</td>
<td>V or mV</td>
</tr>
<tr>
<td>$E_e$</td>
<td>equilibrium potential</td>
<td>V or mV</td>
</tr>
<tr>
<td>$E'_e$</td>
<td>formal electrode potential (i.e. the equilibrium potential when $c_0 = c_1$)</td>
<td>V or mV</td>
</tr>
<tr>
<td>$\Delta E^o$, $U''$</td>
<td>cell potential</td>
<td>V or mV</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant</td>
<td>C mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta G^o$</td>
<td>standard Gibbs free energy</td>
<td>J mol$^{-1}$</td>
</tr>
<tr>
<td>$I$</td>
<td>electric current</td>
<td>A</td>
</tr>
<tr>
<td>$i_m$</td>
<td>specific current</td>
<td>A g$^{-1}$</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant</td>
<td>J K$^{-1}$</td>
</tr>
<tr>
<td>$M, m_i$</td>
<td>mass</td>
<td>kg</td>
</tr>
<tr>
<td>$M_e$</td>
<td>molar mass</td>
<td>kg mol$^{-1}$</td>
</tr>
<tr>
<td>$n$</td>
<td>number of electrons exchanged</td>
<td>(dimensionless)</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro constant</td>
<td>mol$^{-1}$</td>
</tr>
<tr>
<td>$p$</td>
<td>specific power</td>
<td>W kg$^{-1}$</td>
</tr>
<tr>
<td>$P_v$</td>
<td>power density</td>
<td>W dm$^{-3}$</td>
</tr>
<tr>
<td>$Q$</td>
<td>charge capacity</td>
<td>C or Ah</td>
</tr>
<tr>
<td>$q_{th}$</td>
<td>theoretical specific charge capacity</td>
<td>Ah kg$^{-1}$</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$R_{eff}$</td>
<td>effective series resistance</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>$V, V_i$</td>
<td>volume</td>
<td>dm$^{-3}$</td>
</tr>
<tr>
<td>$w_{th}$</td>
<td>theoretical specific energy</td>
<td>Wh kg$^{-1}$</td>
</tr>
<tr>
<td>$W_{V,th}$</td>
<td>theoretical energy density</td>
<td>Wh dm$^{-3}$</td>
</tr>
<tr>
<td>Quantity</td>
<td>Symbol</td>
<td>Value</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>dielectric constant</td>
<td>$\varepsilon$</td>
<td></td>
</tr>
<tr>
<td>wavelength of light</td>
<td>$\lambda$</td>
<td></td>
</tr>
<tr>
<td>viscosity</td>
<td>$\eta$</td>
<td></td>
</tr>
<tr>
<td>magnetic permeability</td>
<td>$\mu$</td>
<td></td>
</tr>
<tr>
<td>electrochemical potential</td>
<td>$\mu_e$</td>
<td></td>
</tr>
<tr>
<td>potential scan rate</td>
<td>$\nu$</td>
<td></td>
</tr>
<tr>
<td>conductivity</td>
<td>$\sigma$</td>
<td></td>
</tr>
<tr>
<td>wavenumber</td>
<td>$\nu$</td>
<td></td>
</tr>
<tr>
<td>inverse of wavelength $(\omega = 1/\lambda)$</td>
<td>$\omega$</td>
<td></td>
</tr>
</tbody>
</table>

### Constants

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
<th>Power of ten</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>speed of light</td>
<td>$c$</td>
<td>2.998</td>
<td>$10^8$</td>
<td>m s$^{-1}$</td>
</tr>
<tr>
<td>elementary charge</td>
<td>$e$</td>
<td>1.602</td>
<td>$10^{-19}$</td>
<td>C</td>
</tr>
<tr>
<td>Faraday constant</td>
<td>$F = N_A e$</td>
<td>9.649</td>
<td>$10^4$</td>
<td>C mol$^{-1}$</td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>$k$</td>
<td>1.381</td>
<td>$10^{-23}$</td>
<td>J K$^{-1}$</td>
</tr>
<tr>
<td>Gas constant</td>
<td>$R = N_A k$</td>
<td>8.319</td>
<td></td>
<td>J K$^{-1}$ mol$^{-1}$</td>
</tr>
<tr>
<td>Planck constant</td>
<td>$h$</td>
<td>6.626</td>
<td>$10^{34}$</td>
<td>J s</td>
</tr>
<tr>
<td>$h = h/2\pi$</td>
<td></td>
<td>1.055</td>
<td>$10^{34}$</td>
<td>J s</td>
</tr>
<tr>
<td>Avogadro constant</td>
<td>$N_A$</td>
<td>6.022</td>
<td>$10^{23}$</td>
<td>mol$^{-1}$</td>
</tr>
</tbody>
</table>

### Conversion factors

- 1 eV = 1.602 x $10^{-19}$ J
- 86.5 kJ mol$^{-1}$
- 8066 cm$^{-1}$
- 1 cm$^{-1}$ = 1.986 x $10^{-23}$ J
- 1 Å = 1 x $10^{-10}$ m
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>AMPC</td>
<td>KOH activated mesophase pitch based coal</td>
</tr>
<tr>
<td>AN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>ASA</td>
<td>Active surface area</td>
</tr>
<tr>
<td>a.u.</td>
<td>arbitrary unit</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer Emmett Teller</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge coupled device</td>
</tr>
<tr>
<td>CCTV</td>
<td>Closed circuit television</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CV</td>
<td>Cylic voltammetry</td>
</tr>
<tr>
<td>DBP</td>
<td>Dibutyl phthalate</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>DEMS</td>
<td>Differential electrochemical mass spectrometry</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>DME</td>
<td>1,2-dimethoxythane</td>
</tr>
<tr>
<td>DWNT</td>
<td>Double-walled nanotube</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>EDLC</td>
<td>Electrochemical double layer capacitor</td>
</tr>
<tr>
<td>EMC</td>
<td>Ethyl-methyl carbonate</td>
</tr>
<tr>
<td>EMI</td>
<td>1-ethyl 3-methyl imidazolium salt</td>
</tr>
<tr>
<td>EPDM</td>
<td>Ethylene propylene diene monomer</td>
</tr>
<tr>
<td>ESR</td>
<td>Effective series resistance</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>GBL</td>
<td>Gamma butyrolactone</td>
</tr>
<tr>
<td>GIC</td>
<td>Graphite intercalation compound</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly ordered pyrolytic graphite</td>
</tr>
<tr>
<td>HSAG</td>
<td>High surface area graphite</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>MCMB</td>
<td>Mesocarbon microbead</td>
</tr>
<tr>
<td>MPC</td>
<td>Mesophase pitch based coal</td>
</tr>
<tr>
<td>MWNT</td>
<td>Multi-walled nanotube</td>
</tr>
<tr>
<td>OCP</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>PEEK</td>
<td>Polyetheretherketone</td>
</tr>
<tr>
<td>PVdF</td>
<td>Polyvinylidenefluoride</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SERS</td>
<td>Surface enhanced Raman spectroscopy</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single-walled nanotube</td>
</tr>
<tr>
<td>TA</td>
<td>Transverse acoustic</td>
</tr>
<tr>
<td>TEA</td>
<td>Tetraethyl ammonium</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TERS</td>
<td>Tip-enhanced Raman spectroscopy</td>
</tr>
<tr>
<td>TFSI</td>
<td>Bis-(trifluoromethanesulphone)imide</td>
</tr>
<tr>
<td>TO</td>
<td>Transverse optical</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VC</td>
<td>Vinylene carbonate</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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CURRICULUM VITAE
1

INTRODUCTION

"Quotation is a serviceable substitute for wit."
Oscar Wilde

1.1 Motivation

On March 20th 1800 a letter was dispatched from Como in Italy to the Royal Society of London. The letter was written in French, but it carried an intriguing English title "On the Electricity excited by the mere Contact of conducting Substances of different kinds". The author of this communication was Alessandro Volta and the contents bore the discovery of constant current generation from a pile of dissimilar metals [1]. On June 26 of the same year the letter was read and later reported in Philosophical Transactions [2], and thus the electric battery materialised into the world of science and heralded the birth of portable energy. However, because of the low energy and power densities of the subsequently developed battery systems, wide application of the battery was limited. Fast-forward two centuries to the present day and one can observe that the battery is going through a renaissance in the form of the lithium-ion battery. Of all the rechargeable battery systems, the lithium-ion battery possesses the greatest energy density and has a power density close to the nickel-cadmium battery [3]. In Western societies, portable energy, stored by the lithium-ion battery, is now
used by the majority of their populations as the power source of mobile phones, laptops, digital cameras and music-playing devices. Nevertheless, the growing market size and escalating number of existing and potential applications have created a cyclical demand for an even more superior battery system. Hence the goal of lithium-ion battery development is on one hand to develop a more energy dense system to satisfy the portable-electronics market, and on the other hand to offer greater power densities in order to have a commercially viable battery to operate as the sole power source in an automotive vehicle. In the short term the attainable goal is the mass-market penetration of lithium-ion battery powered hybrid cars combined with a petrol engine or a fuel cell. Encouraging signs are evident today in comparative success of the petrol/ nickel metal-hydride battery hybrid cars: Toyota Prius and Lexus RX 400h [4, 5]. Clearly a demand for energy-efficient low-emission transportation exists. A possible evolutionary development of the battery/ petrol hybrid would be the decrease of the volume of the petrol engine coupled with an increase of the battery output. The term “plug-in hybrid” has been coined to describe this system [6]. Useful battery lifetime, size and weight (relating to the power and energy densities of the battery) and most importantly cost remains the limiting factors and challenges to overcome to allow for this development.

Nonetheless the next great leap forward in the progress of the lithium-ion battery will not only depend on the discovery of new electrode materials, but also on the improved fundamental understanding on the surface region of battery electrodes. A stable electrode surface would contribute to the creation of a stable and long-life battery.

The lithium-ion battery is a thermodynamically unstable system; today’s challenge is to learn how to manage the kinetics.
1.2 Aim of this work

The driving question behind the work of this dissertation is how does the lithium-ion battery operate under standard conditions? Once this question is understood one can then ask, how can one subsequently improve the operation of this battery? As stated in the introduction, one of the challenges faced by lithium-ion batteries is to understand the surface region of battery electrodes. This thesis will focus on this problem by utilising the surface sensitive technique of Raman spectroscopy to characterise the chemical behaviour of the exterior of battery electrodes. The objective for this work is therefore to monitor the course of ion insertion/de-insertion and its effect on the host material structure at the surface region of lithium-ion battery electrodes.

Firstly this work will begin by the examination of the ex situ Raman mapping technique to record electrode surface variations with micrometer resolution. Secondly in situ Raman microscopy will be used to monitor the structural changes of electrodes during lithium insertion and extraction. Following the change of the Raman signal during insertion electrode reactions provides local composition and chemical information under real battery operation conditions. Thirdly these two techniques will be combined initially with small maps of four points to record possible heterogeneities during lithium incorporation. Later on larger maps will be employed to evidence the relationship between structure and intercalation behaviour. Specifically negative electrode materials, such as graphitic carbons, silicon, titanium dioxide (TiO$_2$), and positive electrode materials lithium cobalt oxide (LiCoO$_2$) and lithium manganese oxide (LiMn$_2$O$_4$), are investigated.

Lastly the question of ion intercalation in graphitic domains of carbon materials of interest to the supercapacitor community will be explored. The electrochemical double layer capacitor (EDLC) is another emergent electrochemical energy storage system. Even though EDLCs possess low energy densities, advantages over current batteries include a much greater electrode stability and device cycle life performance, since charge storage is based on double-layer charging rather than faradaic reactions. In situ Raman microscopy will be used to demonstrate that not only double-layer charging occurs but also insertion reactions.
1.3 Electrochemistry

Electrochemistry covers all reactions in which a chemical change is the result of electric forces and in the reverse case, where an electric force is generated by a chemical process [7].

1.3.1 Galvanic cells

A galvanic or voltaic cell is an electrochemical cell that generates electricity as result of the spontaneous reaction occurring inside it. The cell consists of two dissimilar electrodes (the anode and the cathode) immersed in an electrolyte solution. The electrodes are electronic conductors and the electrolyte solution is an ionic conductor. At the interface between electronic and ionic conductors a passage of electrical charge is coupled with a chemical reaction. This type of reaction is known as a redox reaction, where there is a transfer of electrons from one species to another. These are two half reactions and involve at the anode the oxidation of one species (the removal of electrons) and at the cathode the reduction of another (the addition of electrons).

At the anode: \( \text{Red}_1 \rightarrow \text{Ox}_1 + e^- \)  
At the cathode: \( \text{Ox}_2 + e^- \rightarrow \text{Red}_2 \)

Overall reaction: \( \text{Red}_1 + \text{Ox}_2 \rightarrow \text{Ox}_1 + \text{Red}_2 \)

Each of these reactions is related to a standard electrode potential, \( E^o \), which can be calculated from the thermodynamic data of the reaction. Under equilibrium conditions:

\[
E^o = -\frac{\Delta G^o}{nF} \tag{1.4}
\]

\(-\Delta G^o = \text{standard Gibbs free energy}\)

\(n = \text{number of electrons}\)

\(F = \text{Faraday constant}\)

The Nernst equation is used to calculate the equilibrium potential, \( E_e \), of half-reactions:

\[
E_e = E^o + \frac{2.3RT}{nF} \log \frac{c_e}{c_r} \tag{1.5}
\]
Where $E_e^o$ is the formal potential for the couple in the phase under consideration (i.e. the equilibrium potential when $c_a = c_r$), $R$ is the gas constant and $T$ is temperature. More precisely, this thermodynamic equation should be written in terms of a ratio of activities. For the general electrode reaction:

$$pP + qQ + ne^\prime \leftrightarrow xX + yY$$  \hspace{1cm} (1.6)

The Nernst equation is therefore written in its most exact form as:

$$E_e = E_e^o + \frac{2.3RT}{nF} \log \frac{(a_p)^p(a_q)^q}{(a_x)^x(a_y)^y}$$  \hspace{1cm} (1.7)

where in this case $E_e^o$ is the standard potential (the equilibrium potential when all reactants and products are in their standard states).

The battery

Batteries, which are made up of two or more cells connected either in parallel or in series, can be separated into two classes: primary or secondary. Primary batteries are non-rechargeable because the electrochemical reactions are irreversible under practical conditions (alkaline-manganese dioxide, zinc-air) and therefore are single use. In secondary batteries the electrochemical reactions are reversible; therefore these types of batteries are reusable (lead acid, lithium-ion). In this type of battery during discharge the chemical energy is transformed into electrical energy. The battery can be reused again once electrical energy has been converted into chemical energy during the charging process. The terms cathode and anode cannot be properly defined in a rechargeable cell since the anode is identified as the electrode which gives electrons to the external circuit, and the cathode is the electrode that receives electrons from the external circuit. Therefore depending on whether the cell is being charged or discharged the two terms are mixed. To avoid confusion the electrodes can be simply categorised as either positive or negative because the term refers to their respective electrode potentials.
1.3.2 Characterisation of electrochemical cells

Cell potential

The maximum accessible energy is simply the free energy of reaction, \( \Delta G \). Consequently, high energy results from the choice of electrode materials. This can be achieved by the selection of electrodes with the greatest difference of electrochemical potential, \( \bar{\mu} \) \(^{[7]}\).

The cell voltage can be derived from the Gibbs free energy of the equivalent chemical reaction:

\[
U^\circ = \Delta E^\circ = \frac{\Delta G^\circ}{nF}
\]  

(1.9)

To evaluate the properties of electrodes in a secondary cell some general concepts are introduced:

Charge capacity

The charge capacity, \( Q \) (Ah), is the total amount of charge obtainable from a cell and can be derived from Faraday’s equation:

\[
Q = \int_{t_i}^{t_f} I(t) dt = mnF
\]  

(1.10)

Theoretical specific charge capacity

The theoretical specific charge capacity, \( q_{th} \) (Ah kg\(^{-1}\)), is the amount of charge per kg of reactants, \( m_i \), and it can be calculated from the stoichiometry of the overall cell reaction:

\[
q_{th} = \frac{nF}{\sum_i m_i}
\]  

(1.11)
It is usually desirable that the amount of energy stored in a given mass or volume is as high as possible. To compare the energy content or energy density content of cells, the terms “specific energy” (Wh kg\(^{-1}\)) or “energy density” (Wh dm\(^{3}\)) are employed, whereas the rate capability is expressed either as “specific power” (W kg\(^{-1}\)) or “power density” (W dm\(^{3}\)):

**Theoretical specific energy**

The theoretical specific energy, \(w_{th}\) (Wh kg\(^{-1}\)) is the amount of electrical energy per unit of mass that a battery is able to deliver and is the function of the cell potential (V) and charge capacity (Ah kg\(^{-1}\)):

\[
w_{th} = \frac{nF \Delta E''}{\sum m_i} 
\]

(1.12)

**Theoretical energy density**

The theoretical specific energy, \(W_{V,th}\) (Wh dm\(^{3}\)) is the amount of electrical energy per unit of volume:

\[
W_{V,th} = \frac{nF \Delta E''}{\sum V_i} 
\]

(1.13)

**Specific power**

The specific power, \(p\) (W kg\(^{-1}\)), is the ability of the cell to deliver power per mass:

\[
p = \frac{I \Delta E''}{\sum m_i} 
\]

(1.14)
Power density

The power density, $P_v$ (W dm$^{-3}$), is the power divided by the volume of the cell:

$$P_v = \frac{l \Delta E^\prime}{\sum V_i} \quad (1.15)$$

The charge/discharge rate

When electrochemically cycling a cell the term charge/discharge rate or C-rate ($C/\Delta t$) is often employed to describe the time-frame for either one full charge or discharge. $C$ denotes either a theoretical charge capacity of a cell or battery (Ah) or the nominal capacity of a cell or battery as indicated by the manufacturer. For example $C/37$ therefore means a current theoretically allowing a full discharge in 37 hours.

Irreversible capacity

It is also important to define how much capacity is lost after each cycle. Irreversible capacity loss is therefore explained by the following equation:

$$\text{Irreversible Capacity} = \frac{n_{th \, \text{Charge}} - n_{th \, \text{Discharge}}}{n_{th \, \text{Charge}}} \times 100 \% \quad (1.16)$$
1.4 The lithium-ion battery

Lithium is desirable for negative electrodes of high energy density batteries because it combines a very negative redox potential, -3.04 V vs. SHE, with a low comparable weight of ca. 7 g mol\(^{-1}\) [3, 8, 9]. Early lithium systems involved a lithium metal negative electrode, a non-aqueous lithium-ion conducting electrolyte and a transition metal oxide as the positive electrode material, which was capable of lithium insertion; examples of these are MnO\(_2\), MoS\(_2\), and TiS\(_2\). These materials generally have rigid lattices with layer, tunnel or open structures, which allow insertion of lithium-ions without major structural modification of the host material. These lithium cells offered a light-weight, high energy system, but could only be used as a primary cell, because of formation of dendrites during the re-plating of lithium metal in the charging process. This created serious safety problems, such as the overheating of the cell, which in some cases led to cell ignition and/or explosion.

The solution was to replace the metallic lithium negative electrode with another insertion host. This then stored lithium-ions from the intercalation compound of the positive electrode.

Since the electrochemical potentials (\(\bar{\mu}\)) for the lithium insertion/extraction processes of both electrodes are different, the role of the more negative electrode is to uptake lithium-ions from the more positive lithium intercalation host during the charge step and then to release the lithium-ions in the discharge step (Equations 1.17-1.19). During discharge the lithium-ions go from a high energy state in the negative electrode to a low energy state in the positive electrode while the electrons pass through an external circuit with a release of energy. The electrolyte takes no part in the reaction except for the conveyance of the electroactive lithium ions in between both electrodes (Figure 1.1). Replacement of metallic lithium by a lithium insertion compound improves both cell life and safety, but the trade-off is a lower specific charge and cell voltage.

Positive:  \[ LiMO_2 \leftrightarrow Li_{1-x}MO_2 + xLi^+ + xe^- \]  \hspace{1cm} (1.17)

Negative:  \[ C + xLi^+ + xe^- \leftrightarrow Li_xC \]  \hspace{1cm} (1.18)

Overall:  \[ LiMO_2 + C \leftrightarrow Li_xC + Li_{1-x}MO_2 \]  \hspace{1cm} (1.19)
Figure 1.1: Schematic of the electrochemical process in the lithium-ion cell.

At the time of writing the present specific power and energy densities for commercial lithium-ion batteries at the cell level stands at ca. 100 W kg\(^{-1}\) and 160 Wh kg\(^{-1}\). High power lithium-ion cells can reach power densities of 3000 W kg\(^{-1}\) but with the exchange being a lower energy density of 80 Wh kg\(^{-1}\) [10]. The Ragone plot (Figure 1.2) furthermore shows the superior performance of the lithium ion battery compared to alternative battery systems such as lead acid and nickel/metal-hydride, where their maximum respective energy densities are only 30 and 70 Wh kg\(^{-1}\) respectively. An outline of the different reaction potentials of common electrode materials for the lithium-ion battery is illustrated in Figure 1.3.
Introduction

Figure 1.2: Ragone plot of numerous battery systems and supercapacitors, redrawn from [10].

Figure 1.3: Overview of the different reaction potentials of electrode materials of the lithium-ion battery. White rectangles represent the positive electrode materials and shaded rectangles the negative electrode material. On the left y-axis the materials are plotted against Potential vs. Li/Li⁺ and on the right y-axis against potential vs. the standard hydrogen electrode (SHE) [3, 8, 11].
1.4.1 Negative electrode materials

Graphitic carbons are at the present time the most often employed material for the negative electrode, because of their low cost and non-toxicity [8, 12, 13]. Table 1.1 lists possible alternative materials for the negative electrode.

Table 1.1: Negative electrode materials [8, 12, 13].

<table>
<thead>
<tr>
<th>Negative Electrode Material (Reduced phase in brackets)</th>
<th>Molar mass/ g mol⁻¹ (Related to lithium-free material)</th>
<th>Theoretical specific charge capacity/ Ah kg⁻¹ (Related to lithium-free material)</th>
<th>Potential of reaction/ V vs. Li/Li⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li metal</td>
<td>6.94</td>
<td>3862</td>
<td>0</td>
</tr>
<tr>
<td>Graphite (LiC₆)</td>
<td>72.06</td>
<td>372</td>
<td>0.1</td>
</tr>
<tr>
<td>Graphite (LiC₆)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hard carbons (LiC₆)</td>
<td>-</td>
<td>400-2000</td>
<td>0·1 V</td>
</tr>
<tr>
<td>Al (LiAl)</td>
<td>26.98</td>
<td>993</td>
<td>0.35</td>
</tr>
<tr>
<td>Sn (Li₂Sn₃)</td>
<td>593.55</td>
<td>948</td>
<td>0.42 - 0.66</td>
</tr>
<tr>
<td>Sb (Li₃Sb)</td>
<td>121.75</td>
<td>660</td>
<td>0.9</td>
</tr>
<tr>
<td>Si (Li₂₂Si)</td>
<td>28.09</td>
<td>4200</td>
<td>0.5</td>
</tr>
<tr>
<td>Cu₆Sn₅ (Li₂₂Sn₅ + 6Cu)</td>
<td>974.73</td>
<td>605</td>
<td>0.1</td>
</tr>
<tr>
<td>WO₂ (LiWO₂)</td>
<td>215.85</td>
<td>124</td>
<td>0.3 - 1.4</td>
</tr>
<tr>
<td>MoO₂ (LiMoO₂)</td>
<td>127.94</td>
<td>209</td>
<td>0.8 - 2.0</td>
</tr>
<tr>
<td>MoS₂ (LiMoS₂)</td>
<td>160</td>
<td>168</td>
<td>1.3 - 2.3</td>
</tr>
<tr>
<td>TiS₂ (LiTiS₂)</td>
<td>112.01</td>
<td>239</td>
<td>1.5 - 2.7</td>
</tr>
<tr>
<td>Spinel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li₄Ti₅O₁₂ (Li₇Ti₅O₁₂)</td>
<td>459.26</td>
<td>175</td>
<td>1.56</td>
</tr>
<tr>
<td>Anatase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂ (Li₀.₅TiO₂)</td>
<td>80</td>
<td>168</td>
<td>1.78</td>
</tr>
</tbody>
</table>

Carbonaceous materials

The great advantage of carbon materials is that the redox potential of lithiated carbon materials is almost identical to that of metallic lithium at ca. 0.2 V vs. Li/Li⁺. The insertion of lithium into carbon will be referred throughout this thesis as intercalation; intercalation being formally described as the insertion of a guest species into layered host structure, without any major resulting structural changes. In half-cell reactions against metallic lithium, lithium ion
intercalation into carbon is referred as the discharge step and de-intercalation process is the charge step.

\[ C_n + xLi^+ + xe^- \leftrightarrow Li_xC_n \]  \hspace{1cm} (1.20)

At ambient temperature, graphitic carbon intercalates one lithium atom per six carbon atoms to form the compound, LiC₆ [8]. The maximum attainable specific charge capacity of the LiC₆ electrode is 372 Ah kg⁻¹ (based on the carbon weight only). Particularly during the first charge step of graphite electrodes, some amount of charge is consumed in an irreversible way. This is typical for all types of carbon electrodes. It is caused by side reactions involving the decomposition of the electrolyte, which induces the formation of a solid electrolyte interphase (SEI) on the electrode surface [14]. The SEI prevents further electrolyte decomposition and allows the transfer of ions from the electrolyte into the electrode [15-18]. The type of electrolyte used strongly affects the formation of the SEI film. A common electrolyte solvent, propylene carbonate (PC), undergoes reduction at around 0.8 V vs. Li/Li⁺ [19, 20]. At a slightly more positive potential the intercalation of PC solvated lithium ions intercalate into graphite takes place. This leads to an expansion of the graphene layers. Therefore exfoliation of the graphite will take place before a stable SEI film is able to be formed. On the other hand, ethylene carbonate (EC) is reduced much faster than PC. Thus, the SEI is formed rapidly and prevents further solvated intercalation of lithium [21].

Amongst the non-graphitic carbons there are hard carbons. Here the lithium can be inserted not only between the graphene layers but also into the voids of this material and onto the sides of isolated graphene layers. Such carbons show specific charge capacities of around 400 to 2000 Ah kg⁻¹ and are mainly obtained by pyrolysis of sugars or polymers. The main problem of these hard carbons is the high irreversibility leading to poor cycling stability. This suggests that lithium becomes trapped with the carbon matrix and indicates possible formation of stable LiCₓ compounds [8].
**Lithium-metal alloys**

Due to their much higher theoretical specific charge capacities compared to graphite, binary or ternary lithium-metal alloys, such as tin [22, 23], aluminium [24], antinomy [23], silicon [25] and copper-tin [26] are one of the most well investigated classes of materials. However the main problem encountered with these alloys are the huge volume changes when lithium is either incorporated or removed [27]. As a result, mechanical stress and cracks occur during cycling, which lead to electrochemically inactive particles leading to considerably poor cycle stabilities.

**Layered Transition Metal Oxides**

Transition metal oxides with a layered structure favourably permit lithium intercalation or de-intercalation. Nevertheless the potentials at which this process takes place often occurs at potentials in the region much above the Li/Li⁺ couple and much lower than the 4V positive electrode material. Therefore a greatly reduced voltage is obtained when these materials are combined in the cell resulting in low energy and power densities for these systems [8].

**Titanium compounds**

Titanium containing compounds such as the anatase form of titanium dioxide (TiO₂) [28] and the titanium spinel (Li₄Ti₅O₁₂) insert lithium at potentials around 1.78 and 1.56 V vs. Li/Li⁺ respectively [29]. This potential would lead to a low overall cell voltage and poor energy densities. Nevertheless these materials are of interest because of their rapid discharge and charge properties, due to a high diffusion rate of lithium within these materials. Li₄Ti₅O₁₂ is under serious consideration as the negative electrode in high-power cells since a lithium insertion potential of 1.56 V avoids the danger of lithium metal deposition at high charge rates, which may occur if graphitic carbon is used [11].
1.4.2 Positive electrode materials

The good cyclability and stability of lithium cobalt oxide (LiCoO$_2$) has allowed it to become the most widely used positive electrode material in commercial lithium-ion batteries [3, 8, 11, 12]. Alternatives to the use of LiCoO$_2$ are being investigated due to its high toxicity and low natural abundance. It has the $\alpha$-NaFeO$_2$ structure with the oxygens in cubic close-packed arrangement. Though the energy density of LiCoO$_2$ containing commercial cells have doubled since their introduction to 400 Wh dm$^{-3}$, the high price of this material limits its use to the small cells found in mobile phones and laptops. LiNiO$_2$ is isostructural with LiCoO$_2$, its use as a viable electrode material is limited due to safety issues due to its instability at low lithium content.

Lithium manganese spinel (LiMn$_2$O$_4$) and the lithium iron phosphate (LiFePO$_4$) are possible replacements [3]. LiMn$_2$O$_4$ is non-toxic and relatively abundant and therefore cheaper than cobalt containing materials, though it does have a lower specific charge capacity and poorer cyclability. The anionic lattice of LiMn$_2$O$_4$ contains cubic close-packed oxygen ions and is closely related to the $\alpha$-NaFeO$_2$ layer structure, differing only in the distribution of the cations amongst the available tetrahedral and octahedral holes. This material is of particular interest as the positive electrode of a high-power lithium-ion battery for hybrid electric vehicles. Though at high charge rates this material only has a specific charge capacity of only 80 Ah kg$^{-1}$.

LiFePO$_4$ has the olivine structure, which consists of corner sharing FeO$_6$ octahedra and PO$_4^{3-}$ tetrahedral anions, with lithium occupying the octahedral holes. Though pure LiFePO$_4$ has a very low conductivity ($10^{-9}$ S cm$^{-1}$), it can be used at 90% of its theoretical charge capacity (165 Ah kg$^{-1}$) by reducing the particle size (< 1 $\mu$m) and ensuring that electrodes possess a well dispersed conductive carbon matrix. Table 1.2 displays the other candidate materials for the positive electrode.

The reaction at the positive electrode can be described as follows:

$$\Delta xLi^+ + \Delta xe^- + Li_x(HOST) \leftrightarrow Li_{x+\Delta}(HOST)$$ (1.21)

where (HOST) is an insertion cathode.
### Table 1.2: Positive electrode materials [3, 8, 11, 12].

<table>
<thead>
<tr>
<th>Positive Electrode Material (Oxidised phase in brackets)</th>
<th>Molar mass/ g mol⁻¹ (Related to lithiated material)</th>
<th>Theoretical specific charge capacity/ Ah kg⁻¹ (Related to lithiated material)</th>
<th>Potential of reaction/ V vs. Li/Li⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMnO₂ (LiₓMnO₂)</td>
<td>93.88</td>
<td>140 (0.5 &lt; x &lt; 1)</td>
<td>2.8 - 3.5</td>
</tr>
<tr>
<td>LiCoO₂ (LiₓCoO₂)</td>
<td>97.87</td>
<td>137 (0.5 &lt; x &lt; 1)</td>
<td>3.5 - 4.3</td>
</tr>
<tr>
<td>LiNiO₂ (LiₓNiO₂)</td>
<td>97.63</td>
<td>192 (0.3 &lt; x &lt; 1)</td>
<td>3.5 - 4.2</td>
</tr>
<tr>
<td>LiNi₁ₓCoₓO₂ (LiₓNi₁₋ₓCoₓO₂)</td>
<td>97.75ᵃ</td>
<td>200 (0.5 &lt; x &lt; 1)</td>
<td>3.5 - 4.0</td>
</tr>
<tr>
<td>LiMn₀.₃₃Ni₀.₃₃Co₀.₃₃O₂ (LiₓMn₀.₃₃Ni₀.₃₃Co₀.₃₃O₂)</td>
<td>96.46</td>
<td>167 (0.4 &lt; x &lt; 1)</td>
<td>3.6 - 4.1</td>
</tr>
<tr>
<td>LiMn₂O₄ (LiₓMn₂O₄)</td>
<td>180.82</td>
<td>148 (0 &lt; x &lt; 1)</td>
<td>3.7 - 4.3</td>
</tr>
<tr>
<td>LiFe₅O₈ (LiₓFe₅O₈)</td>
<td>414.17</td>
<td>130</td>
<td>1.7</td>
</tr>
<tr>
<td>LiFePO₄ (LiₓFePO₄)</td>
<td>157.76</td>
<td>170 (0 &lt; x &lt; 1)</td>
<td>3.1</td>
</tr>
<tr>
<td>LiMnPPO₄ (LiₓMnPPO₄)</td>
<td>156.85</td>
<td>171 (0 &lt; x &lt; 1)</td>
<td>4.2</td>
</tr>
<tr>
<td>LiCoPO₄ (LiₓCoPO₄)</td>
<td>160.83</td>
<td>167 (0 &lt; x &lt; 1)</td>
<td>4.7</td>
</tr>
<tr>
<td>LiV₂O₅ (LiₓV₂O₅)</td>
<td>188.82</td>
<td>142 (0 &lt; x &lt; 1)</td>
<td>2.8</td>
</tr>
<tr>
<td>Li₃.₆V₆O₁₃ (LiₓV₆O₁₃)</td>
<td>538.62</td>
<td>179 (0 &lt; x &lt; 3.6)</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Key requirements for the positive electrode are [8]:

- High free energy of reaction with lithium
- Wide range of x (amount of insertion)
- A reasonably low mass and volume per Faraday charge stored
- Small structural change on reaction
- Good reversibility of reaction
- Rapid diffusion of lithium within the host lattice
- Good electronic conductivity
- Non-solubility in electrolyte
- Ease and low cost of synthesis
1.4.3 Electrolyte

In this work, the term electrolyte refers to the solution of both the solvent and the salt. This is contrary to the nomenclature in physical chemistry, which defines the electrolyte as only the salt alone.

The characteristics which a suitable lithium-ion battery electrolyte must fulfil are listed below [12, 18]:

- It should be able to dissolve salts to sufficient concentration. In other words it should have a high dielectric constant ($\varepsilon$).
- A good ionic conductivity ($>1\text{ mS cm}^{-1}$) in order to minimise internal resistance
- It should be fluid (low viscosity $\eta$), so that facile transport can occur
- Stable in a wide electrochemical potential window from 0 to 5 V vs. Li/Li$^+$
- Good thermal (up to 90 °C) and chemical stability
- Compatibility with other cell components
- Low cost, low toxicity and low flammability

Three classes of electrolytes are used or under development in lithium-ion batteries:

*Liquid organic electrolytes*

Liquid organic electrolytes consist of pure or mixtures of aprotic organic solvents into which a lithium salt is dissolved. Organic electrolytes of interest include ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) [18].
Polymer electrolytes

A liquid electrolyte must be contained in a porous solid or elastomeric separator which prevents direct contact between the electrodes [30]. The problems of mechanical mobility in electrolytes are offered a solution through the use of polymer electrolytes with elastomeric qualities. The polymer electrolyte, where the lithium ions are incorporated into a polymer matrix gives the advantage that the polymer is solid but flexible, so that the design and assembly of the battery is kept simple. Polyethylene oxide was found to solvate most metal salts with easily dissociable anions to form elastomeric solutions with conductivities up to $10^{-4}$ S cm$^{-1}$ above the melting point of $65 \, ^\circ\text{C}$ [9].

Ionic electrolytes

Ionic liquids are substances, which are made up only from ions and have a melting point of $<100 \, ^\circ\text{C}$ or are, ideally, even liquid at room temperature ca. $20 \, ^\circ\text{C}$ [31-35]. They have recently found application for lithium metal and lithium-ion batteries because they have shown a relatively good electrochemical stability [36-44] with a high ionic conductivity [33, 45-47]. But these electrolytes possess a large viscosity which limits high-rate cycling [33, 34, 48, 49].
The interest in the utilisation of ionic liquids as battery electrolytes results from their following properties:

- They show a much reduced or even non-existent flammability. Therefore the risks of burning and/or explosion of a misused battery is considerably lower, hence the safety of the battery is enhanced.

- They do not show a noticeable vapour pressure, even at elevated temperatures and are thermally [40, 41] and chemically [34] very stable. This could increase the upper limit of the temperature and hence safety limits in which a battery could be used.

- They have comparatively high electrochemical stability at highly oxidising potentials [36, 50]. This reduces the problems of the use of 4 V transition metal oxides against overcharge.

- In general they are not environmentally hazardous [37, 51, 52].

- They possess a high conductivity.

Of which the ionic liquid salt 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl) imide (EMI TFSI) when used with a lithium salt (such as LiTFSI) is one of the most promising candidates for use in lithium metal, lithium-ion batteries [53]. It has been recently shown that when vinylene carbonate (VC) is used as an additive it is possible to intercalate lithium into microcrystalline graphite with good cycle stability. VC ensures that a stable film formation forms on the graphite before any reduction of the EMI cation can occur [54]. Furthermore good cycling behaviour of lithium-ion batteries containing LiCoO₂ [55] or LiFePO₄ [56] against Li₄Ti₅O₁₂ in ionic liquids has been demonstrated.

*Properties of lithium-ion battery electrolytes*

The majority of the liquid solvents used in the lithium-ion battery are either organic esters or ethers. The most commonly used solvents are listed with a selection of physical properties in Table 1.3 [12, 18, 57].
Table 1.3: Properties of some organic and ionic liquid solvents used in electrolytes for lithium-ion batteries and supercapacitors [12, 18, 57].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Molar mass/ g mol⁻¹</th>
<th>m.p./ °C</th>
<th>b.p./ °C</th>
<th>Dielectric constant</th>
<th>Viscosity/ cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene carbonate (EC)</td>
<td>88</td>
<td>39-40</td>
<td>248</td>
<td>89.6</td>
<td>1.90 (40°C)</td>
</tr>
<tr>
<td>Propylene carbonate (PC)</td>
<td>102</td>
<td>-49</td>
<td>240</td>
<td>64.9</td>
<td>2.53</td>
</tr>
<tr>
<td>Dimethyl carbonate (DMC)</td>
<td>90</td>
<td>3</td>
<td>90</td>
<td>3.1</td>
<td>0.59 (20°C)</td>
</tr>
<tr>
<td>Ethyl-methyl carbonate (EMC)</td>
<td>104</td>
<td>-55</td>
<td>108</td>
<td>3.0</td>
<td>0.65</td>
</tr>
<tr>
<td>Diethyl carbonate (DEC)</td>
<td>118</td>
<td>-74.3</td>
<td>127</td>
<td>2.8</td>
<td>0.75</td>
</tr>
<tr>
<td>1, 2-Dimethoxyethane (DME)</td>
<td>90</td>
<td>-58</td>
<td>84</td>
<td>7.2</td>
<td>0.455</td>
</tr>
<tr>
<td>γ-butyrolactone (GBL)</td>
<td>86</td>
<td>-43</td>
<td>203</td>
<td>39.1</td>
<td>1.75</td>
</tr>
<tr>
<td>Acetonitrile (ACN)</td>
<td>41</td>
<td>-45.7</td>
<td>81.6</td>
<td>35.95</td>
<td>0.3409</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl) imide (EMI TFSI)</td>
<td>391</td>
<td>-15</td>
<td>Thermal decomposition</td>
<td>&lt; 200</td>
<td></td>
</tr>
</tbody>
</table>

The lithium salt also has to fulfil some criteria: it should be inexpensive, able dissolve and dissociate in non-aqueous media, be non-toxic and stable against thermal and oxidative decomposition and should remain inert with other cell components. Also an important factor for the overall performance of the battery is the conductivity of the resulting electrolyte (Table 1.4) [12, 18, 57]. Of all the lithium salts listed in the table, the salt of choice is lithium hexafluorophosphate (LiPF₆) because it is the only salt to just satisfy each major requirement [18]. Lithium perchlorate (LiClO₄) is possibly explosive, lithium tetrafluoroborate (LiBF₄) has a moderate ion conductivity, lithium hexafluoroarsenate (LiAsF₆) is potentially toxic and lithium bis(trifluoromethylsulfonyl) imide causes severe aluminium (positive electrode current collector) corrosion.

Table 1.4: Conductivity of solvents and salts (mS cm⁻¹) [12, 18, 57].

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>LiPF₆</th>
<th>LiClO₄</th>
<th>LiBF₄</th>
<th>LiAsF₆</th>
<th>Li Imide (LiTFSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>5.8</td>
<td>5.6</td>
<td>3.4</td>
<td>5.7</td>
<td>5.1</td>
</tr>
<tr>
<td>DMC</td>
<td>3.0</td>
<td>3.0</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EC:DMC 1:1</td>
<td>10.7</td>
<td>8.4</td>
<td>4.9</td>
<td>11.1</td>
<td>9</td>
</tr>
<tr>
<td>EC:PC 1:1</td>
<td>6.6</td>
<td>14</td>
<td>4.3</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
1.5 Electrochemical double-layer capacitors

In contrary to batteries, energy storage in electrochemical double-layer capacitors (EDLCs), also referred to as supercapacitors, is based on charge separation at the interface between an electronic conductor and an electrolyte solution with ionic conductivity [58-61]. Energy is stored in the electric field established in the double-layer consisting of electronic charges in the electrode and the according counter-ions in the electrolyte (Figure 1.4) [7]. The use of high surface area carbon electrodes results in a considerable charge storage capability and therefore can provide high specific capacitances and power densities (see Ragone Plot; Figure 1.1). When the energy storage occurs solely via double-layer charging and discharging, the lifetime of an EDLC device is expected to be considerable. Indeed EDLCs can be cycled for 500,000-1,000,000 cycles with a very low change in characteristics [60]. Consequently, relative to batteries, the advantages of EDLCs as pulse power devices are a high power density (ca. 1000-10000 W kg\(^{-1}\)) [60], a high efficiency, and long shelf and cycle life [60]. However the main disadvantage is their low energy densities (ca. 5-10 Wh kg\(^{-1}\)) [59, 60], especially when compared with the lithium-ion battery (ca. 160 Wh kg\(^{-1}\)) [8]. This drawback limits their use to applications that require a relatively small amount of energy before the EDLC can be recharged, which takes place in a matter of seconds.

The energy \(W\) stored in a capacitor is given by:

\[
W = \frac{1}{2} C U^2
\]

(1.22)

where, \(C\) is its capacitance and \(U\) is the cell voltage.

The most standard approach to determine maximum power, \(P\), is at the matched impedance condition where one-half the energy of the discharge is in the form of electricity and the other half is in heat. The maximum power at this point is given by:

\[
P = \frac{U^2}{4 R_{\text{eff}}}
\]

(1.23)

where, \(R_{\text{eff}}\) is the total effective series resistance (ESR).
Figure 1.4: Principle of an electrochemical double-layer capacitor and illustration of the potential drop at the electrode/electrolyte interface. Adapted from [59].

Possible future applications for the EDLC could be in a hybrid car [62] either providing energy for acceleration or regenerative breaking. The main present applications are in consumer electronic products where they provide backup power to memory devices during a power outage (e.g. in video recorders, TV satellite receivers) [59]. Electrochemical capacitors also provide the main part of the pulse power to start Siberian Diesel locomotives [59].
1.6 Raman spectroscopy

Electrochemical reactions occur at the surface of electrodes. The main scientific challenge lies in improving the basic understanding of the electrode-electrolyte interface in the hope of devising new solid-solid or solid-liquid interfaces [63-65]. Surface sensitive techniques are therefore applicable in following the course of these reactions in order to improve fundamental knowledge of the chemical processes occurring. Raman spectroscopy has been shown to have been a useful method to follow the electrode surface changes during ion insertion and extraction [66]. It can offer specific chemical information about variations in bond lengths and coordination environments, as well as monitoring local disorder on the electrode surface [67].

Raman scattering is the inelastic scattering of light by matter. When a photon of light \((h\nu_0)\), too low in energy to excite an electronic transition, interacts with a molecule it can be elastically or in-elastically scattered. The elastically scattered light is called Rayleigh scattering; it is strong and has the same frequency as the incident beam \((\nu_0)\) (usually from a laser source). The in-elastically scattered light is called Raman scattering, it is very weak (approximately \(10^9\) of the intensity of the incident exciting radiation) and has frequencies \(\nu_0 \pm \nu_m\), where \(\nu_m\) is a vibrational frequency of a molecule. The \(\nu_0 - \nu_m\) and \(\nu_0 + \nu_m\) lines are called the Stokes and anti-Stokes lines respectively (Figure 1.5).

![Raman Scattering Diagram](image-url)

**Figure 1.5:** Idealised model of Rayleigh scattering and Stokes and anti-Stokes Raman scattering.
Therefore, in Raman spectroscopy, the vibrational frequency \( (v_m) \) is measured as a shift from the incident beam frequency \( (v_0) \) (Figure 1.6). In Raman spectroscopy a vibration will be visible in the Raman spectra if during the course of the vibration, there is a change in polarisability [68].

![Raman spectrum of anatase form of titanium dioxide (TiO₂) showing Rayleigh line, and stokes and anti-stokes lines.](image)

**Figure 1.6:** Raman spectrum of anatase form of titanium dioxide (TiO₂) showing Rayleigh line, and stokes and anti-stokes lines.

Schematic descriptions to clarify which vibrational modes are Raman active and which ones are inactive are illustrated in Figure 1.7. Furthermore the figure compares Raman activity with infrared activity of carbon dioxide (CO₂). Group theory can be used to predict which modes are Raman active [69, 70] and the correlation method in particular can be employed to predict these modes in solids [71]. The following references [68, 72, 73] provide further reading into the classical and quantum theory of Raman spectroscopy which will not be discussed any further here.
From a historical perspective the Raman scattering was first predicted in 1923 by A. Smekal [74]. This phenomenon was then first observed in 1928 in liquids by C. V. Raman and K. S. Krishnan [75]. C. V. Raman later received the Nobel Prize for physics for his discovery in 1935 and the honour of having the discovered effect named after him. But Raman spectroscopy did not come into more general and widespread use in academic and industrial research until the 1960s with the development of the laser. With the advent of an intense, reliable, coherent light source, spectra could be recorded in a short time from very small sample volumes, coloured samples, solids, liquids, gases, at extreme high or low temperatures and pressures and other non-standard conditions.

The latest development in Raman spectroscopy is tip-enhanced near-field Raman microscopy (TERS) [76-81]. This method makes use of the electric field enhancement effect at the proximity of a metal coated atomic force microscope (AFM) tip which allows for Raman nano-imaging. The effect is similar to the one seen in the detection of molecules on the metal-island film, known as surface-enhanced Raman spectroscopy (SERS) [82, 83]. Kawata et al. [80, 84-89] in particular have demonstrated nano-scale Raman measurements of individual carbon nanotubes and deoxyribose nucleic acid (DNA) clusters.

The recent emergence of ultraviolet-wavelength-excited Raman spectroscopy as a tool for characterisation of metal oxides is also noted [90-95].
### Figure 1.7

Raman and infrared active modes for CO₂, adapted from [68].
2

EXPERIMENTAL

2.1 Electrochemical methods

In an electrochemical experiment the electrode process on one electrode, the working electrode is usually studied. Such investigations are carried out by either controlling the cell potential (potentiostatic control) or the current that passes through the cell (galvanostatic control). The other electrode, the counter electrode, is used to complete the circuit. Occasionally a third electrode is employed, the reference electrode. When this is the case the electrode potential is monitored with respect to the reference electrode. During the electrochemical measurements, cells were either under potentiostatic or galvanostatic control and the appropriate potential or current was regulated by a Computer Controlled Cell Capture device (CCCC, Astrol Electronics AG, Oberrrohrdorf, Switzerland).

2.1.1 Cyclic voltammetry

Cyclic voltammetry is a widely used method for studying electrode processes; the determination of the thermodynamics and kinetics of electron transfer at the electrode-solution interface. It is often employed as the first method to characterise new systems. The cell is cycled in a potential window, where the potential applied on the working electrode is continuously changed with a constant rate. Essentially, the potential is swept through the potential range where an electrode reaction occurs before the direction of scan is
reversed in order to define whether (a) the product of electron transfer is stable or (b) reaction intermediates or the final products are electroactive. The change of potential as a function of time is called \textit{scan rate}. The potential sweep can be described by its initial ($E_i$), switching ($E_s$), final ($E_f$) potentials, and sweep (scan) rate $v$. The potential as a function of time ($t$) is:

\begin{equation}
E = E_i + vt \quad \text{(forward sweep)} \tag{2.1}
\end{equation}

\begin{equation}
E = E_s - vt \quad \text{(reverse sweep)} \tag{2.2}
\end{equation}

With scan rate defined as:

\begin{equation}
\nu = \frac{\Delta E}{\Delta t} \quad \Delta E/\Delta t \ (mV \ s^{-1}) \tag{2.3}
\end{equation}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{potential_waveform.png}
\caption{Potential waveform of cyclic voltammetry}
\end{figure}

Other important parameters are the maximum and minimum potential ranges which define the potential window. The choice of this potential window must take into account the stability range of the chosen electrolyte, to therefore avoid its decomposition. In Figure 2.2 an example of the cyclic voltammogram of the graphite SFG44 is shown.
Figure 2.2: Example of a cyclic voltammogram of graphite SFG44. Scan rate = 0.5 mV s⁻¹ from 3 V to 0.3 V vs. Li/Li⁺ in 1 mol dm⁻³ tetraethylammonium-tetrafluoroborate (TEABF₄) in acetonitrile.

2.1.2 Galvanostatic measurements

In a galvanostatic measurement a constant current is applied between the working and counter electrodes. The current is applied until the set upper or lower potential limits are reached. For the working electrode a negative current would cause reduction and the positive current oxidation. The examination of the variation of potential with time is also called chronopotentiometry. This method has an important advantage over cyclic voltammetry, because the current or current density is kept constant, the electrode process is investigated under real battery working conditions (Figure 2.3).
For an insertion/de-insertion process into a compound $M$:

$$L_i x M + \Delta x Li^+ + \Delta x e^- \leftrightarrow L_i x+\Delta x M$$  \hspace{1cm} (2.4)

The amount of the guest species can be calculated as follows:

$$\Delta x = \frac{I \Delta t M_r}{n F m}$$  \hspace{1cm} (2.5)

$I = \text{current (A)}$  \hspace{1cm} $M_r = \text{molecular mass (g mol}^{-1}\text{)}$

$\Delta t = \text{time interval (s)}$  \hspace{1cm} $m = \text{mass of the active component (g)}$

Figure 2.3: Example of a galvanostatic measurement. The potential-time curve (---) of the first lithiation and de-lithiation cycles of graphite SFG15 in 1M LiClO$_4$ in w/w 1:1 EC:DMC are shown at 10 mA/g, which corresponds to a C/37 charge rate. The current-time plot is in addition displayed (---).
2.2 Raman instrumentation

Raman spectra were collected at room temperature (ca. 23°C) by a confocal Raman microscope (Labram series, Jobin Yvon SA, ex DILOR SA) using a helium-neon (HeNe) laser 632.8 nm with around 1 mW laser power as the excitation source. Raman band positions were calibrated against the spectrum of a neon lamp (Penray, Oriel) with a resolution of 1 cm⁻¹.

The set-up (Figure 2.4) allowed samples to be mounted upon an X-Y computer controlled moveable table. A closed circuit television camera (CCTV) permitted the magnified viewing of the surface of the electrode onto a television screen. This allowed the selection of measurement points, as well as ensuring that the laser was focused directly upon the surface. During measurement an autofocus unit selects the optimum focal position to allow for the strongest Raman signal. The scattered light is then back-scattered through the objective and then passes through a notch filter and beam splitter where it is sent through two pin-holes (the hole and the slit), which control the size of the confocal volume (i.e. the volume of light scattered from the sample surface which is to be evaluated). The non discriminated light passes into the spectrometer where a grating splits the scattered light into range of energy which it is counted by a charge coupled device (CCD). CCDs are silicon-based integrated circuit chips that are very sensitive to light. Each chip contains thousands of pixels that allow the whole spectrum to be taken at once in less than a second. The spectrum measured is then analysed and subsequently displayed on a computer [68, 72, 73].
2.3 **Ex situ Raman microscopy**

Measurement *ex situ* is the most straightforward Raman experiment. The sample of interest is mounted onto a glass slide and the objective focuses the laser onto the surface and the Raman spectrum of a single point is collected in the back-scattering configuration.

2.3.1 **Ex situ Raman mapping**

Direct Raman imaging or mapping of samples results in the creation of a two-dimensional (2D) picture at a chosen wavelength which is characteristic of a molecular compound within the fully illuminated specimen (Figure 2.5). Mapping of graphite or oxide electrodes were carried out on a computer controlled X-Y table. For *ex situ* mapping experiments, in order to obtain the highest confocal resolution of around (1 μm)$^3$, the 100x objective was used.
Figure 2.5: Principle of Raman imaging adapted from [73].
2.4 In situ Raman microscopy

Electrochemical experiments can be performed in order to understand electrode processes, but they can rarely deliver information on what is happening at a molecular or microscopic level on the electrode surface and or bulk. In situ techniques are a powerful tool to investigate electrode processes. The main advantage is that contrary to most ex situ methods, the exposure of the working electrode to moisture, air or vacuum, which may change the properties and surface of the electrode, is avoided. Investigations of electrode reactions therefore benefit substantially when it is possible to record spectra for the electrode/solution interface as the electrochemical response is obtained. Spectroelectrochemistry is a subset of in situ methods and other examples as well as Raman microscopy also include uv-visible (UV-vis) and infra-red (IR) spectroscopies [7].

During in situ Raman microscopic measurements a wide angle 80x objective (Olympus) was used to focus the laser light onto the electrode surface. The wide angle allowed the focal point to be inside the cell, at the electrode surface without the objective pressing on the glass window, which is used to seal the Raman cell. Measurement is made in a backscattering configuration through the thin glass window onto the upper electrode that is visible through the hole in the current collector. The laser power was lowered to ca. 0.25 mW with a filter to avoid significant heating of the electrode. The confocal hole and slit set at 3 μm and 2 μm respectively, allowed measurement of a confocal volume of (2 - 3 μm)$^3$ on the surface. This led to each spectrum requiring between 60 - 180 seconds measurement time and usually because of the good signal to noise ratio with one or two accumulations, with little or no detection of electrolyte bands. The spectroelectrochemical cell was electrochemically cycled either under potentiostatic or galvanostatic conditions.
2.4.1 In situ Raman cells

Three types of in situ Raman cells were used during this thesis: a two-electrode cell, a three-electrode cell and a three-electrode temperature-variable cell. The following information provides a description of each cell and the standard method of cell assembly and set-up. All in situ cells used in this study have the system set up in a coin-cell arrangement with a circular counter electrode covered with an electrolyte soaked polymer separator and opposite a circular working electrode. Essentially each in situ cell must fulfil two primary functions to allow good electronic contact between the electrodes, whilst preventing short circuits and to seal the electrodes from moisture and air for a reasonable measurement time-frame of at least one week. Other considerations are that the cell is practical and easy to assemble, the cell is flexible enough to investigate various systems and it is designed such that a thin optical window can be used and that the working electrode is placed that the laser does not have to pass through a too thick layer of electrolyte. The perchlorate salt (LiClO₄) was used as the lithium salt instead of the standard lithium hexafluorophosphate (LiPF₆), because of the occurrence of fluorescence effects when using the later salt.

Two-electrode in situ Raman cell

The two electrode in situ Raman cell consists of a stainless steel body (Figure 2.6). The in situ cell set up consisted of a working electrode (active mass < 1 mg) against lithium counter and reference electrode (Aldrich, thickness 0.175 mm, diameter 6 mm). The lithium counter/reference electrode sits on a moveable titanium current collector, which its height can be controlled with a screw to optimise contact. The copper current collector for the working electrode possesses a hole < 1 mm diameter from which the backside of the working electrode can be viewed and measured. Two polypropylene separators (Aldrich) were employed between the electrodes and were wetted with a few drops of electrolyte. Rubber seals (EPDM, KARLREZ) ensure that the cell is air and moisture tight.
The three-electrode Raman cell differs from the two-electrode Raman cell because it permits measurement with a reference electrode. This allows for the investigation of electrochemical double-layer capacitors (EDLC) systems where a separate reference electrode is necessary in order to control the potential.

The cell (Figure 2.7) is comprised of two electrodes with a separator in-between and a reference electrode positioned on the edge of the separator. The working electrode is covered by an aluminium foil also serving as a current collector. The exciting laser beam shines onto the backside of this electrode through a small hole in the centre of the metal foil.

During standard cell preparation, the adjustable spring-loaded screw was positioned so that
the titanium current collector sits almost level within the cell body (PEEK). The O-ring (EPDM) around the current collector (titanium) allows a small vertical freedom of movement when pressure is applied. Onto this was placed the carbon (M150) counter electrode (diameter 9 mm, thickness 0.3 mm, mass ca. 12 mg) over which a glass fibre separator was located. A small amount (ca. 0.5 mg) of the material acting as the working electrode is positioned on the centre of the separator. An aluminium current collector (thickness 15 μm), which contains a small hole in its middle (diameter ca. 1 mm) is placed over the material and pressed down. Electrical contact with the working electrode is achieved via an aluminium wire pushed onto the Al current collector. The reference electrode consisted of a carbon plug (M150) pressed onto a titanium wire covered with a glass fibre cloth, preventing possible short circuit. The inclusion of the counter electrode on a spring allows the pressure within the cell to remain constant if expansion of the graphite material occurs during cycling. The cell was sealed with a thin optical glass window (0.15 mm) and is made air-tight with a rubber seal (EPDM). The cell was assembled in air and was dried for 24 hour at 140 °C and < 0.01 mbar in a vacuum oven, then cooled down to ambient temperature in argon atmosphere, transferred to a glove box (argon, < 1 ppm water), where it was filled with electrolyte solution.
Figure 2.7: Three electrode *in situ* Raman cell in (A) the fully assembled stage, (B) three-dimensional perspective and (C) an enlarged area showing the separate components (expanded, not to scale).
Three-electrode in situ Raman temperature-variable cell

In some in situ experiments, a useful parameter to control and vary is the temperature to investigate different intercalation pathways and the operation/kinetics of batteries at high or low temperatures. The temperature variable in situ cell was developed to operate in the temperature range of 0 to 70 °C, which is the practical temperature limit when using liquid electrolyte. The top half of the cell (Figure 2.8) resembles the basic set-up of the three-electrode in situ Raman cell. Except now the adjustable screw and spring-loaded contact are replaced with a heat-exchanger attachment which can pass through water to either cool or heat the cell. A thermal couple sits just below the counter electrode to monitor the internal temperature of the cell. The cell cover and cell body are both constructed from PEEK to act as an insulator. Assembly of the cell is identical to the three-electrode in situ Raman cell.

Figure 2.8: Three-electrode in situ Raman temperature-variable cell in (A) the fully assembled stage and (B) the three-dimensional perspective.
2.4.2 Methods of Raman electrode preparation

Producing an electrode which is easy to manufacture, has a low active mass and can reproduce the electrochemical performance as good as standard test cell electrodes was carried out in variety of methods of which all have their respective advantages and disadvantages, and have their application in different types of experiments (Table 2.1).

Table 2.1: Methods of Raman electrode preparation.

<table>
<thead>
<tr>
<th>Raman Electrode</th>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doctor-blade</td>
<td>Standard method of electrode preparation for both lab-based test-cell measurements and scaled-up industrial preparation of commercial electrodes. In essence electrode slurry consisting of active material, binder and solvent is evenly spread onto a thin metal sheet (copper or aluminium), which acts as both the current collector and support for the electrode. The thickness of the electrode can be precisely controlled leading to uniform electrode sheet from which circular electrodes of desired diameter can be punched. For in situ Raman microscopy this type of electrode can be used in the position usually occupied by the lithium counter electrode on the base of the cell.</td>
<td>Easy production of many electrodes of uniform thickness.</td>
<td>The assembly of the cell is complicated. For the laser to reach the surface of the electrode, both separator and lithium counter electrode require a hole in the centre. Moreover the layer of electrode required to be measured through is relatively thick resulting in a poor signal to noise ratio.</td>
</tr>
<tr>
<td>Copper-foam</td>
<td>By placing a drop of electrode slurry onto a copper-foam (a spongy association of thin copper threads), the working electrode can be placed next to the glass window.</td>
<td>Removes the requirement of holed separator and lithium counter.</td>
<td>Electrodes used were always too thick to use inside in situ cells, leading to frequent breakages of the glass window. Furthermore producing a reliable electrode is also complex with either too small active mass or too large leading to cracking of electrode during construction or during electrochemical experimentation which causes dissociated particles.</td>
</tr>
<tr>
<td>Method</td>
<td>Description</td>
<td>Example</td>
<td></td>
</tr>
<tr>
<td>-------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Drop</strong></td>
<td>A drop of electrode slurry was placed onto a circular current collector (diameter ca. 15 mm) with a small hole punched in its centre (&lt; 1 mm).</td>
<td>Eliminates the necessity of holed separator and lithium counter electrode and can produce thin electrodes. Electrode can be placed in the top position close to the glass window, allowing for an improved signal to noise ratio, as the laser only has to pass through a thin electrolyte layer. Method is poor in creating many electrodes of similar thickness and active mass. Moreover slurry preparation needs to be the correct viscosity, too viscous the solvent evaporates too fast and the slurry blocks the pipette, too liquid the slurry runs off the current collector and does not fully cover the hole in the current collector.</td>
<td></td>
</tr>
<tr>
<td><strong>Doctor-blade-press</strong></td>
<td>Free standing electrode films are produced. Electrode slurries consisting of active material, carbon black (when the active material is not carbon), binder, co-polymer (dibutyl phthalate, DBP) and solvent (acetone) are used. The slurry is mechanically mixed and doctor-bladed at a thickness of 200 µm onto an aluminium sheet (15 µm). The acetone solvent quickly evaporates to give a film which is poorly adhesive to the aluminium. DBP is then extracted from the electrode with ether, to give a free-standing film. From this film circular electrodes can be punched from and then pressed with a rolling machine onto a holed-copper current collector (diameter of hole ca. 1 mm).</td>
<td>Electrodes of uniform active mass and thickness can be easily produced. This is the optimum method for producing Raman electrodes. Method is more time-consuming, but produces the best uniform electrodes of low active mass (&lt; 1 mg).</td>
<td></td>
</tr>
<tr>
<td><strong>Powder</strong></td>
<td>During cell construction a pre-determined amount of active material (&lt; 1 mg) can be placed onto the separator and the holed current collector is brought down upon it. Method is employed in measurements of super-capacitor systems with the three electrode <em>in situ</em> cell.</td>
<td>Ease of cell construction. Behaviour of active material rather than the whole electrode is measured. Only for materials with good conductivity i.e. graphitic carbons. Behaviour of active material rather than the whole electrode is measured.</td>
<td></td>
</tr>
<tr>
<td><strong>Industrial Electrodes</strong></td>
<td>Industrial electrodes are a sandwich of both electrodes and separator.</td>
<td>Measure the state-of-the-art industrial electrode. View changes in both electrodes and separator. Re-think of <em>in situ</em> cell design required to measure cross-section of electrode sandwich layer.</td>
<td></td>
</tr>
</tbody>
</table>
2.5 Scanning electron microscopy (SEM)

A complimentary method to Raman microscopy is scanning electron microscopy (SEM) because the Raman spectra collected can be related with the visual image of the material. Furthermore this techniques used in combination, can be very powerful in the case of detecting surface film formation or monitoring material degradation.

SEM is used primarily to observe the surface topography of samples. In scanning electron microscopy the sample is bombarded with a scanning beam of electrons. The slow moving electrons, generated by the specimen, are collected. These are then amplified and displayed on a cathode ray tube. The electron beam and the cathode ray tube scan synchronously so that an image of the surface of the specimen is formed.

Electrodes for the post mortem SEM study were first washed with a solvent to remove the electrolyte, and dried in an argon atmosphere. SEM images shown in chapters 4, 5 and 6 were performed on a LEO 1530 Gemini microscope, which was operated at low voltage (usually 1 kV) to achieve a suitable contrast of the surface details in the secondary electron images and to minimise charging of the uncoated samples [19]. SEM was also carried out on a field-emission scanning electron microscope (FE-SEM), model Supra 55VP (Carl Zeiss) functioning at an accelerating voltage of 4 kV using an in-lens detector to obtain the secondary electron images. These SEM images are shown in chapter 6. All SEM measurements were carried out with the kind collaboration of Dr. Frank Krumeich, Dr. Hilmi Buqa and Patrick Ruch.
2.6 Transmission electron microscopy (TEM)

In Transmission Electron Microscopy (TEM) the sample is again bombarded with a beam of electrons and the intensity of diffraction of these electrons depends on the orientation of the planes of atoms in a crystal relative to the electron beam. At certain angles the electron beam is diffracted strongly, sending electrons away from the axis of the incoming beam, while at other angles the beam is largely transmitted. The sample can be tilted with respect to the electron beam in order to obtain specific diffraction conditions. A high contrast image can be created by blocking electrons deflected away from the optical axis of the microscope by placing the aperture to allow only non-scattered electrons through. This allows a resolution in the order of Angstroms, which allows the imaging of individual atoms in a crystal. The main drawback to TEM is the extensive sample preparation in order to produce a thin enough sample to be electron transparent. Textural and micro-textural characterisations of powders were performed by means of high resolution TEM with a FEI TECNAI F20 ST microscope. TEM measurements were carried out with the kind collaboration of Dr. Emmanuel Baudrin and Dr. Loïc Dupont.
2.7 X-ray diffraction (XRD)

X-ray diffraction (XRD) is generally used to study bulk structures of materials. XRD is a non-destructive technique, which can be used to identify crystalline phases. The X-rays are scattered by each set of lattice planes at a characteristic angle, and the scattered intensity is a function of the arrangement of atoms in the crystal. The scattering from all the different sets of planes results in a pattern which is unique to the crystal structure of a given compound [96].

X-rays are formed in X-ray tubes when the anode material (usually copper) is irradiated with a beam of high-energy electrons. When the electrons collide with the anode, a continuous spectrum of X-rays is emitted. In addition, photons with energy characteristic of the target material are emitted. A monochromator is used that preferentially suppresses photons with other energies than the characteristic one. Produced X-rays are directed to the sample of study and X-rays with wavelength of the order of lattice spacing are elastically diffracted from the atomic planes in a crystalline material [96]. Re-emitted X-rays interfere, giving constructive or destructive interferences. Bragg’s law describes the diffraction condition from planes with spacing, \( d \):

\[
n\lambda = 2d \sin \theta
\]  

(2.6)

This equation was determined by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913 to describe why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta, \( \theta \)) [97]. The variable \( d \) is the distance between atomic layers in a crystal, and the variable lambda \( \lambda \) is the wavelength of the incident X-ray beam; \( n \) is an integer [98]. Figure 2.10 schematically illustrates interference between waves scattered from two adjacent planes of atoms in a crystal.
Figure 2.10: Reflection of X-rays against lattice planes according to Bragg, \( d \) is the lattice plane distance, \( \theta \) is the reflecting angle, redrawn from [99].

In addition to identify crystalline phases, X-ray diffraction can be used to determine crystal size. This can be obtained from the broadening of the peaks according to the Scherrer formulae [100]:

\[
L = \frac{K\lambda}{\beta \cos \theta}
\]  

(2.7)

where, \( L \) is the crystal size, \( \lambda \) is the x-ray wavelength used, \( K \) is the shape factor of the average crystallite (expected shape factor is 0.9), \( \beta \) is the full width at half maximum (FWHM) in radians and \( \theta \) is the peak position.

XRD patterns were collected in a \( \theta \) \( 2\theta \) configuration using a Philips PW 1729 diffractometer (Cu K\(_\alpha\) radiation, \( \lambda = 1.5418 \) Å). The pattern matching refinements were accomplished using FullProf software. XRD measurements reported in this thesis were carried out with the kind collaboration of Dr. Emmanuel Baudrin and Dr. Loïc Dupont.
EX SITU RAMAN MAPPING OF LITHIUM-ION BATTERY ELECTRODE MATERIALS

The determination of the causes for capacity fading and even more seriously, cell failure, is great incentive to try to understand how materials in composite battery electrodes age with time and with number of intercalation cycles. Ex situ spatial monitoring of surface with Raman microscopy allows the investigation of how the material changes or degrades and furthermore how the distribution of materials on the surface change. In this chapter the Raman spectrum of graphite (the negative electrode) is introduced and explained. Maps examining how the crystallite size varies in an electrode are undertaken. For the positive electrode, the distribution of either lithium cobalt oxide (LiCoO₂) or lithium manganese oxide spinel (LiMn₂O₄) with carbon in composite electrodes is investigated. These are the primary results in order to determine the feasibility of electrode mapping.

3.1 Raman mapping of the graphitic negative electrode

3.1.1 Structure of graphite

Graphite has a layered structure in which sp² hybridised carbon atoms are arranged in a hexagonal pattern within each layer; with the graphene layers stacked ABAB (Figure 3.1i) corresponding to the space group P6₃/mmc (D₆h) [101-105]. A hexagonal unit cell results,
with dimensions \( a = b = 2.46 \, \text{Å} \) and \( c = 6.71 \, \text{Å} \), with four atoms per unit cell. In graphite the C-C bond distance is 1.42 Å, whilst the distance between the graphene sheets is 3.35 Å [106]. Graphite can also crystallise in the rhombohedral form with a stacking sequence of ABCABC (Figure 3.1(ii)). Unless otherwise stated the term graphite will only refer to the hexagonal form of graphite.

![Figure 3.1: Crystal structure of (i) hexagonal and (ii) rhombohedral forms of graphite, redrawn from [107].](image)

### 3.1.2 Raman spectrum of graphite

*Introduction*

Single-crystal graphite belongs to the space group \( D_{6h}^4 \) and possesses the reducible representation [108-110]:

\[
\Gamma_{\text{opt}} = 2B_{2g} + 2E_{2g} + A_{2u} + E_{1u}
\]

Of which only the \( 2E_{2g} \) modes are Raman active. For highly orientated pyrolytic graphite (HOPG) these two bands appear at 42 and 1575 cm\(^{-1}\) respectively. The \( A_{2u} \) (868 cm\(^{-1}\)) and \( E_{1u} \) (1588 cm\(^{-1}\)) modes are infrared active and the \( 2B_{2g} \) are silent [111] (Figure 3.2). The low frequency Raman active collective, \( E_{2g1} \), shear mode at 42 cm\(^{-1}\) is difficult to observe because of its proximity to the Raleigh line.
Tuinstra and Koenig were the first to report the Raman spectrum of graphite [108]. Their work showed that a single crystal of graphite produces one peak, the $E_{2g2}$, at 1580 cm$^{-1}$, whereas in all other graphitic-type materials (microcrystalline graphite, amorphous carbon, and carbon black) a second feature appears at 1330 cm$^{-1}$.

The 1580 cm$^{-1}$ peak, called the G-band, after crystalline graphite, is the only Raman active mode of the infinite lattice. The G mode is due to the relative motion of $sp^2$ carbon atoms in rings as well as chains. The other peak, named the D-band from disordered graphite, can be attributed to the breathing motion of $sp^2$ atoms in rings at edge planes and defects in the graphene sheet (Figure 3.3). This mode is forbidden for a perfect graphene layer, but is allowed at plane edges [112]. The intensity of the D-band therefore increases relative to the G-band as (a) the amount of disorganised carbon increases and (b) the graphite crystallite size in the $a$ direction ($L_a$) decreases. The relationship between crystallite size and intensity of the D-band can be expressed as [108]:

\[ \text{Intensity of D-band} \propto \frac{1}{L_a}. \]
where \( R_{DG} \) is the intensity ratio of the D- to G-band and \( C \) is the pre-factor which depends on laser wavelength [113].

\[ L_a = \frac{C}{R_{DG}} [nm] \]  

(3.2)

**Figure 3.3:** Raman Spectrum of microcrystalline graphite SFG44 taken with HeNe laser at 632.8 nm. Schematic representations of atomic motions, which give rise to the D- and G-bands, are also shown. These bands appear at 1330 \( \text{cm}^{-1} \) and 1580 \( \text{cm}^{-1} \) respectively. The small shoulder band \( D' \)-band is observed at 1610 \( \text{cm}^{-1} \).

**D- and D' -band**

In order to explain intercalation phenomena observable in the Raman spectra, a more rigorous explanation of the D-band is required [67]. As discussed in chapter 1, Raman scattering is the inelastic scattering of photons by phonons due to the change of polarisation caused by the phonon (or vibrational) mode. Furthermore Raman and IR activity for a crystal can only be
observed in the limit where the wave vector of the electronic transition \( k = 0 \). At the \( \Gamma \) point of the first Brillouin zone of graphite shown in Figure 3.4, \( k = 0 \) has the full symmetry of the lattice, \( D_{0h} \), and gives rise to the observed \( E_{2g} \) mode. Raman modes in single crystals also obey the fundamental selection rule \( q \approx 0 \), where \( q \) is the wave vector of the scattered phonon. For resonance Raman scattering, when the photon energy is above the band gap, electrons of all wave vectors can be excited. However in graphite, the band gap lies in visible range only within a small part of \( k \) space around the \( K \) point (Figure 3.4). All these bands have \( \pi \) character. In this case, photons resonantly excite states only at the \( k \) vector where the band gap equals the photon energy and can be expressed as the \( k = q \) "quasi selection rule". This sets up a polarisation density wave of \( k \) vector. Its intensity is strong because of the long-range polarisability of \( \pi \) states.

The change of bond polarisation with bond length is by far the dominant term in the Raman matrix element for \( \pi \) states. This term is large for the breathing mode of six-fold rings. By symmetry, for a breathing mode of a graphite plane, the contributions from each ring add constructively because of long range polarisation. Conversely, by symmetry, contributions from rings of other orders within a graphite plane tend to cancel. Therefore this wave will be cancelled out completely in the bulk crystal, and only partially at the edge plane. This explains why the D-band is not observable in HOPG and why its intensity enlarges as disorder within the graphite structure increases. In addition it accounts for the experimental observation of the shift of the D-band with laser wavelength [113-115]. This model for the D-band qualitatively explains observed trends, but until lately the physical mechanism behind the resonance was not fully understood. Recent papers have shown that a double resonance process is involved; however the theory is unable yet to completely explain the occurrence of the D-band in all types of graphitic carbons [115, 116].

In addition a small shoulder band assigned as the D'-band is observed at ca. 1610 cm\(^{-1}\). The appearance of D' occurs because the relaxation of the \( q = 0 \) selection rule allows higher-frequency phonons, as phonons disperse upwards away from \( \Gamma \) (Figure 3.5) [117].
Figure 3.4: First Brillouin zone of two dimensional graphite, adapted from [108]. For the derivation of the first Brillouin zone of graphite see [101].

Figure 3.5: (a) Phonon dispersion curve and (b) electronic band structure of a single graphite layer, adapted from [118-120]. The bold line from K to M corresponds to phonons selected by the $k = q$ "quasi selection rule" as shown by the dashed vertical line. The phonons from K to $\Gamma$ mark the region where the $D'$-band is permitted and is also selected by the $k = q$ "quasi selection rule".
3.1.3 Determination of $L_a$ value

As stated in the previous section, *The Raman spectrum of graphite*, the ratio of the G- and D-bands in the Raman spectrum of graphite is related to the amount of disorder within the structure. More specifically it can be related to the length of the graphene sheet with in graphite crystallites known as the $L_a$ value (Figure 3.6). The higher the value of $L_a$ the greater the structural order, because of the larger size of the graphite crystallites.

![Graphite Crystal Schematic](image)

**Figure 3.6** Schematic of a graphite crystal, displaying the graphite crystallites and crystallographic parameters $L_a$ and $L_c$.

The value is derived from the intensity ratios of the area of the D-band over the area of the G-band and the Tuinstra-Koenig formulation [108] (equation 3.2) showed the relationship between the value of $L_a$ and the band ratio $R_{DG}$ with the pre-factor $C$.

Measurements by Knight and White [121] found the pre-factor $C$ to be 4.4 to give:

$$L_a = \frac{4.4}{R_{DG}} \text{[nm]}$$  \hspace{1cm} (3.3)
However this equation is only valid to calculate $L_a$ for the excitation wavelength of 514.5 nm [122]. It was revealed that the wavelength $\lambda_L$ varies linearly with $R_{DG}$ between $(400 < \lambda_L < 700)$. The relationship of the pre-factor $C$ and wavelength was therefore shown to be [113]:

$$C(\lambda_L) = C_0 + \lambda_L C_1$$

(3.4)

where $C_0$ and $C_1$ were estimated to be -12.6 nm and 0.033 respectively. Therefore when using a HeNe laser of wavelength 632.8 nm the pre-factor is calculated to be 8.3:

$$L_a = \frac{8.3}{R_{DG}} [nm]$$

(3.5)

With this formula selected areas of graphite electrodes can be mapped up to 1 $\mu$m$^3$ resolution and have the $L_a$ distribution and average $L_a$ value determined [19].

The use of X-ray diffraction (XRD) is a complementary method and can determine the dimensions of the crystallites in both the $a$ and $c$ direction [123]. XRD has been used to experimentally verify the relationship [121] of $L_a$ and $R_{DG}$ and the minimum value to which this correlation is valid is ca. 20 Å [124]. However recently it has been demonstrated that the $L_a$ value derived from Raman spectroscopy is underestimated because of the dominant effect of small crystallites [125, 126]. Therefore when ever possible it is advised to carry out both Raman and XRD measurements to obtain $L_a$ values on graphitic samples.
3.1.4 Effect of angle of incidence on $L_a$

Figure 3.7 illustrates the potential problem of measuring graphite electrodes because spectra with different D- and G-band intensity ratios can be measured depending on whether the measurement-region of the particle is mainly edge or basal plane. Kawashima and Katagiri [127] showed that there is a difference between edge and basal plane Raman spectra. Therefore in order to ascertain whether Raman mapping of graphite electrodes can measure accurate $L_a$ values on the electrode surface, the influence of the orientation of the graphite crystals within an electrode is investigated. Maps of several particles on electrodes of microcrystalline and disordered graphite samples were collected and had their $L_a$ values determined using equation (3.5) at an angle of 0, 15, 30 and 45$^\circ$ with respect to the horizontal, using an adjustable sample holder. Each map consisted of 225 separate spectra over an area of 50 x 50 μm using a 50x objective.

![Figure 3.7: Sketch demonstrating the method of angle measurement mapping.](image)
Highly crystalline graphite

Figure 3.8 shows only a slight variation in D-band intensity when the angle of measurement is shifted from 0 to 45° with highly crystalline graphitic materials (a) SLX50 and (b) SFG44.

![Graphite spectra](image)

Figure 3.8: Graphite (a) SLX50 and (b) SFG44 spectrum depending on angle.

Disordered graphite

More disordered graphitic structures were also investigated because the more intense D-band in these materials may be more easily affected by the angle of incidence. However Figure 3.9 shows again that there is no variation in D-band intensity.

![Disordered graphite spectra](image)

Figure 3.9: (a) Disordered graphite A angle measurement (b) Mesocarbon microbead (MCMB) angle measurement.
Conclusions

From these measurements it can be concluded that angle of incidence does not have a significant influence on the intensity of the D-band and therefore the value of $L_a$ of graphite electrodes, when a large number of points are mapped on the electrode. It is believed that all the differently orientated crystallites average out to produce the same $L_a$ value. $L_a$ values of several different synthetic graphite products (TIMCAL AG, Bodio Switzerland) have been determined and can be found in the following references [19, 20, 128].

3.1.5 Correlation of $L_a$ with structural features on graphite

Small mapping of graphite electrodes

Intuitively the more crystalline areas with high $L_a$ should reflect the light (lighter areas on the particle) and the more disordered areas with low $L_a$ should scatter light (darker areas on the particle). Therefore the distribution of crystallite size $L_a$ should be correlated to visible graphite particle parameters such as edge planes and particle boundaries (Figure 3.10a). Small contour maps of 225 spectra demonstrated the method with the microcrystalline graphite SLX50. For each spectrum the $L_a$ values were determined using equation (3.5) and the 2D contour maps were generated with Microcal Origin graphical software.

The 2D contour map shows there is indeed a large variation in $L_a$ distributed over the 40 x 40 μm area measured (Figure 3.10b). However because of the low resolution it is impossible to correlate these low number maps with graphite morphology [128]. Therefore more points and greater resolution is required. Furthermore when no spectrum of graphite is measured (i.e. over a gap between two particles) no $L_a$ value can be calculated and is seen on the map as large white areas. If there are too many bad points in the map it is impossible to generate a contour plot.
**Figure 3.10:** (a) Image of graphite SLX50, (b) obtained $L_n$ spatial distribution plot consisting of 225 spectra (dark low $L_n$, light colour high $L_n$), and bad points in white, where no Raman spectra could be measured. Raman spectra were recorded using an x100 objective, with a resolution of ca. (4 $\mu$m)$^3$.

**Figure 3.11:** Spectra of graphite SLX50 of high $L_n$ 48 nm (dark yellow), low $L_n$ 15 nm (dark green), no spectrum (white) collected during mapping of the electrode surface.

**Increasing the resolution of graphite mapping**

Figure 3.12 shows maps of increasing spectral number density of the graphite SLX50. As the number of spectra increases the more visible the correlation of $L_n$ with structural features on the electrode surface becomes. Large mapping of $L_n$ value to a resolution of ca. (1 $\mu$m)$^3$ is able to allow the viewing of edges of the crystals as well as defects at the crystal surface.
Figure 3.12: (a) optical microscope image of graphite SLX50, (b) small map consisting of 225 spectra, spatial resolution approaching (2 μm)³, (c) medium-sized map of 900 spectra, spatial resolution approaching (1 - 2 μm)³, (d) large map of 2500 spectra, spatial resolution approaching ca. (1 μm)³. Bad points are shown in white, where no Raman spectra could be measured. Raman spectra were recorded using an x100 objective.

**Large mapping of various graphite electrodes**

To demonstrate the reproducibility of large spectral mapping graphite, SLX50 (Figure 3.13a, b) as well as graphite E-KM44 (Figure 3.13c, d) and disordered graphite A (Figure 3.14), were also mapped with a resolution approaching (1 μm)³. All samples show reasonable correlation between morphology shown in the optical image and Iₐ maps.
Figure 3.13: (a) Image of the graphite sample SLX50, (b) calculated spatial distribution plot (2500 spectra) showing the $L_{\alpha}$ values of SLX50, (c) Image of the graphite sample E-KM44, (d) calculated spatial distribution plot (10000 spectra) showing the $L_{\alpha}$ values of E-KM44. Bad points are shown in white, where no Raman spectra could be measured. Raman spectra were recorded using an x100 objective, with a resolution approaching $(1 \mu m)^3$. 
Figure 3.14: (a) Image of disordered graphite sample A. (b) obtained $L_{\alpha}$ spatial distribution plot from LabRam software (dark low $L_{\alpha}$, light colour high $L_{\alpha}$), (c) enlarged calculated spatial distribution plot (2500 spectra) showing the $L_{\alpha}$ values (bad points in white indicate where no Raman spectra could be measured). Raman spectra were recorded using an x100 objective, with a resolution approaching (1 $\mu$m)$^3$. 
Conclusions

Maps created by mapping the ratio of the D- and G-bands show that a spatial $L_a$ resolution approaching $(1 \mu m)^3$ is obtainable. $L_a$ maps can distinguish between different electrode particles, and defects and edge plans within the particles. This may provide an interesting tool when combined with in situ Raman microscopy, which could be used to simultaneously observe lithium intercalation in the bulk particle, at edge planes and defects. However each spectrum requires ca. 10 - 20 seconds to obtain a reasonable signal to noise ratio. Therefore large maps shown with approaching $(1 \mu m)^3$ resolution require at least 7 hours time to measure over a 30 $\mu$m x 30 $\mu$m area. Assuming in situ spectra only require similar time scales to measure the time is already still too long. Improvements in optics within the Raman spectrometer may in the future reduce measurements times. Use of more powerful lasers will give a greater signal but there is an increased risk of sample heating and destruction. This risk has been previously shown to be enhanced during in situ Raman measurements [67].
3.2 Raman mapping of positive electrodes

To follow how the distribution of lithium cobalt oxide (LiCoO₂) or lithium manganese oxide spinel (LiMn₂O₄) with carbon in composite electrodes changes with time and number of cycles is of great interest because it may provide answers for capacity losses due to the breakdown of the conductive carbon matrix. The method could also be used as a quality control tool [129]. Kostecki et al. [130] have recently demonstrated this imaging technique by mapping at a confocal resolution of below (1 µm)³ composite electrodes of a mixed layered oxide, LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂, graphite and carbon black. The following results are a preliminary investigation to determine the viability of Raman mapping of positive electrodes.

3.2.1 Lithium cobalt oxide (LiCoO₂)

Structure

The structure of LiCoO₂ is made up from a cubic close-packed oxygen array [8, 131, 132]. The lithium and transition-metal atoms are distributed in the octahedral interstitial sites in such a way that CoO₂ layers are formed consisting of edge sharing (CoO₆) octahedra. In-between these layers lithium resides in octahedral holes which give LiO₆ coordination (Figure 3.15) [133].

![Figure 3.15](image)

**Figure 3.15:** (a) Structure of layered lithium cobalt oxide (LiCoO₂) (b) schematic diagram of the layered LiCoO₂ structure showing the ABCABC stacking of the O-Li-O-Co-O-Li-O layers, adapted from [8, 131].
Point group analysis

Layered lithium cobalt oxide has the factor group \( D_{3d}^5 \) and the crystal space group \( R\bar{3}m \). The factor group analysis gives the irreducible representation:

\[
\Gamma_{opt} = A_{1g} + E_g + 2A_{2u} + 2E_u \quad (3.6)
\]

Of which the \( A_{1g} \) and \( E_g \) modes are Raman active and the \( 2A_{2u} + 2E_u \) are infrared active [134, 135]. Figure 3.16 shows the Raman spectrum of LiCoO\(_2\) powder (Ferro) from 350 to 1250 cm\(^{-1}\), two prominent bands are observed. These are the \( E_g \) mode at 483 cm\(^{-1}\) and the \( A_{1g} \) mode at 593 cm\(^{-1}\). Weak overtones of the \( E_g + A_{1g} \) bands can be seen at ca. 920 and 1150 cm\(^{-1}\) respectively.

![Figure 3.16: Raman spectrum of lithium cobalt oxide powder (LiCoO\(_2\), Ferro).](image)

Figure 3.17 demonstrates the mapping of a cobalt oxide electrode. The optical image allows no differentiation between oxide and graphite particle. However Raman mapping can allow you to distinguish between the oxide peak at 600 cm\(^{-1}\) and the graphitic peaks, D and G, at 1350 and 1580 cm\(^{-1}\) respectively. The map is constructed by plotting the integrated intensity ratios of the carbon bands divided by main oxide band. Blue areas on the map are from the oxide signal, red area from the carbon signal and colours in-between, such as purple, show a mixture of both materials. The map therefore shows a random distribution of oxide and graphite/carbon black over the 50 x 50 \( \mu \text{m} \) area measured.
Figure 3.17  Optical image (x50) and example Raman map of the ratio of LiCoO$_2$ and carbon of the composite electrode (85% LiCoO$_2$ (Ferro) 5% binder (Oppanol) 9% graphite SFG6 and 1% carbon black (Super P)), map consists of 2500 spectra.

The Ratio, $R$ is defined as $R = I(D$ and G$)/I(E_g$ and $A_{1g}$). Four representative spectra showing the varying intensity ratios between the oxide and carbon bands are shown. Blue areas on the map indicate the presence of LiCoO$_2$ and red areas occurrence of carbon.
3.2.2 Lithium manganese oxide spinel (LiMn_2O_4)

Structure

Lithium manganese oxide (LiMn_2O_4) has a cubic spinel structure (Figure 3.18). The structure can be expressed as a cubic close-packed oxygen array with the oxygen anions on the crystallographic 32e sites of the Fd3m space group. The manganese cations reside in half of the octahedral interstitial sites, 16d, and the lithium cations one eighth of the tetrahedral sites, 8a. The interstitial space in the Mn_2O_4 framework corresponds to a diamond-type network of tetrahedral 8a and surrounding octahedral 16c sites. These vacant tetrahedra and octahedra are interconnected with one another by common faces and edges to form 3D diffusion pathways for the lithium ions [8, 11, 136, 137].

Figure 3.18: (a) The three-dimensional structure of LiMn_2O_4 spinel and (b) crystal structure of typical spinel structure AB_2O_4. Hatched, solid and open circles refer to Li^+, Mn^{3+/4+} and O^{2-} ions respectively for LiMn_2O_4. The numbers refer to various crystallographic position in the spinel structure, adapted from [8, 138].
**Point group analysis**

The factor group analysis for LiMn$_2$O$_4$ spinel produces five Raman active modes [139]:

$$
\Gamma_{\text{Raman}} = A_{ig} + E_g + 3T_{2g}
$$

(3.7)

Figure 3.19 shows that only a signal broad band at ca. 600 cm$^{-1}$ is detected for LiMn$_2$O$_4$. Peak fitting this band with two lorentzians produce two bands centred at 568 and 614 cm$^{-1}$, which have been assigned as the $T_{2g}(3)$ and $A_{ig}$ modes respectively.

**Figure 3.19:** Raman spectrum of lithium manganese oxide spinel (LiMn$_2$O$_4$, Honeywell).

The wavenumber positions of these bands are much lower than previously measured (Table 3.1) [139] and even these values differ from other publications [140, 141]. Recently it has been shown that the Raman spectrum measured depends on the power of the laser [142]. If the laser power is too high laser-induced thermal decomposition of LiMn$_2$O$_4$ occurs. They propose that the correct spectrum consists of a broad peak around 580 cm$^{-1}$, which agrees more closely with the calculated wavenumber for the $A_{ig}$ mode [139].
Table 3.1: Observed bands for LiMn$_2$O$_4$ from [139].

<table>
<thead>
<tr>
<th>LiMn$_2$O$_4$ Band Position/ cm$^{-1}$</th>
<th>Symmetry species</th>
</tr>
</thead>
<tbody>
<tr>
<td>365</td>
<td>$T_{2g}(1)$</td>
</tr>
<tr>
<td>432</td>
<td>$T_{2g}(2)$</td>
</tr>
<tr>
<td>480</td>
<td>$E_g$</td>
</tr>
<tr>
<td>590</td>
<td>$T_{2g}(3)$</td>
</tr>
<tr>
<td>625</td>
<td>$A_{1g}$</td>
</tr>
</tbody>
</table>

Therefore even though the laser power for these measurements was below 1 mW, it maybe that the peak measured, contains some signal from unwanted decomposition products. However at this point in time the correct spectrum of LiMn$_2$O$_4$ remains controversial and the original assignment will be continued to be used in this thesis with caution. None of the lower wavenumber bands are observed, though it is well known that these features are very weak and difficult to detect above the signal to noise ratio [142].

The Raman mapping results of the integrated intensity ratio of carbon peaks (D and G-bands) against the broad LiMn$_2$O$_4$ $A_{1g}$ peak (ca. 600 cm$^{-1}$) is shown in Figure 3.20. Clumps of red areas, the graphite particles are observed around the oxide particle (blue areas). A well dispersed conductive carbon matrix can be seen.
Figure 3.20 Optical image (x50) and example Raman map of the ratio of LiMn$_2$O$_4$ and carbon of the composite electrode (85% LiMn$_2$O$_4$ (Honeywell) 5% binder (Oppanol) 9% graphite SFG6 and 1% carbon black (Super P)), map consists of 2500 spectra. The Ratio, $R$ is defined as $R = I(D \text{ and } G)/I(A_{1g})$. Four representative spectra showing the varying intensity ratios between the oxide and carbon bands are shown. Blue areas on the map indicate the presence of LiMn$_2$O$_4$ and red areas occurrence of carbon.

Conclusions

Raman mapping of fresh LiCoO$_2$ and LiMn$_2$O$_4$ composite electrodes demonstrate the feasibility of measuring the distribution of oxide and carbon particles. The next stage would be to map cycled electrodes and electrodes which failed, to observe any possible changes in the arrangement of these particles.
4

IN SITU RAMAN MICROSCOPY
OF GRAPHITIC CARBONS
AS LITHIUM-ION BATTERY
NEGATIVE ELECTRODES

4.1 Introduction

As discussed in chapter 3, Raman mapping and therefore imaging of composite electrodes can provide spatial information on the distribution of materials on the electrode surface. The graphite electrode in particular was demonstrated to have a heterogeneous composition with a wide variation of crystallite size. The chief aim of this chapter is therefore to demonstrate the necessity of carrying out in situ measurements on more than one point in order to obtain a more detailed picture on the intercalation processes taking place. Numerous in situ Raman studies have been carried out on various graphitic carbons and the intercalation process is well known [66, 143, 144], however some features seen in the Raman spectrum remain poorly understood [67, 145] and further investigation is necessary. In particular in this work, the D-band disappearance (chapter 4.4) [145], local influence of La (chapter 4.5) [146], influence of graphite particle size and rhombohedral fraction (chapter 4.6) [143, 147], graphite exfoliation (chapter 4.7) [143] and influence on temperature on appearance of stage 2 liquid phase (chapter 4.8) [148] are explored in further detail.
4.1.1 Graphite intercalation compounds

Due to the weak van der Waals interlayer forces in graphite, graphite intercalation compounds (GICs) may be formed by the insertion of layers of guest species between the layers of the graphite host material [8, 104]. Lithium-GICs produced chemically have been known since the 1950s, through the work of Hérold [149, 150]. However man’s involvement in intercalation processes dates back even further and historical evidence shows the intercalation of urea into kaolin was crucial in the manufacture of egg-shell porcelain in China as far back as 7th century AD [151].

In these chemical intercalation reactions charge transfer occurs and graphite can behave either as an electron donor or an electron acceptor, as demonstrated in the following equations [106]:

\[ xC + D \rightarrow D^+ C^- \]  \hspace{1cm} (4.1)

\[ xC + A \rightarrow C^+ A^- \]  \hspace{1cm} (4.2)

where C, D and A are graphite, donor and acceptor respectively.

In donor GICs, electrons are transferred from the donor intercalated species into the graphite layers, and leaves the intercalate layer positively charged. In acceptor GICs, the opposite occurs, and electrons are transferred to the acceptor intercalated into the graphite layer, and leaves the intercalate layer negatively charged. For donor GICs, electrons are transferred from donor to graphite atoms occupy the anti-bonding \( \pi^* \) band, while in acceptor GICs, the charge transfer from graphite to acceptor empties the top of the \( \pi \) bonding band. The charge transfer between graphite and the intercalate increases the number of electrons or holes around the Fermi energy, \( E_F \), and makes GICs metallic [101]. The electronic structures of graphene, graphite and donor and acceptor GICs are correspondingly represented in Figure 4.1.
However in galvanic cells, formation of GICs is achieved electrochemically, here the electron is not donated or accepted from intercalated species, but instead the electron comes from or is taken up by the external circuit:

\[ xC + D^+ + e^- \rightarrow D^+ C_x^- \]  

(4.3)

\[ xC + A^- - e^- \rightarrow C_x^+ A^- \]  

(4.4)

The end point of chemical and electrochemical formation of GICs is identical. Therefore, as an example, LiC₆ is always referred to as a donor GIC irrespective of whether it was formed chemically from Li or electrochemically from Li⁺.

Figure 4.1: The electronic structures of (a) graphene, (b) graphite, (c) donor GICs, (d) acceptor GICs, where \( D(E) \) is the density of states and \( E_F \) is the Fermi energy, redrawn from [106].
4.1.2 GICs as lithium-ion battery negative electrodes

Highly crystalline graphitic materials are routinely used as the negative electrodes in lithium-ion batteries. Their positive features include a high reversible specific charge of up to the theoretical value of 372 Ah kg\(^{-1}\) (of carbon) for the formation of the donor GIC, LiC\(_6\), a good cycling stability, as well as high electronic conductivity [8]. The structure of LiC\(_6\) is shown in Figure 4.2 and illustrates the distribution of lithium between the graphene sheets. During lithium intercalation into graphite there is a volume change of ca. 10% as the distance between graphene sheets increases from 3.35 to 3.7 Å [152]. Furthermore the stacking order of graphene layers switches from ABAB to AAAA. In LiC\(_6\) the stacking order of the lithium interlayers is \(\alpha\alpha\), leading to Li-C\(_6\)-Li-C\(_6\)-Li chains along the c-axis, with each lithium being a minimum distance of 4.3 Å apart [153].

\[\text{Figure 4.2: Structure of LiC}_6\text{. a) Left: schematic drawing showing the AA layer stacking and the } \alpha\alpha \text{ interlayer ordering of the intercalated lithium. Right: simplified representation. b) View perpendicular to the basal plane of LiC}_6\text{ (redrawn from [8]).}\]
The most central and distinctive property of GICs is the stepwise formation of a periodic array of unoccupied layer gaps at low concentrations of guest species, called stage formation [154, 155]. This stepwise process can be described by the stage index, \( n \), which is equal to the number of graphene layers between two nearest guest layers. Staging is a thermodynamic phenomena related to the energy required to expand the van der Waals gap between two graphene layers and the repulsive interactions between guest species. Thus as a rule, few but highly occupied van der Waals gaps are energetically favoured over a random distribution of guests [8]. The stage formation during electrochemical lithium insertion is shown in Figure 4.3. Four potential plateaus can be observed at around 0.22, 0.15, 0.13 and 0.09 V. These are correspondingly assigned as the formation of a stage 3 GIC from a dilute stage 1, via stage 4, the change of stage 3 first to a stage 2 liquid phase (no in-plane ordering) then to an ordered stage 2 phase and finally to a stage 1 GIC [8, 148].

![Figure 4.3](image.png)

**Figure 4.3:** Schematic galvanostatic curve showing stage formation during electrochemical intercalation of lithium into graphite at 25 °C (redrawn from [8, 148]).
The Raman spectrum for GICs with stage \( n > 2 \) are acknowledged for showing a doublet G-band. The lower (\( E_{2g2}(i) \)) and upper (\( E_{2g2}(b) \)) frequency components are correspondingly associated with carbon-atom vibrations in interior graphite layers (not adjacent to intercalate layer planes) and in bounding graphite layers (adjacent to intercalate planes). The split in \( E_{2g2} \) mode upon intercalation occurs primarily from changes in symmetry at the boundary layer and secondarily from electronic effects of the intercalate molecule. The \( E_{2g2}(i) \) band disappears for stage 1 and 2, where no graphite interior layer exists.

A quantitative measure of the intercalation stage index, \( n \) can be derived from the relative intensities of the Raman doublet, \( R \) by the following equation [156]:

\[
R = \frac{I_i}{I_b} = \frac{\sigma_i}{\sigma_b} \frac{n - 2}{2} \quad (n > 2)
\]

Where \( I_i \) and \( I_b \) represent the intensities of the interior \( E_{2g2}(i) \) and bounding \( E_{2g2}(b) \) layer modes respectively, and \( \sigma_i/\sigma_b \) is the ratio of the cross section for Raman scattering from the interior and bounding layers (a stage independent constant), which in the case of lithium intercalation is equal to 1.

The cycling programme used for all graphite samples during cycling is displayed in Table 4.1. The specific charge/discharge currents employed were 10 mA g\(^{-1}\) of carbon. This corresponds to a charge rate of \( C/37 \), i.e. the electrode is charged to its full theoretical charge capacity (372 Ah kg\(^{-1}\) for graphite) within 37 hours. All in situ cells had an internal cell resistance of between 50 - 100 \( \Omega \) which leads to a calculated \( iR \) drop of ca. 0.01 V when the working electrode has a mass between 1 - 2 mg of active material. The potentials quoted in this thesis have not been corrected for this \( iR \) drop.

### Table 4.1: Cycling programme for graphite vs. lithium in situ cell.

<table>
<thead>
<tr>
<th>Programme</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific charge current</td>
<td>10 mA g(^{-1}) of carbon</td>
</tr>
<tr>
<td>Specific discharge current</td>
<td>-10 mA g(^{-1}) of carbon</td>
</tr>
<tr>
<td>Charge potential limit</td>
<td>1.5 V vs. Li/Li(^+)</td>
</tr>
<tr>
<td>Discharge potential limit</td>
<td>0.005 V vs. Li/Li(^+)</td>
</tr>
</tbody>
</table>
4.1.3 Electrochromism in GICs

The degree of intercalation can also be qualitatively determined by the observation of the particular colour of the graphite particle surface [104, 157]. For lithium GICs stage 3 and 4 graphite, is blue in colour, stage 2, LiC_{12} is red, and stage 1 LiC_6 appears yellow [158]. The colour change is associated with the up-shift of the Drude reflectance edge in the visible region with increasing charge transfer to the carbon π conduction bands from the intercalated layers [159]. For acceptor GICs only the stage 1 compound is coloured, which is often blue [104]. Figure 4.4 shows the surface of the graphite electrode SFG44 at 0.12 V.

![Graphite SFG44 at 0.12 V vs. Li/Li⁺, C/5 75 mA g⁻¹, adapted from [157]](image)

**Figure 4.4:** Graphite SFG44 at 0.12 V vs. Li/Li⁺, C/5 75 mA g⁻¹, adapted from [157].
4.2 Single point in situ Raman microscopy on graphite SFG44

The first and second lithiation and de-lithiation galvanostatic curves of graphite SFG44 cycled in the two electrode in situ cell are shown in Figure 4.5. As with other graphitic materials, the charge consumed for the formation of LiC₆ in first cycle exceeds the theoretical maximum of 372 Ah kg⁻¹ (Table 4.2), due to the formation of the passivation film called the solid electrode interphase (SEI) [8]. The electrochemical performance of the in situ Raman cell matches the performance of this material reported in the literature [54, 160].

![Graph of galvanostatic curves](image)

**Figure 4.5:** Galvanostatic first and second lithiation and de-lithiation curves of graphite SFG44 against metallic lithium counter/reference, cycled in the in situ Raman cell, with a constant specific current 10 mA g⁻¹ in 1M LiClO₄, 1:1 EC:DMC (charge rate C/37).

**Table 4.2:** Specific charge capacity (Ah kg⁻¹) of graphite (SFG44) vs. lithium in situ Raman cell during the first cycle in 1M LiClO₄, 1:1 EC:DMC.

<table>
<thead>
<tr>
<th></th>
<th>Specific charge capacity/ Ah kg⁻¹ of carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Lithiation</td>
<td>396</td>
</tr>
<tr>
<td>1st De-lithiation</td>
<td>349</td>
</tr>
</tbody>
</table>

The optical picture of graphite SFG44 (Figure 4.6) shows the measurement point used from which the Raman spectra were obtained.
The results from the first and second lithium intercalation and de-intercalation cycle are shown (Figures 4.7 to 4.10). The spectra compare well to the literature [66, 67, 143, 145, 161-163]. On each figure the potential (V) and specific charge capacity (Ah kg⁻¹ of carbon) of when each spectrum was measured is displayed. All the spectra are base-line corrected and stacked arbitrarily up the y-axis to allow for clear visualisation. Bands due to the electrolyte are either not detected or negligible because of the confocal set-up, which allows a confocal resolution of (2-3 μm)³. Furthermore the thin glass window (0.1 mm) used, allows close sample measurement onto the holed-electrode. The first observation which is noted is the degradation of the Raman signal as cycle number increases. The signal to noise ratio becomes poorer because of an increased background base line, the cause maybe due to increased fluorescence from degradation products of the electrolyte. Therefore Raman measurements are best undertaken during the first cycle.
The first lithium intercalation Raman spectra are illustrated in Figure 4.7. At 3 V the G-band is seen at 1585 cm\(^{-1}\), a weak D-band and D'-band are also correspondingly noted at 1330 cm\(^{-1}\) and 1610 cm\(^{-1}\). This spectral series of any highly graphitic material can be split into four stages of specific interest [66, 67, 145]:

- Loss of D- and D'-bands between potentials ca. 3 - 0.6 V
- Shift of G-band from 1585 cm\(^{-1}\) to 1595 cm\(^{-1}\) ca. 0.6 - 0.2 V
- Split of G-band into \(E_{2g}(i)\) (1578 cm\(^{-1}\)) and \(E_{2g}(b)\) (1601 cm\(^{-1}\)) bands ca. 0.16 - 0.09 V
- Loss of band signal as low stage number compounds are formed ca. 0.09 - 0.005 V and appearance of new bands at 1370 cm\(^{-1}\) and 1850 cm\(^{-1}\).
Figure 4.7: *In situ* Raman spectra series of graphite SFG44 of the first lithium intercalation from open circuit potential (3 V) to 0.005 V. Spectra are shifted arbitrarily up the intensity axis. The arrow on the right-hand side indicates the direction of the scan (charge rate C/37).
The first lithium de-intercalation is illustrated in Figure 4.8. At ca. 0.12 V only a weak band at 1370 cm\(^{-1}\), a broad band at 1540 cm\(^{-1}\) and strong band at 1850 cm\(^{-1}\) are observed. The reverse spectral can be also split into four stages of specific interest:

- **Weakening of 1370 and 1850 cm\(^{-1}\), red-shift and growth of 1540 cm\(^{-1}\)**
  
  ca. 0.12 - 0.16 V

- **Completion of red-shift of 1540 to 1601 cm\(^{-1}\) to form \(E_{2g2}(b)\) of stage 2 GIC**

  ca. 0.16 - 0.17 V

- **Return of G-band doublet: \(E_{2g2}(i)\) (1578 cm\(^{-1}\)) and \(E_{2g2}(b)\) (1601 cm\(^{-1}\))**

  ca. 0.17 - 0.22 V

- **Return of G-band at 1595 cm\(^{-1}\), which subsequently shifts back to 1585 cm\(^{-1}\)**

  ca. 0.23 - 1.5 V
Figure 4.8: *In situ* Raman spectra series of graphite SFG44 of the first lithium de-intercalation from 0.005 to 1.5 V. Spectra are shifted arbitrarily up the intensity axis. The arrow on the right-hand side indicates the direction of the scan (charge rate \(C/37\)).
The trends for the first intercalation and de-intercalation are repeated for the second cycle and are illustrated in Figures 4.9 and 4.10. The spectral trends are identical to those observed in the first cycle; this therefore demonstrates the reversibility of the intercalation of lithium into graphite.
Figure 4.9: In situ Raman spectra series of graphite SFG44 of the second lithium intercalation from 1.5 to 0.005 V. Spectra are shifted arbitrarily up the intensity axis. The arrow on the right-hand side indicates the direction of the scan (charge rate C/37).
**Figure 4.10:** *In situ* Raman spectra series of graphite SFG44 of the second lithium de-intercalation from 0.005 to 1.5 V. Spectra are shifted arbitrarily up the intensity axis. The arrow on the right-hand side indicates the direction of the scan (charge rate $C/37$).
Conclusions

In situ Raman spectrum of the initial two lithiation and de-lithiation cycles on a single point on a graphite electrode were obtained with excellent signal noise ratio and no detection of electrolyte bands. The spectra match known literature [66, 143]. The spectra of the first cycle match those taken during the second cycle therefore demonstrating identical lithium intercalation with cycle number. However, the quality of spectra and the signal to noise ratio decrease with cycling. The background noise increases, which makes accurate base-line correction difficult. By the third and fourth cycle (not shown) the obtained spectra are of poor quality. Therefore for optimum Raman measurements it is suggested to only use the spectra from the first cycle.
4.3 Four point *in situ* Raman microscopy on graphite SFG44

Due to the heterogeneity of the graphite surface, as shown in chapter 3, *in situ* multipoint mapping of the graphite electrode is advantageous. However because of the too long accumulation times (180 - 300 seconds) required to obtain an *in situ* Raman spectrum of sufficiently low signal to noise ratio, initial maps consisted just of four points. Figure 4.11 shows the optical microscope picture showing the four points measured. The four points lie on a separate graphite particle and the spectra are obtained by continuous Raster scanning of the surface during change in potential. The Raman spectra collected from all four points were relatively similar. Therefore for clarity just the Raman spectrum of point c is shown during the first lithium insertion and extraction. These spectra will illustrate in more detail the trends described in the single point graphite measurement seen previously in chapter 4.2. However the peak-fitting data of all four points during the first lithium insertion and extraction are plotted in Figures 4.16 and 4.21 respectively.

![Optical microscope picture](image)

*Figure 4.11:* Optical microscope picture (x80 objective) of points (a), (b), (c) and (d) measured on uncycled graphite SFG44 surface in 1M LiClO₄ 1:1 EC:DMC. Each point lies on a separate particle.

*Loss of D- and D'-bands*

During the galvanostatic first lithium intercalation the first change in the Raman spectrum observed is the weakening and broadening of the D-band (Figure 4.12) coupled with the
disappearance of the D'-band. The D, G and D' bands are observed at 1330, 1580 and 1610 cm$^{-1}$ respectively. Loss of intensity of the D-band is first observed to occur below 1.0 V. It steadily decreases with potential until the band is lost into the signal noise below 0.6 V. Figure 4.16a displays the reduction with potential in the area ratio between G- and D-bands. This observation has previously been reported [145], though the reason for the band disappearance up until now is not fully understood. The D-band is seen to begin to weaken below ca. 1.0 V. At around 0.9 V the formation of the SEI is known to begin in EC containing electrolytes. During the formation of a stable film, is lithium co-intercalated with EC, it is believed that the intercalation of ions disrupts the D-band. Lithium intercalation begins at ca. 0.55 V [143], so a reordering of the graphite structure from ABAB to AAAA due to lithium intercalation is unlikely to be the cause of D-band weakening.

![Graphical representation of Raman bands](image)

**Figure 4.12:** Spectral series of point (c) graphite SFG44 displaying loss of D-band as potential is lowered. Spectra are shifted arbitrarily up the intensity axis. The arrow on the right-hand side indicates the direction of the scan (charge rate C/37).
Shift and sharpening of G-Band

The Raman spectra recorded from 0.5 to 0.17 V are shown in Figure 4.13. The position of the G-band is observed to shift from 1582 cm$^{-1}$ to 1592 cm$^{-1}$ (Figure 4.16b). The frequency shift can be attributed to the increase of the force constants of the in-plane C-C bonds of the dilute stage 1 GICs. Within the region 0.19 - 0.6 V the G-band shifted linearly with potential average slope of -22 cm$^{-1}$/V which is slightly lower than the value of -29 cm$^{-1}$/V determined by Shi et al. [144] for graphite KS44. The peak shape also narrows and then widens over the series as shown in Figure 4.14c where variation of G-band FWHM within potential range 3.0 - 0.17 V vs. Li/Li$^+$ is plotted. The G-band of point c has an initial FWHM of ca. 15 cm$^{-1}$ which begins to narrow under ca. 0.6 V down to 6 cm$^{-1}$ at 0.4 V and then increases to 20 cm$^{-1}$ at 0.2 V. The narrowing and shift of the G-band both begin below a potential of 0.6 V. This can be attributed to the beginning of lithium insertion at 0.55 V [143]. The dilute stage 1 continues until 0.2 V, below which starts the formation of low stage number compounds. This causes the broadening of the G-band because it also consists of weak signals from the emerging $E_{2g2}(i)$ (1578 cm$^{-1}$) and $E_{2g2}(b)$ (1601 cm$^{-1}$) bands.
Figure 4.13: Spectral series of point (c) graphite SFG44 displaying up shift of G-band as potential is lowered. Spectra are shifted arbitrarily up the intensity axis. The arrow on the right-hand side indicates the direction of the scan (charge rate C/37).

**Split of the G-band**

As the potential is lowered further to 0.17 V the G-band continues to broaden and two side bands begin to grow and become distinct bands below 0.16 V (Figure 4.14). These peaks can be assigned to the intensities of the interior $E_{2g_2}(i)$ (1578 cm$^{-1}$) and bounding $E_{2g_2}(b)$ (1601 cm$^{-1}$) bands. These two bands quickly become prominent at the detriment of the dilute stage 1 band. This transformation points towards to a phase transition from the dilute stage 1 to a staged phase with $n > 2$. Using equation (4.5) [66] and the intensities of the bands from the peak fitting, the ratio $R$ is calculated to be about 0.9, which signifies the establishment of a stage 4 lithium GIC (graphite intercalation compound) at 0.16 V.
The phase transition is related with the change from a random distribution of lithium ions into a more compact distribution in the staged compound. The shift of the $E_{2\text{g}_2(b)}$ band to 1601 cm$^{-1}$ is due to the further increase of the C-C bond force constants.

![Spectral series of point (C) graphite SFG44 displaying split of G-band into $E_{2\text{g}_2(i)}$ and $E_{2\text{g}_2(b)}$ doublet as potential is lowered. Spectra are shifted arbitrarily up the intensity axis. The arrow on the right-hand side indicates the direction of the scan (charge rate C/37).](image)

**Figure 4.14:** Spectral series of point (C) graphite SFG44 displaying split of G-band into $E_{2\text{g}_2(i)}$ and $E_{2\text{g}_2(b)}$ doublet as potential is lowered. Spectra are shifted arbitrarily up the intensity axis. The arrow on the right-hand side indicates the direction of the scan (charge rate C/37).

**Formation of Stage 2 GIC**

Figure 4.15 first shows the reduction and eventual disappearance of the $E_{2\text{g}_2(i)}$ band at 0.091 V down to 0.088 V. However the $E_{2\text{g}_2(b)}$ band at 1601 cm$^{-1}$ is also seen to disappear. For a stage 2 GIC spectrum it is expected that a single band at ca. 1601 cm$^{-1}$ should be observed as in the case in of stage 2 GIC from chemical synthesis. This is clearly not the case and instead a broad band at 1550 cm$^{-1}$ is seen. This is tentatively assigned as the blue-shifted
$E_{2g}\text{(b)}$ of a stage 2 liquid GIC, where there is no longer ordered distribution of lithium within the planes. This shift can then be explained by charge transfer effects during intercalation of a donor species where electrons occupy the $\pi^*$ orbital and thus weaken the C-C bond strength. Such an effect has been seen for intercalation of donor species into less ordered carbon materials [164-166]. This broad band continues to blue shift and broadens until it disappears into the noise at ca. 1540 cm$^{-1}$. No pure stage 2 band is observed at 1601 cm$^{-1}$ at any of the four points investigated during lithium insertion. Furthermore the stage 1 GIC band for LiC$_6$ was also not observed.

Raman bands are thought to be no longer visible because of the increase of electrical conductivity of these low stage GICs, which leads to a reduction in optical skin depth, and results in a low Raman scattering intensity [66]. The electrical conductivity can be directly correlated to the optical skin depth ($\delta$) of the laser beam [167]:

$$\delta = \sqrt{\frac{2}{\mu \sigma \omega}}$$

(4.6)

Where $\mu$, $\sigma$, and $\omega$ are the magnetic permeability, the electronic conductivity and the inverse of the wavelength, respectively.

Another reason for the non detection of the sharp band of a low stage number lithium-GIC may also be related to the detection of a broad asymmetric line (known as a Fano-Breit-Wigner line [168]) at ca. 1450 cm$^{-1}$ in stage 1 heavy alkali-GICs such as K-, Rb-, and Cs-GICs [104]. But the mechanism for this coupling in the particular case of lithium-GICs is at present unknown [66].
In addition two bands are also observed to appear below potentials of 0.12 V, which are indicated by * in Figure 4.15. An intense band at ca. 1850 cm$^{-1}$ and a very weak sharp band at 1370 cm$^{-1}$. The band at 1850 cm$^{-1}$ was initially assigned to originate from a complex between lithium ions and decomposition products of the ethylene carbonate electrolyte component [67]. The origin of this band has been discussed in the literature [169, 170] and has been described as originating from species containing a carbon-carbon triple bond, with the acetylide Li$_2$C$_2$ as the most likely species formed. It is suggested that it is formed because of laser heating of the graphite surface through the duration of measurement; however as seen in Figures 4.8 and 4.10 this band blue shifts and weakens or disappears during lithium extraction as the potential is raised to 1.5 V.
Recently carbon nanowires have been measured and the band for the carbon-carbon triple bond for these species also has a similar wavenumber position at ca. 1850 cm$^{-1}$ [171, 172].

To the best knowledge the weak band at 1370 cm$^{-1}$ has not been reported in the literature thus far and remains unassigned. The appearance of the band at 1370 cm$^{-1}$ is unlikely to arise from the electrolyte as the closest band of the electrolyte EC:DMC 1:1 M LiClO$_4$ is only a very weak band from a CH$_2$ bending mode seen at 1362 cm$^{-1}$ [173-176], so if the electrolyte has been detected other stronger bands should also have been observed, which is not the case. Laser heating effects could also be the case, but like the 1850 cm$^{-1}$ band this peak is also seen to reversibly appear and disappear at potentials below 0.12 V and above 0.16 V.

**Figure 4.16:** Change in the intensity ratio between the G- and D-bands (a), the shift in G-band position (b) and the variation of G-band FWHM (c) within potential range 3.0 - 0.17 V vs. Li/Li$^+$ for the first lithiation of graphite. Plots of the peak position and full width at half maximum of the G-band extracted from a statistical analysis of spectra collected over the region 3.0 V - 0.175 V. Within the region 0.19 - 0.6 V the G-band shifted linearly with potential (see solid line, average slope -22 cm$^{-1}$/V; correlation coefficient = 0.981).
First de-lithiation

During the first de-lithiation the reverse trend for the Raman spectra is seen (Figure 4.17) as potential is cycled from 0.005 to 1.5 V. At 0.126 V three bands are observed at 1370 cm\(^{-1}\), 1560 cm\(^{-1}\) and 1850 cm\(^{-1}\). The band at 1560 cm\(^{-1}\) is seen to shift and grow in intensity to 1601 cm\(^{-1}\) as the potential is increased. This indicates the formation of the \(E_{2g2}(b)\) and thus the formation of a pure stage 2 GIC. Yet during the first lithium insertion the shifted band at 1560 cm\(^{-1}\) was assigned as a stage 2 liquid phase. This interpretation is confusing as it is expected during de-intercalation that we should go from a stage 2 to stage 2 liquid not the other way around. Unless the shifted \(E_{2g2}(b)\) at 1560 cm\(^{-1}\) can be assigned as both stage 1 and 2 liquid phases, where no periodic order exists between adjacent layers. Both the 1370 and 1850 cm\(^{-1}\) bands have disappeared by 0.16 V.

Figure 4.17: Raman spectral series of point (c) graphite SFG44 displaying the first de-lithiation from 0.126 to 0.160 V. The formation of a stage 2 GIC is displayed as well as presence of new bands at ca. 1370 and 1850 cm\(^{-1}\). Spectra are shifted arbitrarily up the intensity axis. The arrow on the right-hand side indicates the direction of the scan (charge rate C/37). The "*" marks bands at 1370 and 1850 cm\(^{-1}\).
Above 0.16 V a second peak emerges at 1575 cm\(^{-1}\) (Figure 4.18), this is the \(E_{2g2}(i)\), which grows at the expense of the \(E_{2g2}(b)\). This marks the return to a stage 3 GIC and then to a stage 4 by ca. 0.2 V.

![Raman spectral series of point (c) graphite SFG44 displaying the first de-lithiation from 0.161 to 0.201 V. The formation of a G-band doublet is displayed. Spectra are shifted arbitrarily up the intensity axis. The arrow on the right-hand side indicates the direction of the scan (charge rate \(C/37\)).](image)

**Figure 4.18:** Raman spectral series of point (c) graphite SFG44 displaying the first de-lithiation from 0.161 to 0.201 V. The formation of a G-band doublet is displayed. Spectra are shifted arbitrarily up the intensity axis. The arrow on the right-hand side indicates the direction of the scan (charge rate \(C/37\)).

Then there is a mixture of stage 4 and dilute stage 1 (Figure 4.19) from 0.22 to 0.24 V and the doublet G-band returns again to the single \(E_{2g2}\) at 1592 cm\(^{-1}\) which then blue shifts back to 1580 cm\(^{-1}\), showing the passage from dilute stage 1 to fully de-intercalated graphite. In Figure 4.20a the shift in G-band position and in Figure 4.20b the variation of G-band FWHM is shown in potential range 0.22 - 1.5 V vs. Li/Li\(^+\). Within the region 0.19 - 0.6 V the G-band shifted linearly with potential and the average gradient was calculated to be -38 cm\(^{-1}\)/V, which is a steeper shift compared to intercalation.
Figure 4.19: Raman spectral series of point (c) graphite SFG44 displaying the first de-lithiation from 0.22 to 1.5 V. The shift and return of the single G-band is displayed. Spectra are shifted arbitrarily up the intensity axis. The arrow on the right-hand side indicates the direction of the scan (charge rate C/37).

At 1.5 V a weak D-band is observed (Figure 4.21). The re-emergence of the D-band may aid in the development of an explanation of why the D-band disappears in the first place. It is suggested that for the ring breathing D-band to be Raman active at the surface/edge it requires the full $D_{6h}$ symmetry [108]. This symmetry is permitted in the graphite as only weak van der Waals forces bind the graphene layers, therefore each graphene layer can be treated separately. However when there is intercalate between the layers there is the much stronger ionic bond between intercalate and graphene sheet. Therefore the symmetry is broken by the redistribution of the $\pi$-electron cloud via this interaction. Instead of the symmetry argument it could also be suggested that the band is lost via the failure of resonance conditions which the D-band intensity depends upon by the change in electron distribution [106]. Therefore it can be proposed that the D-band first disappears below 1 V due to the formation of the SEI,
where lithium is co-intercalated with the electrolyte, namely EC [15]. The D-band remains inactive at lower potentials because the ternary intercalation compound has now reacted and formed a stable SEI and is replaced by the insertion of the naked lithium ion. Only at 1.5 V does the D-band return where no intercalation from either SEI forming processes or from inserted lithium is present (Figure 4.21). However the band is slightly weaker in intensity which may indicate either trapped ions, irreversible distortion of the surface region or suppression by the SEI. Therefore the disappearance of the D-band is thought to be a strong indicator for intercalation of ions between the graphene sheets.

![Figure 4.20:](image)

**Figure 4.20:** Shift in G-band position (a) and the variation of G-band FWHM (b) within potential range 0.22 - 1.5 V vs. Li/Li⁺ for the first de-lithiation of graphite. Plots of the peak position and full width at half maximum of the G-band extracted from a statistical analysis of spectra collected over the region 0.22 - 1.5 V. Within the region 0.19 - 0.6 V the G-band shifted linearly with potential (see solid line, average slope -38 cm⁻¹/V; correlation coefficient = 0.94.
Figure 4.21: Raman spectra of graphite SFG44 of point b, of the initial (3 V), and after first insertion and extraction of lithium (1.5 V).

Conclusions

The Raman spectra measured during the four point study indicate that at the surface regions of graphite the intercalation goes in the following stage order:

Dilute stage 1 → stage 4 → stage 3 → stage 2L → (stage 1)

The major difference being that no stage 2 spectrum was observed during intercalation. This is slightly different to results from XRD [148], where the following staging order is observed with in the bulk crystal:

Dilute stage 1 → stage 4 → stage 3 → stage 2L → stage 2 → stage 1

Furthermore the in situ Raman results of the order of de-intercalation do not completely match the intercalation Raman spectral series and a different de-insertion arrangement is proposed:

(Stage 1) → (stage 1L) → stage 2 → stage 3 → stage 4 → dilute stage 1
In situ Raman Microscopy of Graphitic Carbons

The key difference again involves the stage 2 spectrum where it is observable during de-intercalation.
These results are contradictory especially in the correct assignment of the stage 2L phase, as it appears the liquid phase before stage 2 is reached is indistinguishable. It could be suggested that the Raman spectrum of stage 2L and stage 1L are identical as both have a disordered distribution of lithium with no long range order along the c-axis. Therefore it is suggested that the shift of the G-band can be attributed to either charge transfer effects or a coupling effect similar in other low stage alkali metal GICs.
A new band was observed at 1370 cm\(^{-1}\), and to the best of all knowledge has not yet been previously detected. However, though the electrolyte as the source has been ruled out, its correct assignment remains uncertain.
The band at 1850 cm\(^{-1}\), previously assigned as carbon-carbon triple bonded species, was also detected at potentials below 0.12 V during the first lithiation.
The D-band (1330 cm\(^{-1}\)) was observed start to disappear below 1 V and completely vanish below 0.5 V because of intercalation, first co-intercalation of solvent with lithium during SEI formation and then during lithium intercalation. However the original D-band intensity is very weak and could still be visible at lower potentials but is not detected above the signal noise. Therefore in order to more clearly follow the disappearance of the D-band, this measurement needs to be repeated but using a graphite with a more intense D-band than graphite SFG44.
4.4 D-band disappearance

In order to more clearly follow the D-band disappearance and appearance during in situ measurements, a more disordered graphite sample was chosen to be investigated. The graphite material used in this experiment has been termed “disordered graphite” because it has a prominent D-band (1330 cm\(^{-1}\)) compared with graphite SFG44 (Figure 4.22).

![Raman spectrum of powder samples of graphite SFG44 and disordered graphite A.](image)

**Figure 4.22:** Raman spectrum of powder samples of graphite SFG44 and disordered graphite A.

The SEM image (Figure 4.23) demonstrates the heterogeneous nature of the graphite electrode. The surface consists of particles of various shapes and sizes and as previous mapping of graphite electrodes has shown with high variation in \(L_a\) value (chapter 3 and [177]).
In order to assess the possible heterogeneity of the electrode reaction Raman spectra were collected from four arbitrarily selected points on the disordered graphite electrode surface during the lithium intercalation and de-intercalation processes. The four points lay on two separate graphite particles (Particle 1; points (A) and (B), Particle 2; points (C) and (D)) (Figure 4.24), these were approximately 15 μm apart from one another.

Figure 4.24: An optical microscope picture of the uncycled graphite (disorder graphite A) electrode surface showing the four points measured: (A), (B), (C) and (D) on Particle 1 and Particle 2.
Figure 4.25 displays the first constant current charge of the disordered graphite A. The first lithiation again exceeds the theoretical maximum specific charge of 372 Ah kg\(^{-1}\) because of irreversible charge consumed from the formation of the SEI [14]. Figure 4.26 displays the Raman spectra of the first lithium intercalation into a disordered graphite material within the potential range of open circuit potential (OCP) ca. 3 V to 0.5 V in the top quad and from 0.5 V down to 0.22 V in the bottom quad.

![Graph showing the first constant current charge of disordered graphite A. The first lithiation exceeds the theoretical maximum specific charge of 372 Ah kg\(^{-1}\).](image)

**Figure 4.25:** Galvanostatic charge curve of disordered graphite A with a constant specific current 10 mA g\(^{-1}\) against potential/ V vs. Li/Li\(^+\) in 1M LiClO\(_4\) 1:1 EC:DMC (charge rate C/37).

The first order spectrum of disordered graphite at OCP (Figure 4.26 all four points, 3.0 V) shows two main bands: the D- and G-bands at 1330 cm\(^{-1}\) and 1580 cm\(^{-1}\) respectively. Additionally the small G-band shoulder, the D\(^{\prime}\)-band is observed at 1610 cm\(^{-1}\).
Figure 4.26: In situ Raman spectra series of disordered graphite A of the four points from open circuit potential (3.0 V) to 0.6 V (top) and from 0.5 V to 0.22 V (bottom). Spectra are shifted arbitrarily up the intensity axis. The arrows on the left-hand side of each quad indicate the direction of the scan (charge rate C/37).
Table 4.3: Potential (V), specific charge capacity (Ah kg\(^{-1}\)) and \(x\) in Li\(_x\)C\(_6\) values of the Raman spectra displayed in Figures 4.26 and 4.28.

<table>
<thead>
<tr>
<th>Potential/ V</th>
<th>Specific charge capacity/ Ah kg(^{-1})</th>
<th>(x) in Li(_x)C(_6)</th>
<th>Potential/ V</th>
<th>Specific charge capacity/ Ah kg(^{-1})</th>
<th>(x) in Li(_x)C(_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0 (OCP)</td>
<td>0</td>
<td>0</td>
<td>0.205</td>
<td>44</td>
<td>0.118</td>
</tr>
<tr>
<td>1.25</td>
<td>2</td>
<td>0.005</td>
<td>0.19</td>
<td>46</td>
<td>0.124</td>
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<tr>
<td>0.9</td>
<td>4</td>
<td>0.01</td>
<td>0.18</td>
<td>48</td>
<td>0.129</td>
</tr>
<tr>
<td>0.8</td>
<td>6</td>
<td>0.015</td>
<td>0.175</td>
<td>53</td>
<td>0.142</td>
</tr>
<tr>
<td>0.75</td>
<td>8</td>
<td>0.02</td>
<td>0.175</td>
<td>55</td>
<td>0.148</td>
</tr>
<tr>
<td>0.7</td>
<td>10</td>
<td>0.025</td>
<td>0.175</td>
<td>57</td>
<td>0.153</td>
</tr>
<tr>
<td>0.65</td>
<td>12</td>
<td>0.03</td>
<td>0.175</td>
<td>60</td>
<td>0.161</td>
</tr>
<tr>
<td>0.6</td>
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<td>0.175</td>
<td>64</td>
<td>0.172</td>
</tr>
<tr>
<td>0.5</td>
<td>19</td>
<td>0.05</td>
<td>0.175</td>
<td>66</td>
<td>0.177</td>
</tr>
<tr>
<td>0.46</td>
<td>21</td>
<td>0.056</td>
<td>0.165</td>
<td>82</td>
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</tr>
<tr>
<td>0.39</td>
<td>23</td>
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<td>0.153</td>
<td>89</td>
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<tr>
<td>0.335</td>
<td>29</td>
<td>0.078</td>
<td>0.13</td>
<td>99</td>
<td>0.266</td>
</tr>
<tr>
<td>0.29</td>
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<td>0.125</td>
<td>102</td>
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<tr>
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</tr>
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<td>0.101</td>
<td>126</td>
<td>0.339</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.85</td>
<td>207</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Figure 4.27 displays various band analyses from spectra for all four points (A to D) shown in Figure 4.26. Figure 4.27a shows the increase in the integrated intensity ratio of the G-band to D-band \((I_G/I_D)\) with decreasing potential. The initial \(I_G/I_D\) values give the \(L_a\) values of these points to be: (A) 4 nm, (B) 25 nm, (C) 4 nm, (D) 10 nm respectively when using equation 3.6. The \(I_G/I_D\) ratio stays relatively constant until 1.1 V but is then seen to increase below 0.9 V. As the potential decreases the D- and D’-bands are seen to decline in intensity for all points. By 0.22 V of points (B) and (D), the D-band has disappeared into the signal noise. In contrast points (A) and (C) clearly possess D-bands until about 0.13 V. The variation of D-band loss can again be explained by an initial loss during co-intercalation below 0.9 V and then the start of total disappearance during major lithium intercalation below 0.2 V, where the D-band is disrupted at both defects and edge planes.
Figure 4.27b displays the shift in the G-band position from 1580 cm$^{-1}$ to 1590 cm$^{-1}$. This shift as before is attributed to the formation of dilute stage 1 GIC [66]. Some heterogeneity is observed with the shift of the G-band of point (D) beginning at a higher potential 0.46 V compared to points (A), (B) and (C) at ca. 0.39 V. The average slope of -28.5 cm$^{-1}$/ V corresponds more satisfactorily than graphite SFG44 with a similar measurement on a single KS44 graphite microflake by Shi et al. [144]. In Figure 2.27c, the decrease and then subsequent increase of the full-width-half-maximum (FWHM) of the G-band, is shown with decreasing potential.

The spectra of the four points measured from 0.205 - 0.175 V (top quad) and 0.175 V - 0.085 V (bottom quad) (Figure 4.28) show the variation in potential of the appearance of the G-band doublet that is indicative of the formation of a stage 4 graphite intercalation compound (GIC). For point (A) the stage 4 GIC is first at 0.153 V, point (B) at 0.175 V, point (C) at 0.165 V and point (D) at 0.180 V. The G-band doublet band can be assigned to the intensities of the interior $E_{2g2}(i)$ (1577 cm$^{-1}$) and the bounding $E_{2g2}(b)$ (1602 cm$^{-1}$) bands [66]. This phase transition is related with the change from a random distribution of lithium-ions into a more compact distribution in the staged compound. At 0.108 V, for point C, only a single broad band is observed at 1570 cm$^{-1}$. This band decreases and is unobservable below 0.10 V. These results display the phase transitions from stage 3 through to stage 2L. Again the stage 1 lithium GIC is not observed [66].
Figure 4.27: Change in the intensity ratio between the G- and D-bands (a), the shift in G-Band position (b) and the variation of G-band FWHM (c) within potential range 3.0 - 0.170 V vs. Li/Li⁺. Plots of the peak position and full width at half maximum of the G-band extracted from a statistical analysis of spectra collected over the region 3.0 V - 0.175 V. Within the region 0.175 - 0.550 V the G-band shifted linearly with potential (see solid line, average slope -28.5 cm⁻¹/V; correlation coefficient = 0.9779).
Figure 4.28: *In situ* Raman spectra series of disordered graphite A of the four points from 0.205 to 0.175 V (top) and from 0.175 V to 0.085 V (bottom). Spectra are shifted arbitrarily up the intensity axis. The arrows on the left-hand side of each quad indicate the direction of the scan (charge rate C/37).
The heterogeneity of the intercalation of lithium into graphite can be observed in the optical picture of disordered graphite A (Figure 4.29). The qualitative assessment of the particular stage compound at a particular location has also been demonstrated by Migge et al. [163]. In Figure 4.29A at 0.175 V small areas of blue colour can be noticed on surface of some of the particles (circled), signifying the presence of a stage 3 or 4 GIC. Whilst in Figure 4.29B at 0.086 V patched of red and blues areas can be clearly seen, indicating a mixture of stage 2, 3 and 4.

**Figure 4.29:** Optical microscope image (x80 objective) of disordered graphite A surface during first lithiation at (A) 0.175 and (B) 0.086 V vs. Li/Li⁺.

*First de-lithiation*

Most importantly the reappearance of D-band during lithium de-intercalation is shown in Figure 4.30. The reappearance occurs strongly when the potential is increased above 0.5 V. Interestingly the reappearance of the D-band is coupled with an overall intensity increase of the G-band as well. These results support the assumption that intercalation disrupts the D-band, and first weakens during SEI formation and then completely during lithium intercalation and reappears only when all the lithium is subsequently removed and a stable SEI is in place which prevents any further co-intercalation. Though the de-intercalation spectra are of a poorer quality to the intercalation spectra it can still be clearly seen that the spectral trend is the same as shown previously in chapters 4.2 and 4.3.
The lone $E_{2g2}(b)$ band at 0.18 V shows a stage 2 GIC, this transforms into a doublet G-band ($E_{2g2}(i)$ and $E_{2g2}(b)$) above 0.2 V indicating stage 3 and then stage 4 GICs. The return to a single band ($E_{2g3}(i)$, 1590 cm$^{-1}$) at 0.32 V confirms the presence of a dilute stage 1 which shifts to 1580 cm$^{-1}$ to produce a spectrum of non-intercalated graphite.

Figure 4.30: *In situ* Raman spectra series of first de-lithiation of point (A) of disordered graphite A from 0.18 to 1.5 V. Spectra are shifted arbitrarily up the intensity axis. The arrows on the right-hand side of each quad indicate the direction of the scan (charge rate C/37).
Conclusion

The measurement of the first lithium intercalation into graphite of four separate points on the electrode was successfully undertaken. All points showed the characteristic spectra as discussed previously in the literature and in chapters 4.2 and 4.3 at similar potentials vs. Li/Li⁺. For more the ordered points (B) and (D) ($L_a = 25$ and 10 nm respectively) the D-band was observed to disappear below potentials of ca. 0.29 V, whilst the more disordered points (A) and (C) ($L_a$ both ca. 4 nm) the D-band has disappeared from 0.135 V. The spectra suggest that even at a low charging rate of $C/37$, intercalation does not proceed uniformly over the whole electrode, with some measurement points showing the stage 4 G-band doublet bands at higher potentials. This confirms the same observation by Migge et al. [163], where they measured different staged GIC Raman spectra depending on location on the electrode.
4.5 \( L_a \) correlation with stage number

From the previous measurements on disordered graphite A there seemed to be an indication that the \( L_a \) value may play an important role in determining how much lithium is intercalated under galvanostatic conditions. Therefore the first in situ Raman large number mapping experiment was employed to evaluate whether there is a relationship between \( L_a \) and type of GIC [178]. In the previous 4 point the greatest variation in the Raman spectrum existed at around 0.17 V. Therefore at 100 points within an area of 40 \( \mu \text{m} \times 40 \mu \text{m} \) (Figure 4.31a) had their Raman spectrum first collected at 3 V (OCP) and the \( L_a \) values of each point were determined using equation 3.5. Figure 4.31b shows that the \( L_a \) values have a large distribution of 6 to 50 nm. Then the potential was galvanostatically cycled down to 0.17 V and held at this potential for current to drop to a near zero value in order to be under steady state conditions (around 24 hours). The same 100 points were again mapped at 0.17 V. At this potential a doublet should be observed for all points. Indeed a doublet was observed for most points and using equation (4.5), the spectra indicated staged compound between stages 6 and 3 (Figure 4.31c). At some points a spectrum could not be obtained as these are indicated by white squares. For the points where a spectrum at both 3 V and 0.17 V could be obtained the relationship between \( L_a \) and stage number was plotted (Figure 4.28d). The figure shows that clear relationship could not be obtained. This could be because the position was slightly changed during intercalation because visual correction of position had to be carried out before the second mapping at 0.17 V. The length of the mapping experiment was also too long. Each point required a measurement time of 3 minutes to obtain a spectrum of sufficiently low signal to noise ratio. Therefore including the time required for the auto-focus and time between to move from one point to another the map required 5 - 6 hours to complete. Under a pseudo-steady state, it is unlikely that the measurement of point 1 occurred under similar conditions as point 100. Therefore a significant increase in signal intensity and lowering of mapping time is required for this experiment to produce reliable and reproducible results.
Figure 4.31: (a) optical picture of surface of uncycled disorder graphite A electrode, (b) $L_a$ map generated from 100 Raman spectra obtained using equation (3.5) at 3 V vs. Li/Li$^+$, (c) stage index generated from 100 Raman spectra using equation (4.6) at 0.17 V vs. Li/Li$^+$, (d) plot showing relationship between stage number vs. $L_a$. White points indicate where no spectra could be measured at 0.17 V. Electrolyte used: 1M LiClO$_4$ 1:1 EC:DMC.
4.6 Particle size and rhombohedral fraction

The effect of the particle size and fraction of the rhombohedral phase (3R) in graphite on the mechanism of lithium intercalation was investigated with in situ Raman microscopy. With the ABCABC structure as opposed to ABAB structure the affect of these differing surface properties may be visible in the Raman spectra. The structural and surface properties of the graphite materials investigated are shown in Table 4.4 [19]. The SFG and KS series 44, 15 and 6 are investigated and Table 4.4 shows that these graphitic materials possess a wide range of values for the rhombohedral fraction. These graphite materials differ due to the shape of the particles; SFG particles are anisometric whilst KS are isometric [179].

Rhombohedral form of graphite has the primitive unit cell $R\bar{3}m$ and contains two carbon atoms. The irreducible representation shows two Raman active modes [147]:

$$\Gamma_{\text{Raman}} = A_{1g} + E_g$$  \hspace{1cm} (4.7)

The $A_{1g}$ arises from carbon atom displacements perpendicular to the graphene sheets and the $E_g$ mode to carbon atom displacements within the graphene sheets and is therefore thought to occur at a similar frequency (1580 cm$^{-1}$) as the G-band in hexagonal graphite. However, the $A_{1g}$ mode, which is believed to be active at around 850 cm$^{-1}$, has been so far not detected by Raman [147] because it arises from weak interplanar interactions. This is confirmed in Figures 4.32 - 4.37 where no significant difference in the intercalation spectra are observed when measuring the first lithiation of graphite materials SFG6, 15, 44 and KS6, 15, 44. No $A_{1g}$ band was detected near 850 cm$^{-1}$ for the graphite materials with a high rhombohedral fraction (subsequently this wavenumber region is omitted from the Raman figures). All the materials show identical intercalation spectral trends as seen before in chapters 4.2, 4.3 and 4.4. The potentials at which some features, such as appearance of doublet G-band do vary between materials but this can be attributed to the heterogeneity of lithium intercalation into graphite as previously demonstrated in chapter 4.4.

The effect of particle size can also be ignored as no significant effect is seen which confirm previous conclusions by Huang and Frech [143], when they also compared in situ Raman
spectra of KS6 and KS44. In Table 4.4, for example, SFG6 shows a larger irreversible charge loss in comparison to SFG44 in 1M LiPF$_6$ 1:1 w/w EC:DMC, this trend is also seen during galvanostatic cycling of the Raman cells in 1M LiClO$_4$ 1:1 w/w EC:DMC where the galvanostatic curves of SFG6 (Figure 4.32) shows a much high charge loss due to SEI formation than SFG44 (Figure 4.34). This charge loss has been shown to correlate with the BET surface area of the graphite [180].

Table 4.4: Structural bulk and surface properties of SFG and KS graphite [19].

<table>
<thead>
<tr>
<th>Graphite</th>
<th>BET/m$^2$g$^{-1}$</th>
<th>$d_{50a}$/$\mu$m</th>
<th>Rhombohedral 3R-phase$^b$ (%)</th>
<th>$L_d$/nm Raman</th>
<th>Irreversible charge loss (%)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFG6</td>
<td>17.1</td>
<td>3.3</td>
<td>37</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>SFG15</td>
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<td>9.1</td>
<td>23</td>
<td>76</td>
<td>12</td>
</tr>
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<tr>
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<td>6.2</td>
<td>20.0</td>
<td>12</td>
<td>39</td>
<td>13</td>
</tr>
</tbody>
</table>

$^a$For example, in sample SFG6, 50% of the particles are smaller than 3.3 $\mu$m

$^b$Fraction of the rhombohedral phase (3R) in graphite

$^c$Values from first cycle in 1M LiPF$_6$ 1:1 w/w EC:DMC
Figure 4.32: First graphite lithiation curve and in situ Raman spectral series of SFG6 graphite in 1M LiClO₄ 1:1 w/w EC:DMC during the first electrochemical charge. Numbered points on spectra correspond to position measured on the lithiation curve. Spectra are shifted arbitrarily up the intensity axis (charge rate C/37).

Figure 4.33: First graphite lithiation curve and in situ Raman spectral series of SFG15 graphite in 1M LiClO₄ 1:1 w/w EC:DMC during the first electrochemical charge. Numbered points on spectra correspond to position measured on the lithiation curve. Spectra are shifted arbitrarily up the intensity axis (charge rate C/37).
Figure 4.34: First graphite lithiation curve and in situ Raman spectral series of SFG44 graphite in 1M LiClO₄ 1:1 w/w EC:DMC during the first electrochemical charge. Numbered points on spectra correspond to position measured on the lithiation curve. Spectra are shifted arbitrarily up the intensity axis (charge rate C/37).

Figure 4.35: First graphite lithiation curve and in situ Raman spectral series of KS6 graphite in 1M LiClO₄ 1:1 w/w EC:DMC during the first electrochemical charge. Numbered points on spectra correspond to position measured on the lithiation curve. Spectra are shifted arbitrarily up the intensity axis (charge rate C/37).
Figure 4.36: First graphite lithiation curve and in situ Raman spectral series of KS15 graphite in 1M LiClO$_4$ 1:1 w/w EC:DMC during the first electrochemical charge. Numbered points on spectra correspond to position measured on the lithiation curve. Spectra are shifted arbitrarily up the intensity axis (charge rate C/37).

Figure 4.37: First graphite lithiation curve and in situ Raman spectral series of KS44 graphite in 1M LiClO$_4$ 1:1 w/w EC:DMC during the first electrochemical charge. Numbered points on spectra correspond to position measured on the lithiation curve. Spectra are shifted arbitrarily up the intensity axis (charge rate C/37).
Conclusion

No major variation of Raman spectra is observed according to particle size or rhombohedral fraction. These results indicate that the intercalation mechanism of lithium into graphite is similar irrespective of the micro-scale properties of graphite material.
4.7 Exfoliation of graphite in PC containing electrolyte

Introduction

Highly crystalline graphitic materials are routinely used as the negative electrode in lithium-ion batteries [8]. The stability of highly crystalline graphite materials towards exfoliation during the first electrochemical reduction in mixed ethylene carbonate (EC)/propylene carbonate (PC) electrolyte systems depends on the formation of an efficient passivation film on the graphite particle surface [181]. This is essential for the proper operation of these electrode materials in the lithium-ion battery. Electrochemical exfoliation can be avoided on graphite surfaces with high defect content, since the surface passivation process is sufficiently completed at more positive potentials [19]. If the formation of stable solid electrolyte interphase (SEI) does not take place before the potential range in which solvent co-intercalation reactions occur, then deterioration (exfoliation) of the graphite will result, with a considerably diminished charge storage capability. Subsequent electrochemical reduction of the co-intercalated electrolyte leads to substantial gas formation, whose bubbles result in a build up of local pressure that may crack the graphite particles, causing the breaking up of the crystal lattice (Figure 4.38) [15-17].

Many graphitic parameters have been previously investigated to determine which ones have the greatest influence on whether or not exfoliation occurs. Guerin et al. [147] suggested that graphitic materials with a high rhombohedral fraction do not exfoliate in the presence of PC because of the resultant introduction of disorder into the graphite structure. However, investigations by Spahr et al. [182] with ethylene carbonate (EC) suggest that surface group chemistry plays the active role, and has subsequently lead to the idea of an active surface area (ASA) [20]. The ASA being the cumulative surface area of the various types of defects present at the carbon surface. Graphitic materials with a high ASA tend not to exfoliate because surface passivation is kinetically enhanced [183]. Moreover, the addition of additives to the electrolyte to suppress exfoliation, has been reported [184].

It has been shown [19] that ex situ Raman mapping of numerous graphitic samples determined that microcrystalline graphite materials with a low length of the graphite crystallite in the a-direction ($L_a$) (ca. 20 nm) tended not to exfoliate in PC containing electrolyte (Figure 4.39).
Figure 4.38: Schematic showing the Besenhard model of SEI film formation and exfoliation [15].
Figure 4.39: Relationship between the $L_\alpha$ value and the particle size ($d_v/\mu m$) distribution of the graphite SFG-, KS- and GN powders. Graphite powders circled show no exfoliation in a PC containing electrolyte [19].

**Exfoliation-band**

During an *in situ* Raman study of the intercalation of lithium into a carbon coke anode in the presence of 1.2 M LiAsF$_6$ in PC, an up-shift of the G-band was detected by Irish et al. [185] and was assigned as the co-intercalation of solvent. Inaba et al. [66] commented on this effect, but did not observe solvent co-intercalation in their study on natural graphite powder (NG-7) with 1.0 M LiClO$_4$ in EC/diethyl carbonate (DEC). Through *in situ* Raman measurements of lithium intercalation into microcrystalline graphite (KS44) in 1M LiClO$_4$ in EC/1,2-dimethoxyethane (DME) solutions by Huang and Frech [143], a doublet formation of the G-band at potentials below 0.9 V was observed. The appearance of this doublet suggested that a stage compound ($n > 2$) is formed in the surface layers of the graphite particles. They proposed that, because the frequencies and relative intensities of these two bands do not match the spectrum measured for normal stage compounds, it is likely that lithium ions were co-intercalated with solvent into the top layers of graphite. Therefore the resultant partial exfoliation produced loosely compacted graphite layers. This band can therefore be assigned to the graphite layers on which Li(solvent)$_x$ moieties ($x > 0$) were bound. This band will be referred to as the exfoliation-band or E-band, and if detected by Raman microscopy it will signal the initiation of the exfoliation process.
The graphitic material SFG44 is well known to exfoliate in PC containing electrolyte, whilst this effect is not observed for the graphitic carbons with smaller crystallites and greater ASA such as SFG6 [19, 20]. These two materials will be compared to evaluate possible differences seen in the Raman spectrum.

Results and discussion

The in situ Raman spectra of SFG6 in LiClO₄ EC:PC (Figure 4.40) is identical to SFG44 in EC:DMC shown in chapter 4.2 and the G-band split is noted to begin at 0.17 V as the G-band broadens.

Figure 4.40: First graphite lithiation curve and in situ Raman spectral series of SFG6 graphite in 1M LiClO₄ 1:1 w/w EC:PC during the first electrochemical lithiation (charge rate C/37). Numbered points on spectra correspond to position measured on the lithiation curve. Spectra are shifted arbitrarily up the intensity axis.
In situ Raman spectra of SFG44 in LiClO₄ EC:PC during the first lithiation are shown in Figure 4.41. The G-band appears again at 1584 cm⁻¹ at OCP. During the first lithiation process the G-band remains unchanged until the cell potential decreases to 0.9 V, where a shoulder appears at 1597 cm⁻¹. The shoulder increases in intensity and becomes the dominant band by 0.785 V. This band, which can be identified as the exfoliation-band or E-band which was described in the introduction, can be allocated to C-C vibrations of graphite layers on which Li(solvent)x moieties (x > 0) were bound [143]. Because the frequencies and relative intensities of these two bands (the G- and E- band) do not match the spectrum measured for normal stage compounds seen for graphite SFG6 (Figure 4.40) at 1578 cm⁻¹ (E₂g₂(i)) and 1602 cm⁻¹ (E₂g₂(b)), it is probable that at the surface regions of the graphitic particles lithium-ions are co-intercalated with PC [186, 187]. Furthermore, together with the appearance of the E-band, is the weakening of the D-band. Below 0.82 V it is no longer detectable. Even though the wavenumber position is similar to the D’ band, the E-band is not related. The D’-band usually appears as a weak-shoulder to the G-band in the range of ca. 1604-1615 cm⁻¹. This band is thought to be linked to the D-band and as such can be related to holes and edge planes on the graphene sheet as opposed to an intercalation effect, as witnessed in these measurements. One would expect that an increase in the D’-band would be coupled to an increase in the D-band [188].

Below 0.2 V the E-band is no longer detected (inset Figure 4.41) and the spectra are identical to those previously observed for SFG6 EC/PC displayed earlier in Figure 4.40. A shifted single band (1594 cm⁻¹) is observed (spectrum 11), indicating the formation of dilute stage 1 GIC. As the cell potential decreases further, the stage-four compound appears which has two equally intense bands at 1578 and 1602 cm⁻¹; these are shown at lower potentials (spectra 12-14). The loss of the E-band would indicate that the Li(solvent)x moieties (x > 0) are no longer present in the four points measured. The appearance of the shifted G-band and doublet G-band indicate that after the exfoliation process is completed, lithium-ion intercalation is now proceeding as in the case of graphite SFG 44 in the electrolyte EC:DMC [66, 143, 146].
Figure 4.41: First graphite lithiation curve and *in situ* Raman spectral series of SFG44 graphite in 1M LiClO$_4$ 1:1 w/w EC:PC during the first electrochemical lithiation (charge rate C/37). Numbered points on spectra correspond to position measured on the lithiation curve. Spectra are shifted arbitrarily up the intensity axis.

In Figure 4.42 the Raman spectra of the four points on the electrode surface measured from 3-0.725 V are shown. The Raman spectra of point (d) were previously shown in more detail in Figure 4.41. Comparing the spectra it can be observed that there is a great variation between the intensities of the measured E-band. Moreover on point (a), the E-band appears below 0.9 V but has disappeared below 0.8 V. These results show that there is a large heterogeneity between points measured on the electrode surface.
Figure 4.42: Optical image of graphite SFG44 surface showing the four points: (a), (b), (c) and (d), measured at the corner of a square 30 μm in length. The *in situ* Raman spectra of the four points in 1M LiClO₄ 1:1 w/w EC:PC are shown in the potential range of 3 - 0.725 V vs. Li/Li⁺. The $I_D/I_G$ ratios at 3.0 V vs. Li/Li⁺ for all four points are displayed by each spectral series.

In fact, inhomogeneity of passivation phenomena on graphitic electrodes with Raman spectroscopy has already been established by Kostecki et al. [162]. They demonstrated that, the more disordered the local graphitic material, the stronger the Raman signal at 1000-1200 cm⁻¹ from inorganic decomposition products is. In this investigation these decomposition products are not present, as they arise from the PF₆⁻, whereas here LiClO₄ was employed as the electrolyte salt. However, the relationship of the E-band can still be examined by comparison with the D-band/ G-band ratio ($I_D/I_G$) of the four individual points. For graphitic carbons the evaluation of the D/ G ratio gives an indication of surface disorder [162].
In Figure 4.43 the $I_d/I_G$ ratio of all four points are plotted against the ratio of E-band/ G-band ($I_e/I_G$) taken at both the initiation of PC co-intercalation at 0.88 V and when the co-intercalation process is well under way at 0.725 V. From the plot point (b) displays the lowest $I_d/I_G$ value of 0.16 indicating that the local graphite structure is fairly ordered. Interestingly this point also displays the highest $I_d/I_G$ ratios at both of the potentials. Therefore point (b) suggests that the more ordered the graphite structure, the lower amount of ASA or passivation kinetics, and consequently the more likely it is to exfoliate. Points (c) and (d) follow this trend, they both respectively have higher $I_d/I_G$ ratios of 0.24 and 0.44 and lower $I_d/I_G$ values. However the small number of points recorded in this work cannot reliable demonstrate a precise relationship. Indeed point (a), which has a similar $I_d/I_G$ value to point (b) of 0.19, initially possesses only a weak E-band at 0.88 V. However, as stated earlier, by 0.725 V only the G-band is present, suggesting that this site has formed a stable SEI and no more solvent co-intercalation is occurring.

Figure 4.43: Plot of $I_d/I_G$ vs. $I_d/I_G$ values of the four points (a), (b), (c) and (d) measured. $I_d/I_G$ at 0.88 V and 0.725 V are shown.
The exfoliation of the graphite SFG44 can be confirmed by the SEM images shown in Figure 4.44. In Figure 4.44a, the SEM picture shows a number of fully exfoliated graphite particles covered with a tightly bound SEI layer. The particles seem to be connected with a spider-web like features. This is considered to be the binder, because it has been determined with the SEM to be non-conductive, and because it stretches out between the particles, holding the particles together. Furthermore it can be seen in Figure 4.44b that the SEI has also precipitated over the binder, this is seen as the white globules on the binder.

Figure 4.44: Post Mortem SEM images of SFG44 graphite negative electrode after completion of the 3rd de-lithiation, cycling between the potential limits of 0.005 V and 1.5 V in 1M LiClO₄ 1:1 w/w EC:PC electrolyte.
The solvent has therefore been decomposed on the graphite surface, this can be confirmed by
differential electrochemical mass spectrometry (DEMS) [19], where the rate of ethylene and
propylene gas formation (decomposition products of EC and PC) were shown to increase with
decreasing potential. Therefore once the potential lowers below 0.85 V decomposition of the
electrolyte at the graphite electrode is the favoured process compared to solvent co-
intercalation. Furthermore decomposition of electrolyte already within the graphite causes
further separation and expansion of the graphite layers.

To study this process in more detail SFG44 was galvanostatically charged at 10 mA g\(^{-1}\) of
carbon to 0.8, 0.6 and 0.3 V and then equilibrated at this potential for 24 hours, until the
current had been reduced to zero and the electrode was under steady state conditions.
Figure 4.45 demonstrates the G- and E-bands blue-shift with decreasing potential
correspondingly from 1584 and 1597 cm\(^{-1}\) at 0.8 V to 1589 and 1607 cm\(^{-1}\) at 0.3 V (Table 4.5). In the case of the G-band shift it is known that at 0.3 V a dilute stage 1 compound
containing bare lithium is present because the shift of the G-band of dilute stage 1 GICs can
be attributed to an in-plane C-C bonds force constant increase [143, 146]. For the occurrence
of the migrating E-band, this could be due to an increase of solvent co-intercalation at the 100
nm thick skin depth layer at the graphite surface region, detectable by Raman spectroscopy.
However, although it has been shown by XRD that there is significant PC co-intercalation at
0.8 V [187], it is difficult to believe that this is still the case at 0.3 V. As reduction of
propylene carbonate is very favourable at this low potential.
Table 4.5: The positions of the bands shown in Figure 4.44, SFG44 graphite in 1:1 w/w 1M LiClO₄ EC:PC, when the electrode was galvanostatically charged at 10 mA g⁻¹ of carbon to 0.8, 0.6 and 0.3 V respectively.

<table>
<thead>
<tr>
<th>Holding potential/ V vs. Li/Li⁺</th>
<th>G-band/cm⁻¹</th>
<th>E-band/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>1584</td>
<td>1597</td>
</tr>
<tr>
<td>0.6</td>
<td>1583</td>
<td>1604</td>
</tr>
<tr>
<td>0.3</td>
<td>1589</td>
<td>1607</td>
</tr>
</tbody>
</table>

Figure 4.45: Results of Raman measurements after stabilisation at 0.8, 0.6 and 0.3 V vs. Li/Li⁺ in 1M LiClO₄ 1:1 w/w EC:PC electrolyte. The Raman spectrum of SFG44 graphite at 3.0 V (OCP) is also shown for comparison.

Each of these electrodes went under post mortem investigation with SEM and the resultant images are shown in Figure 4.46. At 0.8 V (images a, b and c) a tightly formed SEI film is observed on the surface of the graphite particles. This is seen as the white film in the SEM and in image (a) is observed to be formed on all graphite particles. In image (b) a small amount of exfoliation is observable on the edge plains of the flat graphite particles. At 0.8 V
partial exfoliation of the graphite particles is detectable. Exfoliation is mainly evident on large particles and particles with high $L_a$ and $L_c$ values. This observation is supported by XRD and Raman measurements previously carried out by us, which showed that materials with lower particle size and lower $L_a$ and $L_c$ values tended not to exfoliate in PC containing electrolyte [19]. One exfoliated particle is displayed in image (c); under the SEI layer the graphite layers have expanded. At 0.6 V (images d, e, and f) it is apparent that exfoliation has continued. Both large and small particles are now heavily exfoliated. Again what has previously been considered to be the binder is also present in image (d). In images (e) and (f), the fully exfoliated accordion-like particles, can be clearly seen. In (f) the filaments of either the SEI or binder can also be distinguished; stretched out along the edge plain (most likely it is the binder that is observed as it should be more elastic than the SEI). It could be supposed that the SEI or binder is trying to hold the particle together, but the exfoliation is too heavy. The images for 0.3 V (g, h and i) show no large differences from those taken at 0.6 V. Full exfoliation of the graphite particles has been completed. Because of the large extent of exfoliation the SEI layer (though still present) is no longer visible to the SEM.

These SEM pictures help to explain the heterogeneities measured between the Raman spectra during mapping experiments. At 0.8 V not all particles exfoliate or undergo the same amount of exfoliation, this corresponds to the non-detection of the E-band at some positions and the different intensities measured for this band.
Figure 4.46: Post mortem SEM images of SFG44 graphite negative electrode after stabilisation at 0.8 V (a, b, c) 0.6 V (d, e, f) and 0.3 V (g, h, i) vs. Li/Li\(^+\) in 1M LiClO\(_4\) 1:1 w/w EC:PC electrolyte.
Conclusions

In SFG44 graphite in EC:PC a band at 1597 cm\(^{-1}\), labelled as the E-band was detected by \textit{in situ} Raman microscopy, which can be related to the presence of Li(solvent)\(_x\) moieties (x > 0). Exfoliation of SFG44 in EC:PC was confirmed by SEM. Multipoint mapping of the electrode surface demonstrated the variation in intensity of this band with respect to the unchanged G-band at 1584 cm\(^{-1}\). Moreover some points measured did not show the E-band and only contained the G-band at potentials below 0.8 V. The variation of the appearance of the E-band in the Raman spectra was supported by SEM images, which suggest that not all graphite particles exfoliate.

Potential stabilisation studies show that the E-band shifts from 1597 to 1607 cm\(^{-1}\) when the potential is held at 0.8 then 0.3 V vs. Li/Li\(^+\). This could be due to a greater amount of lithium solvent co-intercalation at the surface region of the graphite crystal. SEM images show different stages of exfoliation at these potentials. At 0.8 V exfoliation takes place preferentially on larger particles. However, by 0.6 V full exfoliation on all graphite particles is observable.
4.8 Detection of the stage 2L phase disappearance at 0 °C

Introduction

The phase diagram of Li\textsubscript{x}C\textsubscript{6} was determined by Dahn [148] by detailed in situ XRD measurements (Figure 4.47). A curious part of this phase diagram, which has not yet been fully investigated for electrochemical formation of lithium-GICs, is the apparent disappearance of the stage 2L phase at temperatures below 10 °C. The earlier phase diagrams reported by Fischer [105] illustrated this phase change to occur at the lower temperature of under −13 °C for lithium-GICs made by chemical intercalation. Moreover Doll et al. [158] have successfully monitored this phase change with Raman spectroscopy. They saw a reversible change using HOPG from a dilute stage 2, LiC\textsubscript{17} change to a mixture of pure stage 2, LiC\textsubscript{12} and stage 3, LiC\textsubscript{18} and back again. In chapters 4.2, 4.3 and 4.4, in situ Raman microscopy was shown to be able to clearly differentiate the three different stage GICs during electrochemical intercalation: stage 3, stage 2L and stage 2 (Figure 4.48). Stage 3 has a doublet G-band, stage 2L a broad band ca. 1540 cm\textsuperscript{-1} and stage 2, the \( E_{2\text{g}}(b) \) at 1600 cm\textsuperscript{-1}. Therefore this phase transition is investigated with in situ Raman microscopy to see if it occurs, as Dahn [148] indicates at, ca. 10 °C by measuring the Raman spectrum at 23 and 0 °C at the phase transition boundary, ca. Li\textsubscript{0.25}C\textsubscript{6}.

![Figure 4.47: The phase diagram of Li\textsubscript{x}C\textsubscript{6} in the range 0 °C < T < 70 °C. Dots show where in situ XRD measurements were obtained (redrawn from [148]).](image-url)
In situ Raman Microscopy of Graphitic Carbons

Figure 4.48: A comparison of the Raman spectra of stage 3, stage 2L and stage 2 GICs for graphite SFG6. Note the stage 2L and 3 GIC Raman spectra are taken from the first lithiation, whilst the stage 2 spectrum is from the first de-lithiation. This is because no stage 2 GIC spectra were recorded during lithiation; therefore this is why the potential at which this spectrum was measured (0.16 V) is higher than for the stage 3 GIC spectra (0.13 V).

Experimental

In view of the fact that the graphite surface is very heterogeneous and different Raman spectra can be collected at different locations, in situ Raman mapping of 25 points on the surface was undertaken in order to seek to obtain a representative picture (Figure 4.49). The in situ Raman temperature variable cell was employed in this experiment with lithium metal acting as both counter and reference and graphite SFG6 as the working electrode. Graphite SFG6 was chosen for this experiment because it is stable and does not exfoliate in the PC containing electrolyte, 1M LiClO₄ 1:1 w/w EC:PC, which is liquid below 10°C with acceptable conductivity that is comparable to room temperature.
Figure 4.49: Optical microscope image of uncycled graphite SFG6 electrode surface (x80 objective) displaying the 25 points measured.

The Raman cell was under galvanostatic control from 3 V to 0.12 V (Figure 4.50) under a constant current of 0.025 mA. At 0.12 V it is expected that the graphite is in the region of the phase diagram where $x = 0.25$ for $\text{Li}_x\text{C}_6$, at the boundary of stage 3/stage 2 $\rightarrow$ stage 2L/stage 2. The potential is held at 0.12 V and the current dropped towards 0 mA as the cell reaches steady state conditions. The cell was put under open circuit before the steady state was reached (ca. 0.005 mA, 20 % of the original current) because of the compromise between lifetime of the Raman cell and length of experiment with waiting for the true steady state. Raman spectra were then collected from the 25 points at 1 (23 °C), 6 (0 °C) and 27 (23 °C) hours after the circuit was broken. Each spectrum required 300s to acquire an acceptable signal to noise ratio, leading each 25 point map to require 2 hours to accomplish. For each temperature change, the map was repeated twice, in order to verify that no relaxation processes are occurring during the long-time measurement. The temperature was reduced to 0 °C as an estimated error of $\pm 3 \, ^\circ\text{C}$ is attributed to the experimental set-up. The position of the thermal couple is situated below the current collector of the lithium counter electrode; therefore a temperature gradient is expected through the electrolyte towards the graphite
working electrode. Consequently, to be confident that the graphite electrode is below the phase transition temperature boundary of 10 °C (which also carries an error of ± 2 °C), the cell was cooled to 0 °C down from the ambient room temperature of 23 °C (after completion of map a). Once the measurements at 0 °C (map b) were completed the temperature was allowed to increase naturally back to room temperature before the last mapping was untaken (map c).

**Figure 4.50:** The potential-time curve plot of the first lithiation of graphite SFG6 from 3.0 V to 0.12 V in 1M LiClO₄ in w/w 1:1 EC:PC at 10 mA g⁻¹ of carbon (charge rate C/37). Cell was put to open circuit after 9 hours at 0.12 V.
Results and discussion

The results of six representative points from map a (23 °C), b (0 °C) and c (23 °C) are displayed in Figure 4.51. Each map is the first map of each temperature measurement because the repeat map displayed no variation. The results of map a show three different types of Raman spectra, points 3, 6 and 9 show a broad band on to which three recognisable peaks are located at ca. 1263, 1429 and 1537 cm⁻¹. Only the 1537 cm⁻¹ band can be tentatively assigned as the shifted $E_{2g}^2(b)$ of the stage 2L GIC. The origin of the other two bands origin remains unknown. This band is also present at points 15 and 20, where the previously reported (chapters 4.2 and 4.3) stage 2L spectra is shown. Point 24 shows the G-band doublet of the stage 3 GIC. Therefore the spectra from map a compliment Dahn’s XRD results [148] which predict the presence of both stage 3 and 2L at 0.12 V at this temperature. Map b shows the results after cooling the cell to 0 °C. All six points display dissimilar spectra after this temperature change (in fact all 25 points changed, not shown). The spectra observed for all points can be assigned to the stage 3 doublet (1580 cm⁻¹ and 1601 cm⁻¹), or the broad single stage 2 GIC band at 1601 cm⁻¹. The cooling down lowered the intensity of the spectra at all points. Map b therefore implies the disappearance of the stage 2L phase at 0 °C, again in agreement with Dahn [148].

When the graphite was again mapped at room temperature (23 °C), map c, some of the spectra have changed back, points 15, 20 and 24, some have partially returned, point 9, whilst other points have remained the same, points 3 and 6. These measurements therefore indicate the return of the stage 2L phase at some positions on the graphite electrode. Doll et al. [158] observed the return transition was sluggish and was only observed to be complete after a time of 96 h upon return to room temperature. As map c was measured only 9 hours after returning to room temperature this may explain the partial reversal seen.
Figure 4.51: Raman spectra of representative points of the different variations of the Raman spectra observed during temperature change of graphite SFG6. All Raman spectra displayed have not undergone base-line correction. Arrows on the right-hand side indicate which direction to read the spectra.

Conclusions

Reversing the temperature between 23 and 0 °C, the Raman spectrum displays at some points of the graphite electrode, the loss and reappearance of the stage 2L phase at 0.12 V. These results concur with the established phase diagram of Li_xC_6. Mapping the graphite surface at 25 points reveals markedly different spectra according to position, reaffirming the heterogeneous nature of lithium intercalation into this material. Indeed some of the spectra displayed previously unreported bands at 1263 cm⁻¹ and 1429 cm⁻¹, whose assignment is unknown.
5

IN SITU RAMAN MICROSCOPY
OF FURTHER MATERIALS FOR
LITHIUM-ION BATTERIES

5.1 Introduction

After the successful measurement of graphitic materials with multipoint in situ Raman microscopy, this technique was further employed in the investigation of other promising lithium-ion battery negative electrode materials. Again the method was used to study how the material changes during lithiation and de-lithiation and the detection of any possible heterogeneous electrode intercalation behaviour. Four points on the electrode surface were followed during lithium insertion and de-insertion in the method developed and effectively implemented for the graphite samples as discussed earlier in chapter 4. Two negative electrode materials, under development for use in the lithium-ion battery, were studied: nano silicon and both the micro and nano forms of titanium dioxide anatase (TiO₂).

As the positive electrode is the greater challenge in the lithium-ion battery, concerning lower specific capacities, cost and cyclability, it would be now advantageous to turn our attention with this technique to these electrode materials. Two standard cathode materials lithium cobalt oxide (LiCoO₂) and lithium manganese oxide spinel (LiMn₂O₄) were initially investigated to see how our results compare to the literature.
5.2 Negative electrode materials

5.2.1 Nano silicon

Introduction

As stated previously in the introduction for chapter 4, graphitic carbon is the material of current choice for the negative electrode in the lithium-ion battery because it shows relative safety upon cycling when compared to lithium metal. Due to graphite’s relatively low electrochemical charge capacity (theoretical value: 372 Ah kg⁻¹), however, the search for alternative negative electrode materials with a greater charge capacity has now become an important goal in lithium-ion battery research. One of the main areas of interest is in the field of lithium-metal alloys [189]. Well-known examples are aluminium [24], tin [22, 23], antimony [23], for binary alloys, or copper-tin [26], copper-antimony [190] for ternary alloys. In these systems, the metal reversibly forms alloys with lithium [190], which have very high capacities. A general disadvantage of alloy electrodes, however, is the huge volume change which occurs upon the insertion/de-insertion of the lithium. It can attain values of more than 200-300% [27] and leads to mechanical fatigue upon prolonged cycling.

Much research has been conducted on silicon, as it reversibly forms, like tin, electrochemically active binary alloys with lithium [191-193]. These alloys can show a very high lithium insertion capacity of approx. 4200 Ah kg⁻¹ based on silicon (for a theoretical composition of Li₄.₂Si). This very high lithium content is however accompanied by a huge volume change (of more than 300%), which leads to strong mechanical stress on the crystallites and, thus, to breaking and amorphisation of the particles and loss of the electrical contact [8, 194, 195]. A rapid loss of the reversible capacity upon prolonged cycling (fading) generally results.

A reduction of the particle size into the nanometre range can reduce the mechanical stress. An early study [25], showed the favourable behaviour of nano-silicon/carbon composites. Recent literature [196-198] shows that with nano-scale materials charge capacities up to 1700 Ah kg⁻¹, together with reduced fading can be reached. However, such materials are not
yet comparable to common graphite electrodes as they suffer from low cycle life and high fading. Wang et al. [199] recently presented composite electrodes based on nano silicon inclusions in carbon aerogel. These electrodes show a stable charge capacity of 1450 Ah kg\(^{-1}\). The same group prepared also a promising high-capacity composite electrode by ball-milling, but these electrodes still suffer from a relatively high fading [200]. Of late silicon-disordered carbon nano-composites have provided reversible capacities above 600 Ah kg\(^{-1}\) [201].

Dahn et al. [202] have developed an effective combinatorial chemistry approach in order to test different silicon alloy materials in a wide composition window. Examples of these bimetal alloy systems include Si/Zn [203], Si/Sn and Si/Ag [204] and with multi-metal alloys Si-(Cr, Fe, Mn, Ni) [205] and Si-Al-(Cr, Fe, Mn, Ni) [206].

In our laboratory Holzapfel et al. [207] have previously investigated two types of nano silicon composite electrodes electrochemically. One with 80 weight % and the other with 20 weight % nano silicon. The composite electrode was based on an intimate mixture of the nano silicon with small particle graphite (KS6, TIMCAL, AG). For material and electrode preparation see [207, 208]. For the 80 wt% silicon electrode also 2% of Super P carbon black (TIMCAL, AG) has been added. The silicon material (20 wt%) is mixed with 70 wt% of KS6 and 10% of SOLEF® PVdF 1015 binder (Solvay SA, Belgium) in a N-methylpyrrolidone solution. In another study they investigated a nano silicon graphite material produced by chemical vapour deposition [208].

The SEM image of the composite electrode, using 20 wt% of nano-silicon (Figure 5.1) shows a homogeneous mixture of the silicon particles and the graphite matrix. The silicon particles form long aggregates which are well connected to the larger graphite particles.

**Figure 5.1:** SEM-image of the nano-silicon/graphite composite electrode [207].
Electrochemical behaviour

Figure 5.2 shows the electrochemical cycling of both types of electrodes. For the 80 % Si composite electrode a relatively high irreversible capacity of about 35 % can be noted for the first cycle, but to a much less extent upon the subsequent cycles and a tendency to fall with increasing cycle number up to 60 cycles. The reversible capacity during the subsequent cycles remains very high with an average of 1350 Ah kg\(^{-1}\) during more than 60 cycles. This behaviour is new when the present results are compared to literature data where capacities more than 1000 Ah kg\(^{-1}\) are seldom obtained and, if, for a much smaller number of cycles. The nano silicon seem to show a much smaller mechanical degradation upon the intercalation/ de-intercalation process, which is probably due to the very small particle size and the good interaction with the supporting graphite/ carbon black matrix (Liu et al. [209]). The 20 % Si composite electrode shows a stable specific charge capacity of ca. 1000 Ah kg\(^{-1}\) for around 120 cycles and also shows a large irreversible capacity during the first cycle of around 20 %. Both these composites show a performance which is a factor of three greater than graphite.

![Graph showing electrochemical cycling behaviour](image)

**Figure 5.2:** Electrochemical cycling behaviour of composite electrodes with 80% and 20% nano silicon, respectively, compared to a graphite electrode [207].
From electrochemical analysis (Figure 5.2) of these two composite electrode materials the 20% nano silicon composite was investigated with *in situ* Raman microscopy because it showed the most impressive results with respect to their high reversible charge capacity (1000 Ah kg\(^{-1}\)), low irreversible capacity upon prolonged cycling and both, long cycle life and low capacity fading.

**Structure of silicon**

Silicon has the identical crystal structure as diamond; it is based on the cubic close packed structure and has the crystal group *Fd3m*. Each silicon atom is at the centre of a tetrahedron and is covalently bonded to four other silicon atoms. The unit cell of silicon is displayed in Figure 5.3.

![Unit cell of Silicon](image)

**Figure 5.3:** Unit cell of Silicon. Crystal group *Fd3m*. Grey spheres = Si.

**Point group analysis**

Silicon has the tetrahedral point group (*T_d*). Point group analysis predicts the appearance of one band. This intense sharp band is seen at 520 cm\(^{-1}\) that results from the scattering of the first order optical phonon (TO) is illustrated in the Raman spectrum of silicon (Figure 5.4). Two weaker peaks either side of this band can also be seen at around 300 and 950 cm\(^{-1}\). These are respectively the second-order transverse acoustic mode (2TA) and the second-order optical phonon mode (2TO) [210, 211].
**Results and discussion**

The optical image of the composite nano silicon electrode surface (Figure 5.5) displays the four points, labelled (a), (b), (c) and (d), which were measured by *in situ* Raman microscopy during galvanostatic cycling. The four points lie on the corners of a square that are approximately 15 μm apart. Only the graphite KS6 particles can be observed. Neither the nano silicon nor the binder is visually detectable with an optical microscope. The SEM image in Figure 5.1 previously showed that the nano silicon is evenly dispersed around the graphite particles.

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**Figure 5.4:** The Raman spectrum of nano silicon powder.

**Figure 5.5:** Optical image of the surface of nano silicon composite electrode showing the four points measured. Only the graphite KS6 can be seen on the electrode surface.
In Figure 5.6 the first charge vs. potential curve can be seen and the first discharge obtains a charge capacity greater than 1100 Ah kg\(^{-1}\). This result compares well with electrochemical measurements of standard test cells under optimum conditions, where the first discharge provides capacities around 1300 Ah kg\(^{-1}\) [207]. The first charge capacity though is much lower than for the standard test cells. The Raman cell was 700 Ah kg\(^{-1}\) compared to the standard test cell measurement of ca. 1000 Ah kg\(^{-1}\) (Figure 5.2) [207].

![Graphical representation of the first lithiation and de-lithiation curve for 20% nano Si electrode.](image)

**Figure 5.6:** First lithiation and de-lithiation curve for 20% nano Si electrode. Galvanostatically cycled from 3 V to 0.005 V at 50 mA g\(^{-1}\) of silicon. The numbers close to the curve show where the Raman spectra displayed in Figures 5.7 and 5.9 were measured.

The *in situ* Raman spectral series of the 20% nano Si composite is shown in Figure 5.7, with Table 5.1 listing at which potential and capacity each spectrum was measured. All four points display the first order optical phonon mode (TO) of silicon at ca. 520 cm\(^{-1}\) with a full width at half maximum (FWHM) of 6 cm\(^{-1}\). For points (a) and (c) this band is much more prominent than points (b) and (d) (spectrum 1 all points). The second-order transverse acoustic phonon mode (2TA) and the second order optical phonon mode (2TO) can also be seen at ca. 300 and 950 cm\(^{-1}\) [211-213]. The main bands of graphite are also observed, with the D-band seen at
1330 cm\(^{-1}\) and the G-band at 1585 cm\(^{-1}\) [108]. During the first lithium insertion into this material from the open circuit potential (ca. 3 V vs. Li/Li\(^+\)) to 0.165 V vs. Li/Li\(^+\) the three silicon lines at 300, 520 and 950 cm\(^{-1}\) are seen to rapidly diminish (spectrum 3) and then disappear completely at most of the points of the surface (represented most clearly by points (a) and (c)). This is because of the inserted lithium breaks down the tetrahedral symmetry of the structure. The diamond-like structure of silicon becomes amorphous through lithium insertion. Another explanation of the intensity loss is the conversion of Si from a semiconductor to alloy metal during lithium insertion which will lead to a significant reduction on the optical skin depth, as seen with graphite [66]. This observation is in agreement with previous Raman measurements upon nano silicon, where a decrease of the 520 cm\(^{-1}\) band was also detected [214]. The decrease in intensity of the TO mode of silicon, for all points, can be observed. The intercalation spectral characteristics of graphite are also seen, especially at 0.165 V vs. Li/Li\(^+\) where the stage 3 and 4 GIC G-Band doublet appears [66, 143, 146] (represented most clearly by points (b) and (d)).

Table 5.1: The potential (V) and specific charge capacity (Ah kg\(^{-1}\)) of nano silicon composite of the measured corresponding numbered Raman spectra.

<table>
<thead>
<tr>
<th>Spectrum Number</th>
<th>Potential/ V</th>
<th>Specific charge capacity/ Ah kg(^{-1})</th>
<th>Spectrum Number</th>
<th>Potential/ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0</td>
<td>0</td>
<td>11</td>
<td>0.115</td>
</tr>
<tr>
<td>2</td>
<td>0.70</td>
<td>110</td>
<td>12</td>
<td>0.145</td>
</tr>
<tr>
<td>3</td>
<td>0.60</td>
<td>125</td>
<td>13</td>
<td>0.155</td>
</tr>
<tr>
<td>4</td>
<td>0.50</td>
<td>140</td>
<td>14</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>165</td>
<td>15</td>
<td>0.23</td>
</tr>
<tr>
<td>6</td>
<td>0.34</td>
<td>175</td>
<td>16</td>
<td>0.25</td>
</tr>
<tr>
<td>7</td>
<td>0.27</td>
<td>190</td>
<td>17</td>
<td>0.28</td>
</tr>
<tr>
<td>8</td>
<td>0.205</td>
<td>210</td>
<td>18</td>
<td>0.29</td>
</tr>
<tr>
<td>9</td>
<td>0.18</td>
<td>220</td>
<td>19</td>
<td>0.32</td>
</tr>
<tr>
<td>10</td>
<td>0.165</td>
<td>240</td>
<td>20</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Figure 5.7: *In situ* Raman spectral series of the first lithiation of 20% nano silicon composite electrode of four points from 3 V to 0.165 V. Spectra are shifted arbitrarily along the intensity axis.

The decrease in intensity of the TO mode of silicon, for all points, can be observed in Figure 5.8. The band intensity decreases steadily for points (a) and (c) below a potential of 0.7 V vs. Li/Li+. No band can be detected above the noise level below 0.15 V vs. Li/Li+. Under 0.1 V vs. Li/Li+ no strong graphite signal can be detected which agrees with previous measurements on graphite [66].
Figure 5.8: Decrease in the intensity of the TO mode of silicon (520 cm$^{-1}$) from 3.0 V to 0.155 V vs. Li/Li$^+$. For the first de-lithiation no reappearance of a silicon line, at 520 cm$^{-1}$, was detected for any of the points measured during the cycling of potential from 0.005 V to 1.5 V vs. Li/Li$^+$ (Figure 5.9, shows point (d) as an example). With the early decrease of the silicon line during the first lithium insertion it is unlikely a sufficient amount of lithium leaves the silicon for the initial crystalline structure to return for the TO mode of silicon to be detectable. Only at point (d) were any Raman bands measured. The reappearance of graphite doublet G-band returning to singlet G-band (ca. 1580 cm$^{-1}$) is observed. This indicates that lithium is de-intercalating from the graphite present in the electrode. The return to the single G- band at 1590 cm$^{-1}$ is observed in spectra 17-20 above potentials of 0.2 V. Additionally the band at 1850 cm$^{-1}$, previously detected by our group [67], and later identified to be a carbon-carbon triple bond species [169, 170] is observed in spectra 11-13.
Figure 5.9: In situ Raman spectral series of the first de-lithiation of 20% nano silicon composite electrode of point (d) from 0.005 V to 1.5 V. Spectra are shifted arbitrarily along the intensity axis and are not base line corrected.

During the first lithiation of nano silicon some points which were measured still displayed a typical open circuit potential spectrum for the silicon (Figure 5.10) at 0.05 V vs. Li/Li+. At this potential no signal from either the silicon or graphite should be observable. These measurement points could have been isolated particles. In order to evaluate how frequent the occurrence non-contacted particles are, 100 points on the electrode surface were mapped in an area of 50 μm x 50 μm at 3.0 V and 0.05 V vs. Li/Li+ with a confocal volume of (2 μm)^3. The detection of non-contacted particles could explain the lower capacity expected for this material and the subsequent capacity loss during the first cycle.
The number of Si signals at 520 cm$^{-1}$ present at 100 points was compared at 3 V and at 0.05 V. Because the intensity of the Si signal can vary significantly, the signal detected was divided into two classes: strong signal where the intensity (arbitrary units), $I > 500$ and weak signal where, $I < 500$. The number of silicon 520 cm$^{-1}$ peaks still detectable from the mapping experiments show that a significant amount of the nano-silicon material becomes isolated and electrochemically inactive during cycling (Table 5.2). The results show that around 20% of the particles at the electrode surface intercalate little or no lithium (strong: $I > 500$ values).

**Table 5.2:** Number of Si peaks (520 cm$^{-1}$) detected during cycling in a nano-Si vs. Li in situ Raman cell. Strong peaks have intensity > 500 and weak peaks, intensity < 500.

<table>
<thead>
<tr>
<th>Potential vs. Li/Li$^+$</th>
<th>Number of TO Si Peaks (520 cm$^{-1}$) detected</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>1st lithiation</td>
<td></td>
</tr>
<tr>
<td>OCP ca. 3.0 V</td>
<td>100</td>
</tr>
<tr>
<td>0.05 V</td>
<td>35</td>
</tr>
</tbody>
</table>
Conclusions and outlook

The first lithiation Raman spectra of nano-silicon vs. Li *in situ* cell were successfully measured. Results show the decrease in intensity of the TO silicon band at 520 cm⁻¹, when the potential is reduced from 3 V to 0.005 V. Additionally the intercalation spectra of lithium into graphite are displayed, which correspond to previous measurements.

The spectra measured during the first de-lithiation shows no reappearance of the silicon band at 520 cm⁻¹. Given the rapid disappearance of the silicon band (i.e. at low specific charge capacity) it is unlikely that enough lithium could be extracted to completely restore the silicon structure. Reversible intercalation into graphite is demonstrated by the reappearance of the G-band.

Some points on the electrode still displayed a typical spectrum for the silicon at potentials at which lithium intercalation should be proceeding. These measurement points could have been isolated particles. The detection of non-contacted particles may provide an explanation for the lower reversible charge capacity of the electrode observed.

Further investigations could include mapping studies on future nano-silicon composite electrode materials since the detection with Raman microscopy of non-contacted particles in the electrode has been successfully demonstrated. The mapping of electrodes would allow the evaluation of the correlation between electrochemical performances of electrodes with detection of non contacted particles.
5.2.2 Titanium dioxide (TiO$_2$) anatase

Introduction

While put aside a few years ago because of possible enhanced side reactions (mainly from electrolyte decomposition), nano-textured materials were recently investigated both as negative [215] and positive [3, 216] electrodes. Amongst these, titanium dioxide (TiO$_2$) has been largely investigated [28, 217]. In bulk anatase-type TiO$_2$ a specific charge capacity of 168 Ah kg$^{-1}$ is classically obtained with lithium is inserted into half the vacant octahedral holes, giving a composition of Li$_{0.5}$TiO$_2$, according to equation 5.1:

$$\text{TiO}_2 + xe^- + x\text{Li}^+ \leftrightarrow \text{Li}_x\text{TiO}_2 \quad (5.1)$$

Though the potential plateau is ca. 1.5 V higher compared to the currently preferred graphite negative electrode, possible advantages maybe its rapid discharge and charge properties [218, 219]. Furthermore akin to graphite, TiO$_2$ is cheap and non-toxic. Besides these properties, it was shown recently that reducing the size induces the extension of the composition range of the initial solid solution domain [28], further confirmed by neutron diffraction studies [220]. Thus there is still a need to properly study and understand the effect of the size on the electrochemical reactivity of such systems.

Three TiO$_2$ anatase materials of varying nano-sized particles were investigated. Two commercially available samples: Prolabo and AK1 (both from BASF) and a sol-gel prepared titanium oxide referred as MTi5 [28]. MTi5 was synthesised by a two-step method consisting firstly of the preparation of a solid precursor through hydrolysis of titanium alkoxide (titanium tetra-isopropoxide) followed by heat treatment at 250 °C under ambient air for 1 hour. This method led to a highly porous material with a 200 nm homogenous particle size [28]. For TiO$_2$ anatase only a couple of comprehensive Raman studies can be found in the literature: a detailed ex situ study on TiO$_2$ composite electrodes [221], and an in situ investigation on thin films of Li$_x$TiO$_2$ [222].
Structure

Tetragonal anatase TiO₂ (symmetry group I₄₁/amd- \( D_{3h}^{19} \)) is composed of TiO₆ octahedra that share two adjacent edges in the ac- and bc- planes. Between the octahedra, there are potential lithium intercalation sites of two types, having either octahedral or tetrahedral oxygen coordination (Figure 5.11) [223].

Figure 5.11: (a) Building unit (b) unit cell and (c) structure of anatase TiO₂ [223].

Yellow spheres = Ti, Red spheres = O. Images created by Balsac software, courtesy of Dr. I. Czekaj.
Materials characterisation

The two commercial samples were well crystallized X-ray pure white TiO₂ powders. AK1 shows a broadening of the Bragg peaks characteristic of the presence of small crystallites (Figure 5.12). Indeed, this latter is formed from the aggregation of crystallites of about 10 - 20 nm diameter (Figure 5.13a). Smaller particles/crystallites were obtained from our synthesis process in agreement with Sudant et al. [28]. By a simple annealing treatment for 1 hour at 250 °C well defined homogeneous crystallites of 8 nm diameter can be prepared (the value determined by Scherrer's method is in good agreement with the TEM images, Figure 5.13b). Whatever the sample, close lattice parameters with a cell volume of about 136.3 Å³ (Table 5.3) were found. There is thus no major structural difference between these three samples. However a textural evolution linked to the decrease of crystallite sizes from more than 80 nm to 8 nm for the Prolabo samples and MTi5, respectively, is noticed [28]. This decrease is also correlated to the increase of specific Brunauer-Emmett-Teller (BET) surface area (10 m² g⁻¹, 51 m² g⁻¹ and 223 m² g⁻¹ for Prolabo, AK1 and MTi5, respectively).

![X-ray diffraction patterns of AK1 and MTi5 TiO₂ samples.](image)

Figure 5.12: X-ray diffraction patterns of AK1 and MTi5 TiO₂ samples.
Table 5.3: Cell parameters (S.G.: 14/amd) obtained by refinement of the X-ray diffraction patterns in a pattern matching mode using the Foolprof software.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a) and (b) (Å)</th>
<th>(c) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prolabo</td>
<td>3.7850(6)</td>
<td>9.514(2)</td>
</tr>
<tr>
<td>AK1</td>
<td>3.786(1)</td>
<td>9.507(3)</td>
</tr>
<tr>
<td>MTi5</td>
<td>3.791(3)</td>
<td>9.479(6)</td>
</tr>
</tbody>
</table>

Figure 5.13: High Resolution Transmission Electron Microscopy image of (a) AK1 (b) MTi5.
Electrochemical behaviour

A demonstration of the effect of particle-size on the difference in electrochemical behaviour of anatase TiO$_2$ are shown by the galvanostatic curves of Prolabo and MTi5 at a C/20 rate (Figure 5.14) [28]. Both materials display a well defined plateau at 1.75 V vs. Li/Li$^+$, which is in agreement with known literature [224]. However the main difference is a much longer monotonous potential decrease before this constant potential is reached as the material decrease from micro- to nano-scale. For Prolabo TiO$_2$ the capacity reached at 1.75 V is 0.02 e$^-$ per mole of TiO$_2$, whilst for MTi5 it is ca. 0.2 e$^-$.  

![Figure 5.14: Galvanostatic cycling curves of (a) Prolabo TiO$_2$ and (b) MTi5 TiO$_2$ at C/20 rate between 3 and 1.5 V in 1M LiClO$_4$ PC electrolyte at 20 °C. Adapted from Sudant et al. [28].](image)
The variation between the cycling behaviour of Prolabo and MTi5 TiO$_2$ is shown in Figure 5.15. It can be seen that for Prolabo TiO$_2$ the specific charge capacity decreases dramatically, down from 150 to ca. 10 Ah kg$^{-1}$, only after the first few cycles. Whilst for MTi5 the charge capacity remains stable at 150 Ah kg$^{-1}$ over a 50 cycle period. The good charge capacity retention of MTi5 can be explained by the better accommodation of structural changes occurring during lithium insertion. While for the larger Prolabo, stress could be present in the grains.

![Figure 5.15: Evolution of the specific charge capacity as a function of the cycle number for micro TiO$_2$ (Prolabo) and nano TiO$_2$ (MTi5) at C/20 and 20 °C. Adapted from Sudant et al. [28]. Here discharge means lithiation and charge de-lithiation.](image)

**In situ Raman electrode preparation**

The composite electrode for in situ Raman investigations was formed from 40 wt% of anatase type TiO$_2$ (either Prolabo, AK1 from BASF or MTi5), 10% carbon black, 20% PVdF binder, 30% dibutyl phthalate (DBP, Aldrich). For the working electrode preparation first the active TiO$_2$ anatase material was ball-milled with carbon black for 15 minutes. The addition of the binder, dibutyl phthalate and acetone produced a slurry, which was mechanically mixed and doctor-bladed onto an aluminium sheet (thickness 20 μm). DBP was extracted from the electrode with ether, to give a free-standing film which was hole-punched leading to an electrode of a 57 wt% active material (thickness 100 μm, diameter 6 mm, total electrode mass ca. 1 mg).
**Point group analysis of TiO$_2$ anatase and Li$_x$TiO$_2$**

Tetragonal TiO$_2$ anatase has the factor group $D_{4h}^{19}$ with the symmetry $I4_1/amd$-$D_{4h}^{19}$ and according to the factor group analysis, the 15 optical modes have the irreducible representation [71, 225]:

$$\Gamma_{\text{opt}} = A_{1g} + A_{2u} + 2B_{1g} + B_{2u} + 3E_{g} + 2E_{u} \quad (5.2)$$

The $A_{1g}$, $B_{1g}$ and $E_{g}$ modes are Raman active, therefore six active modes are expected in the Raman spectrum of TiO$_2$ anatase. However, the band at 514 cm$^{-1}$ is resolved into two components at 507 ($A_{1g}$) and 519 ($B_{1g}$) cm$^{-1}$ only below 73 K [225]. The $A_{2u}$ and $E_{u}$ modes are infrared active and the $B_{2u}$ is silent.

The spectrum of the Prolabo TiO$_2$ sample (Figure 5.16) therefore presents these five bands (Table 5.4 for assignment of the bands) with the bands at 143, 195 and 393 cm$^{-1}$ corresponding predominantly to O-Ti-O bending and the bands 514 and 637 cm$^{-1}$ to Ti-O stretching. Comparing the band positions measured in this investigation to previous works by Ohsaka [225] and Baddour-Hadjian [221], it can be seen that for all peak values for Prolabo, AK1 and MTi5 are ca. 2 - 3 cm$^{-1}$ lower than these previously reported literature values.

**Figure 5.16:** Ex situ Raman spectra of Prolabo, AK1 and MTi5 TiO$_2$ anatase powders. Spectra are shifted up the y-axis.
Table 5.4: Band positions and full width at half maximums (FWHM) of ex situ powder measurements of Prolabo, AK1 and MT15 anatase TiO₂ in this study and previously reported measurements of anatase TiO₂ band positions by Ohsaka et al. [225] and Baddour-Hadjéan et al. [221].

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Prolabo</th>
<th>AK1</th>
<th>MT15</th>
<th>Ref [225]</th>
<th>Ref [221]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Band Position/ cm⁻¹</td>
<td>FWHM/ cm⁻¹</td>
<td>Band Position/ cm⁻¹</td>
<td>FWHM/ cm⁻¹</td>
<td>Band Position/ cm⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E₉</td>
<td>143</td>
<td>8</td>
<td>144</td>
<td>12</td>
<td>145</td>
</tr>
<tr>
<td>E₈</td>
<td>195</td>
<td>-</td>
<td>195</td>
<td>-</td>
<td>195</td>
</tr>
<tr>
<td>B₁₈</td>
<td>393</td>
<td>17</td>
<td>393</td>
<td>22</td>
<td>396</td>
</tr>
<tr>
<td>A₁₉, B₁₉</td>
<td>514</td>
<td>17</td>
<td>515</td>
<td>22</td>
<td>515</td>
</tr>
<tr>
<td>E₉</td>
<td>636</td>
<td>19</td>
<td>638</td>
<td>26</td>
<td>639</td>
</tr>
</tbody>
</table>

*Peak values at 73 K

Classically (for bulk materials), when lithium is intercalated, tetragonal TiO₂ anatase (I₄₁/amd- D₁₄₅) (a = b = 3.8 Å, c = 9.51 Å) is transformed to an orthorhombic structure (Imma- D₁₈⁸) (a = 3.81 Å, b = 4.08 Å, c = 9.05 Å) [223, 226]. The main local evolution changing the symmetry from D₁₄₅ to D₁₈⁸ is that two equatorial Ti-O distances are elongated from 1.937 Å to 2.044 Å. Consequently the factor group analysis again produces 15 optical modes with the irreducible representation:

$$\Gamma_{\text{opt}} = 3A_g + 3B_{2g} + 3B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u} \quad (5.3)$$

of which the gerade modes are Raman active and the ungerade modes are infrared active. Nine Raman active bands are therefore predicted for LiₓTiO₂ (orthorhombic):

$$\Gamma_{\text{raman}} = 3A_g + 3B_{2g} + 3B_{3g} \quad (5.4)$$

The A₁₉ and B₁₈ both become A₉ modes and the E₉ modes split into B₂₈ and B₃₈. The in situ Raman spectrum of LiₓTiO₂ (orthorhombic, 1.75 V, x = 0.03 LiₓTiO₂) is compared to pristine anatase TiO₂ (Prolabo) (Figure 5.17 and Table 5.5). Even though more than nine bands are observed, the spectra match reasonably well to the point group analysis predictions. The low wavenumber E₉ bands at 143 and 195 cm⁻¹ split into B₂₈, B₃₈ doublets, seen at 163, 177 cm⁻¹ and 228, 354 cm⁻¹, respectively. The B₁₈ at 393 cm⁻¹ transforms to an A₉, now observed
slightly blue-shifted at 416 cm\(^{-1}\) and the previously overlapping bands at 514 cm\(^{-1}\) \((A_{ig}, B_{ig})\) are also now \(2A_g\) modes seen at 516 and 553 cm\(^{-1}\). The highest \(E_g\) at 636 cm\(^{-1}\) is observed to have red-shifted to 626 cm\(^{-1}\) \((B_{3g})\). The \(E_g\) mode for anatase TiO\(_2\) is the doubly degenerate O-Ti-O\(_{eq}\) stretch in both \(x\) and \(y\) directions [227]. When lithium is inserted the Ti-O distances in both \(x\) and \(y\) directions increase: in the \(y\)-direction both Ti-O bond lengths increase slightly from 1.937 to 1.942 Å. But in the \(x\)-direction the Ti-O bond lengths both enlarge to 2.044 Å [223]. It could therefore be expected that the other band of the doublet is located at a significantly lower wavenumber. The \(B_{2g}\) is therefore tentatively assigned to the band at 527 cm\(^{-1}\), whose shape after band deconvolution is also similar to the 626 cm\(^{-1}\) band (Figure 5.17).

Nevertheless unassigned bands are found at 276, 315, 327, 339, 435 and 464 cm\(^{-1}\). At the present state, the assignment of this Li\(_x\)TiO\(_2\) spectrum is incomplete and uncertain. Based on lattice dynamics simulations, Baddour-Hadjjean et al. [221] suggested that extra bands could result from lithium located in different sites within the TiO\(_2\) framework, but further investigation would be required for such assignment. Furthermore, in their work they observed extra bands in the 639 - 1000 cm\(^{-1}\) region when anatase becomes lithiated. However, contrary to what they previously reported [228] from their \textit{ex situ} and simulated Raman measurements, it was found here that every band observed at these frequencies arises from the electrolyte. This was checked after numerous \textit{in situ} Raman measurements carried out on this system with different electrolytes and by using strict confocal conditions that completely removed the detection of the electrolyte signal.
Figure 5.17: Comparison of the Raman spectrum of TiO$_2$ anatase (Prolabo) and Li$_x$TiO$_2$ orthorhombic (1.75 V, $x = 0.03$ Li$_x$TiO$_2$).
Table 5.5: Band assignment and Raman wavenumbers (cm$^{-1}$) for TiO$_2$ anatase (Prolabo) (1.75 V, x = 0.03 Li$_x$TiO$_2$) *s = strong, w = weak.

<table>
<thead>
<tr>
<th>Band/ cm$^{-1}$ ± 1</th>
<th>FWHM/ cm$^{-1}$ ± 1</th>
<th>Assignment</th>
<th>Strength*</th>
<th>Mode</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>163</td>
<td>4</td>
<td>O-Ti-O bend</td>
<td>s</td>
<td>$B_{2g}$</td>
<td>One of the doublet band of the $E_g$, 143 cm$^{-1}$</td>
</tr>
<tr>
<td>177</td>
<td>6</td>
<td>O-Ti-O bend</td>
<td>s</td>
<td>$B_{3g}$</td>
<td>One of the doublet band of the $E_g$, 143 cm$^{-1}$</td>
</tr>
<tr>
<td>228</td>
<td>13</td>
<td>O-Ti-O bend</td>
<td>s</td>
<td>$B_{2u}$</td>
<td>Arises from the splitting of the $E_g$ mode at 195 cm$^{-1}$</td>
</tr>
<tr>
<td>276</td>
<td>6</td>
<td>Unassigned</td>
<td>w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>314</td>
<td>14</td>
<td>Unassigned</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>328</td>
<td>14</td>
<td>Unassigned</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>337</td>
<td>9</td>
<td>Unassigned</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>354</td>
<td>8</td>
<td>O-Ti-O bend</td>
<td>s</td>
<td>$B_{3g}$</td>
<td>Arises from the splitting of the $E_g$ mode at 195 cm$^{-1}$</td>
</tr>
<tr>
<td>416</td>
<td>21</td>
<td>O-Ti-O bend</td>
<td>w</td>
<td>$A_x$</td>
<td>Assigned as the shifted 394 cm$^{-1}$ $B_{1g}$ band of TiO$_2$ anatase</td>
</tr>
<tr>
<td>435</td>
<td>8</td>
<td>Unassigned</td>
<td>w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>464</td>
<td>12</td>
<td>Unassigned</td>
<td>w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>516</td>
<td>11</td>
<td>O-Ti-O axial</td>
<td>s</td>
<td>$A_g$</td>
<td>Anatase $A_{1g}$ or $B_{1g}$ modes</td>
</tr>
<tr>
<td>529</td>
<td>19</td>
<td>O-Ti-O equatorial</td>
<td>s</td>
<td>$B_{2g}$</td>
<td>Possible doublet band of the $E_g$ 637 cm$^{-1}$</td>
</tr>
<tr>
<td>553</td>
<td>12</td>
<td>O-Ti-O axial</td>
<td>s</td>
<td>$A_g$</td>
<td>Shifted TiO$<em>2$ anatase $A</em>{1g}$ or $B_{1g}$ modes</td>
</tr>
<tr>
<td>626</td>
<td>34</td>
<td>O-Ti-O equatorial</td>
<td>s</td>
<td>$B_{3g}$</td>
<td>Doublet band of the $E_g$ 637 cm$^{-1}$ in TiO$_2$ anatase</td>
</tr>
</tbody>
</table>
Results and discussion

TiO$_2$ anatase lithiation/de-lithiation (Prolabo)

Electrodes are generally heterogeneous surfaces, consisting of the active material, carbon and binder. For each in situ Raman measurement four points on the electrode surface were sequentially measured [146]. Each measurement-point was at the corner of the square of length 50 µm (Figure 5.18). For TiO$_2$ Prolabo, the four particles did not show similar spectral features at similar potentials, and these differences will be highlighted later.

![Figure 5.18 Optical Microscope image of TiO$_2$ composite electrode, 57 wt% of anatase type TiO$_2$ (Prolabo), 14 % carbon black, 29 % PVdF binder (x80 obj), showing 50 x 50 µm measurement square and the four points measured: (a), (b), (c) and (d).](image)

For a C/22 rate, the first discharge process of TiO$_2$ anatase (Prolabo) occurs at approximately 1.77 V (± 0.01 V), while the first charge is observed at a slightly higher potential of around 1.90 V (± 0.01 V) (Figure 5.19). In reduction a capacity of ca. 0.45 lithium ions per mole of oxide (150 Ah kg$^{-1}$) is observed at the cut-off potential of 1 V. At the initial state the five bands of the anatase are clearly obtained (Figure 5.20A, 3 V). As lithium is inserted, a shift of the intense $E_g$ band from 143 to 145 cm$^{-1}$, is noted (1.83 V), the other bands being unchanged.
However, as we reach 1.81 V (x = 0.02 for Li_xTiO_2), many new bands are observed (Table 5.5 and as discussed in the previous section) and E_g has continued to shift to 147 cm^{-1}. This results from the tetragonal to orthorhombic transition on the voltage plateau. Surprisingly, the phase change observed by Raman is found to be finished by 1.75 V (x \sim 0.03), where the E_g band is no longer distinguished. This can be understood as the Raman is surface sensitive to coverage of the particle by the reduced phase. After this transition, only decrease in the bands intensity of "Li_{0.5}TiO_2" phase is observed as the potential is lowered to 1 V, where x = 0.45. On de-insertion (Figure 5.20B), the intensity of the bands goes up as the potential plateau is reached followed by the growth and return shift of the E_g band at 145 cm^{-1} above 1.90 V. This band then increases at the expense to its orthorhombic B_{2g} and B_{3g} doublet from 1.96 to 3 V. It is important to notice that this latter is close to the initial spectrum seen at 3 V (though weak signals from orthorhombic Li_xTiO_2 are still clearly visible) thus showing the good reversibility of the process while some irreversibility is clearly visible on the electrochemical curve (Figure 5.19).

This type of evolution was seen for most points measured on the electrode surface. However sometimes we obtained some discrepancies. For some points after the beginning of phase transition (x > 0.03 for Li_xTiO_2) the shifted E_g at 149 cm^{-1} was still visible at a variation of intensities. This band remained visible throughout the measurement cycle. For some other locations, anatase bands could also still be present. The presence of this band could either indicate the insertion of lithium is not homogenous within this electrode or the measurement was over badly electronically contacted particles.
Figure 5.19: First lithiation/ de-lithiation curves of Prolabo (thick line) AK1 (medium line) and MTi5 (thin line) anatase TiO$_2$ in the 3-1 V potential region, cycled in 1M LiClO$_4$, 1:1 EC:DMC. At C/22, 15 mA g$^{-1}$ of TiO$_2$. 
Figure 5.20: *In situ* Raman spectra series of the first lithium (A) insertion and (B) de-insertion into/from anatase TiO$_2$ (Prolabo) Spectra are shifted up the y-axis. The intensity axis scale is identical for (A) and (B). Numbers indicate band wavenumber (cm$^{-1}$) maximums. The potential/ V vs. Li/Li$^+$ and x in Li$_x$TiO$_2$ values for each spectra are listed. Cycled in 1M LiClO$_4$ 1:1 EC:DMC, at C/22, 15 mA g$^{-1}$ of TiO$_2$. 
Conversely, for the smaller nano-sized samples (AK1 and MTi5) the spectra were similar whatever the location indicating that lithium insertion proceeds homogeneously. Up to 0.85 lithium ions per formula unit were inserted when discharged to 1 V at a C/22 rate for both samples (Figure 5.19.). The main difference is the shape of the curve with a first domain, corresponding to a solid solution [28], extending to larger lithium contents as the particle size decreases, at the expense of the voltage plateau capacity. Indeed, while this plateau was reached at \( x = 0.03 \) for the Prolabo sample, values of ca. \( x = 0.1 \) and \( x = 0.15 \) are observed for AK1 and MTi5, respectively. Furthermore AK1 has a small second plateau at ca. 1.45 V which would correspond to a biphasic phenomenon leading to LiTiO\(_2\) [220]. In contrast for MTi5, below 1.5 V, the potential drops off linearly. This last phenomenon seems to be highly kinetically limited and was found only for electrochemical measurements at 120 °C [229], or for small particles [220].

The Raman spectra evolutions during these electrochemical processes are illustrated for AK1 and MTi5 in Figures 5.21 and 5.22, respectively. Starting with the anatase spectrum, the appearance of new bands are observed at 1.8 V that is for \( x = 0.09 \) (AK1) and \( x = 0.13 \) (MTi5) in agreement with the extension of the solid solution domain. The Raman spectrum for the orthorhombic phase is essentially identical to the one observed on reduction of Prolabo sample except for slight observed shifts in position and lower spectral resolution. On the first domain, the \( E_g \) band at 144 cm\(^{-1}\) shifted to 149 cm\(^{-1}\), simultaneously with an intensity decrease and the appearance of two shoulder bands at 165 and 177 cm\(^{-1}\). Different peaks shift (195 cm\(^{-1}\) to 232 cm\(^{-1}\) and 637 cm\(^{-1}\) to 629 cm\(^{-1}\)) and new peaks are observed at 315, 339, 355, 527 and 554 cm\(^{-1}\). These are again assigned as the new Raman modes associated with a phase transition from tetragonal Li\(_x\)TiO\(_2\) to orthorhombic Li\(_x\)TiO\(_2\).

As described above, upon further lithium insertion (AK1: \( x = 0.1 \); MTi5: \( x = 0.14 \)) the spectrum radically changes. The band at 149 cm\(^{-1}\) disappears and is completely replaced by an intensified doublet peak at 165 and 177 cm\(^{-1}\). The 393 cm\(^{-1}\) peak also vanishes and another new weak peak appears at 416 cm\(^{-1}\). The 629 cm\(^{-1}\) band shift continues down to 626 cm\(^{-1}\). The main difference between the two materials (AK1 and MTi5) thus lies in the extension of the
solid solution domain (note also the lower signal/noise ratio for smaller crystallites). No changes in the Raman spectra are seen once this Li_{0.5}TiO_2 composition is reached with the exception of the decrease of the band intensities leading to a featureless spectrum (Figure 5.21A, 1.60 – 1.03 V and Figure 5.22A, 1.65 – 1.06 V). Upon oxidation, as soon as some lithium is extracted, some broad peaks become again distinguished. At 3 V, the pure anatase TiO_2 spectrum is not observed back for both samples. The E_g peak was however observed back at 143 cm⁻¹ for AK1 and only partially at 153 cm⁻¹ for MTi5 (Figures 5.21B and 5.22B).

![Figure 5.21: In situ Raman spectra series of the first lithium (A) insertion and (B) de-insertion into/from anatase TiO_2 (AK1). Spectra are shifted up the y-axis. The intensity axis scale is dissimilar for the (A) and (B). Numbers indicate band wavenumber (cm⁻¹) maximums. The potential/ V vs. Li/Li⁺ and x in LiₓTiO_2 values for each spectra are listed. Weak band marked with a "*" comes from the electrolyte. Cycled in 1M LiClO_4 1:1 EC:DMC, at C/22, 15 mA g⁻¹ of TiO_2.](image-url)
Comparison between the three nano-sized TiO$_2$ anatase samples

In Figure 5.16 the *ex situ* Raman spectra of Prolabo, AK1 and MTi5 TiO$_2$ anatase powders were shown. No significant difference was observed between the *ex situ* Raman spectrum of the three dry powder samples. As Table 5.4 shows, the most intense $E_g$ peak for MTi5,
145 cm\(^{-1}\) is shifted to a higher wavenumber position and is much broader (full width at half maximum (FWHM) = 16 cm\(^{-1}\)) compared to AK1 (144 cm\(^{-1}\), FWHM = 12 cm\(^{-1}\)) and Prolabo (143 cm\(^{-1}\), FWHM = 8 cm\(^{-1}\)). This peak broadening could be associated with an increase of crystal amorphisation as the crystallite size is reduced. The \textit{in situ} measurements of Prolabo, AK1 and MTi5 (Figures 5.20, 5.21 and 5.22) show similar trends in the Raman spectra, but there are some subtle differences which need to be discussed. Primarily the major variation between the three materials is the amount of lithium ions which are inserted before a phase change from tetragonal Li\_xTiO\_2 to orthorhombic Li\_xTiO\_2 is first observed in the Raman spectrum: Prolabo (0.02), AK1 (0.09) and MTi5 (0.13). This effect can be correlated to the discharge-charge curves (Figure 5.19) in agreement with previous studies on TiO\_2 [28, 220] and is similar to the effect on lithium intercalation on particle size into \(\alpha\)-Fe\_2O\_3 [230].

For Prolabo, however the value is erroneous since the electrode was found to be heterogeneous and thus some particles could be disconnected electronically. Furthermore for this sample the reproducibility in terms of charge capacity was poor (electrochemical cells with higher charge capacities up to 0.75 at 1 V were obtained, not shown). Under optimum conditions the Prolabo TiO\_2 cell performs almost as well as the other two nano materials in the first cycle (Sudant et al. [28]), both materials obtaining specific capacities of 150 Ah kg\(^{-1}\). Possible reasons for the poor performance in the \textit{in situ} Raman cell could be the lower mechanical pressure on the electrode within the Raman cell, therefore leading to loss of contact of some particles within the electrode. Therefore, it is estimated that under optimum cell conditions the phase change for Prolabo occurs ca. \(x = 0.05\) in Li\_xTiO\_2. The variation of lithium content before the occurrence of the phase change is the result of the extension of the solid solution domain, where because of the decrease of the particle size, the material can intercalate more lithium without phase transition [28]. Figure 5.23 displays the Raman spectra illustrating for all three materials the shift of the lowest wavenumber \(E_g\) band (144 cm\(^{-1}\)) with respect to potential and \(x\) in Li\_xTiO\_2. Interestingly, it appears that the \(E_g\) band shift is similar for all three samples. This means that locally, the same critical state (where Li\_xTiO\_2 has either a tetragonal or orthorhombic crystal structure) is reached. However the quantity of lithium ions inserted to reach this state is inversely proportional to the size of the crystallites (Figure 5.24).
Figure 5.23: $E_g$ shift for Prolabo, AK1 and MTi5 TiO$_2$ anatase. The potential (V) and x in Li$_x$TiO$_2$ are shown next to their corresponding spectrum.

Figure 5.24: Trend of TiO$_2$ crystallite particle size and Raman observation of the complete phase transition from Li$_x$TiO$_2$ tetragonal to Li$_x$TiO$_2$ orthorhombic of x in Li$_x$TiO$_2$ (related to the complete disappearance of 144 cm$^{-1}$ $E_g$ band). Included is a suggested curve of best fit (-----).
The shift of low wavenumber $E_g$ mode from ca. 144 to 149 cm$^{-1}$ and the $E_g$ mode at 636 cm$^{-1}$ to 627 cm$^{-1}$ for the example of AK1 (Figure 5.25) with (a) potential and (b) $x$ in Li$_x$TiO$_2$ can be correlated to the shift of the (101) Bragg peak observed by in situ X-ray diffraction (XRD) [28]. For MTi5 the shift of this peak is observed up to $x = 0.15$ for Li$_x$TiO$_2$, which is consistent with the in situ Raman results, which showed the phase change at a similar value of $x = 0.13$ (Figure 5.25). This means that smaller crystallites can better accommodate the strain due to their capacity to expand (“particle breathing”). However, when this is no longer possible, the phase transition occurs. Baddour-Hadjjean et al. [221] did not report any change in the ex situ collected Raman spectra before a composition $x = 0.3$. These results are not consistent with our study since their preparation route (400°C annealing for 5 hours) should lead to larger crystallite sizes (not reported).

In order to study the effect of cyclability on these materials ex situ measurements on electrodes after different cycles were performed (Figure 5.26). For both AK1 and MTi5 the pure anatase spectra are obtained, while during the in situ experiments some irreversibility was underlined. This can thus stress that under ex situ conditions; the lithiated materials are not stable and evolve. Finally, beyond obtaining Li$_{0.5}$TiO$_2$, the intensity of the band decreases up to a complete disappearance of the signal, seen especially for AK1.
Itoh et al. [167] attributes the loss of band intensity to an increase in conductivity which lowers the Raman active skin depth. *In situ* Raman measurements on LiCoO$_2$ illustrated this phenomenon. The electrical conductivity can be directly correlated to the optical skin depth ($\delta$) of the laser beam:

$$\delta = \sqrt{\frac{2}{\mu \sigma \omega}}$$ (5.5)

Where $\mu$, $\sigma$ and $\omega$ are the magnetic permeability, the electronic conductivity and the inverse of the wavelength, respectively. An increase in electronic conductivity will result in a reduction of the optical skin depth. Zachau-Christiansen [229] reported the increase of the conductivity of lithiated anatase by more than 3 orders of magnitude up to compositions $x = 0.59$. As the signal decrease is enhanced after the first plateau one could speculate that the conductivity for higher composition would still evolve to larger values.

**Figure 5.26:** *Ex situ* Raman measurements of cycled AK1 (left) and MTi5 (right) electrodes. With cycle number indicated on each spectrum. 0 indicates a fresh non-cycled electrode. Electrodes were cycled at C/22 rate from 3 V to 1 V and back to 3 V in 1M LiClO$_4$, PC. The cells were dismantled in an argon filled glove box (< 1 ppm water) and the electrodes were washed with pure PC prior to Raman measurement. No change in the Raman spectrum is observed with cycle number.
Conclusions and outlook for this material

In situ Raman spectra have been generated for the lithiation and de-lithiation into and out of micro- and nano-sized anatase TiO$_2$. The biphasic transition from tetragonal TiO$_2$ to orthorhombic titanate Li$_x$TiO$_2$ was clearly evidenced. The phase transition, seen by Raman spectra, occurs at lithium content depending on the crystallite size ($x = 0.03$ for Prolabo, 0.1 for AK1 and 0.14 for MTi5). This is consistent with the extension of the solid solution domain, when particle size is reduced. Moreover results showed the heterogeneous lithium insertion nature of the larger Prolabo (ca. 80 nm) electrodes and the homogenous behaviour of smaller nano-sized electrodes (AK1, ca. 15 nm and MTi5 ca. 8 nm) under electrochemical operation. This can explain the better cyclability observed for the smaller nano-scale TiO$_2$ based electrodes. Furthermore the detected steady decrease in band intensity for the smaller nano-sized TiO$_2$ materials, AK1 and MTi5, when $x > 0.3$, could be related to an increase in conductivity of the lithiated TiO$_2$ anatase, which causes a lowering of the optical skin depth. Finally the assignment of the bands and understanding of the evolution is not simple and further investigation is required.
5.3 Positive electrode materials

5.3.1 Lithium cobalt oxide (LiCoO₂)

Lithium cobalt oxide is the current material of choice for the positive electrode. It has a theoretical specific charge of 137 Ah kg⁻¹ when 0.5 moles of lithium are removed, equation (5.6) [8]:

\[ \text{LiCoO}_2 \leftrightarrow \text{Li}_{0.5}\text{CoO}_2 + 0.5\text{Li}^+ + 0.5\text{e}^- \] (5.6)

LiCoO₂ has a cubic rock salt structure (\(R\bar{3}m\), \(D_{3d}^5\)) [131, 132] which is illustrated in chapter 3, Figure 3.15 [8, 131] and thus is found to have the following irreducible representation [135]:

\[ \Gamma_{opt} = A_{ig} + E_g + 2A_{2u} + 2E_u \] (5.7)

where the Raman active modes are \(A_{ig}\) and \(E_g\) and the infrared modes are \(A_{2u}\) and \(E_u\).

In a previous in situ Raman investigation on LiCoO₂ by Inaba at al. [135] it was speculated that at \(\text{Li}_{0.5}\text{CoO}_2\) the hexagonal phase \((R\bar{3}m)\) changes to a monoclinic phase \((C2/m)\). This leads to a factor group \(C_{2h}^\chi\) with \(Z = 2\). The resulting irreducible representation for all of the vibrational modes is:

\[ \Gamma_{opt} = 2A_g + 2A_{2u} + B_g + 4B_u \] (5.8)

where the Raman active modes are the gerade modes: \(A_{ig}\) and \(B_g\), and the infrared modes are the ungerade modes: \(A_{2u}\) and \(B_u\) [134, 135].

The first de-lithiation curve for LiCoO₂ vs. lithium in situ Raman cell is displayed in Figure 5.27. The cell was cycled between open circuit potential (3 V) and 4.2 V. It however can be observed that the cell only reached a potential of 4.12 V, due to cell failure, corresponding to \(\text{Li}_{0.6}\text{CoO}_2\). It is believed the mechanical pressure on the electrode within the in situ Raman cell is too low. Nevertheless the in situ Raman spectral series of de-lithiation shows that the sharp \(E_g\) and \(A_{ig}\) bands, found correspondingly at 485 and 595 cm⁻¹. These bands weaken as the potential is raised and they disappear completely above 4.07 V.
In situ Raman Microscopy of Further Materials

(Figure 5.28) and are replaced by much broader and weaker bands at 463 and 568 cm$^{-1}$. This intensity decrease is associated with the increase of conductivity of LiCoO$_2$, when a small amount of lithium is removed [231, 232], which reduces the optical skin depth [167, 233].

The measured shift and large decrease in intensity at 4.11 V should indicate the formation of the second hexagonal phase. Given that the space group for the second hexagonal Li$_x$CoO$_2$ (0.75 < x < 0.53) phase is identical as pure LiCoO$_2$, the weakly detected bands are still assigned as the $E_g$ and $A_{1g}$. However Inaba et al. [135] reported that the $E_g$ and $A_{1g}$ bands should be observed at 584 and 480 cm$^{-1}$. Consequently, even though the composition of Li$_{0.5}$CoO$_2$ was not reached according to the de-lithiation curve (Figure 5.27), the Raman spectrum of the monoclinic phase might have been observed at this particular measurement point. Seeing that Inaba et al. [135] observed the monoclinic phase to have weak broad bands at ca. 470 and 570 cm$^{-1}$, which match values obtained by this measurement (463 and 568 cm$^{-1}$). However, peak splitting of the $E_g$ band to $A_g$ and $B_g$ was not detected either by this investigation, or by Inaba et al. [135].

![Figure 5.27](image)

**Figure 5.27:** First de-lithiation curve for lithium cobalt oxide (Ferro) in the *in situ* Raman cell. Galvanostatically cycled from 3 V to 4.12 V at 20 mA g$^{-1}$ of LiCoO$_2$, in 1M LiClO$_4$ 1:1 EC:DMC (Charge rate C/7).
Figure 5.28: *In situ* Raman spectral series of the first de-lithiation of LiCoO$_2$ (Ferro) electrode from 3 V to 4.12 V. Spectra are shifted arbitrarily along the intensity axis (Charge rate C/7).

Table 5.6: Observed Raman band positions and assignments for the first, second hexagonal phases and monoclinic phase of Li$_x$CoO$_2$. Band positions (cm$^{-1}$) without brackets are from Inaba et al. [135] and in brackets are from this study.

<table>
<thead>
<tr>
<th>LiCoO$_2$</th>
<th>Li$_x$CoO$_2$, 0.75 &lt; $x$ &lt; 0.53</th>
<th>Li$_x$CoO$_2$, $x$ = 0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band position/ cm$^{-1}$</td>
<td>Symmetry species</td>
<td>Band position/ cm$^{-1}$</td>
</tr>
<tr>
<td>486 (485)</td>
<td>$E_g$</td>
<td>480</td>
</tr>
<tr>
<td>596 (595)</td>
<td>$A_{g}$</td>
<td>584</td>
</tr>
</tbody>
</table>
5.3.2 Lithium manganese oxide (LiMn$_2$O$_4$)

Lithium manganese oxide spinel (LiMn$_2$O$_4$) is one of the possible replacements to LiCoO$_2$ for the positive electrode. LiMn$_2$O$_4$ possesses an inferior theoretical specific capacity of 124 Ah kg$^{-1}$ for the reaction:

\[
\text{LiMn}_2\text{O}_4 \leftrightarrow 2\text{MnO}_2 + \text{Li}^+ + e^-
\]  

(5.9)

Conversely it has a lower toxicity than LiCoO$_2$ and can be produced more cheaply from more abundant raw materials [8]. LiMn$_2$O$_4$ has a cubic spinel structure, (Fd3m space group, this is illustrated in chapter 3, Figure 3.18 [8, 138]) which leads to the irreducible representation:

\[
\Gamma_{\text{opt}} = A_{1g} + E_g + T_{1g} + 3T_{2g} + A_{2u} + 2E_u + 4T_{1u} + 2T_{2u}
\]  

(5.10)

Of which the $A_{1g}$, $E_g$ and $3T_{2g}$ are Raman active and the $4T_{1u}$ are infrared active [139].

$\lambda$-MnO$_2$ also has the Fd3m space group and the loss of the lithium atom results in the loss of $T_{2g}$ and $T_{1u}$ phonons:

\[
\Gamma_{\text{opt}} = A_{1g} + E_g + T_{1g} + 2T_{2g} + A_{2u} + 2E_u + 3T_{1u} + 2T_{2u}
\]  

(5.11)

For compositions between LiMn$_2$O$_4$ and $\lambda$-MnO$_2$, Ammundsen et al. [139] modelled the Li$_{0.5}$Mn$_2$O$_4$ spinel phase in the $F\bar{4}3m$ space group, which is a lower symmetry subgroup of Fd3m. This assumption leaves every second lithium tetrahedral site vacant, which produces an experimentally observed ordering of Li [234, 235] and gives the irreducible representation:

\[
\Gamma_{\text{opt}} = 3A_1 + 3E + 3T_1 + 6T_2
\]  

(5.12)

The $A_1$, $E$ and $T_2$ modes are all Raman active, the $T_1$ modes are also IR active and the $T_1$ modes are inactive.

The first de-lithiation curve for LiMn$_2$O$_4$ vs. lithium in situ Raman cell is shown in Figure 5.29. The cell was cycled between open circuit potential (ca. 3 V) and 4.2 V. At 4.2 V the curve goes beyond $x = 0$ for Li$_x$Mn$_2$O$_4$, demonstrating that charge was lost in other mechanisms apart from lithium extraction. Therefore x values have been assigned an error of 5 %. Figure 5.30 shows in situ spectra in the frequency range of 400–800 cm$^{-1}$ during the first
de-lithiation and Table 5.7 displays the observed main peaks for LiMn$_2$O$_4$, Li$_{0.5}$Mn$_2$O$_4$ and λ-MnO$_2$. At the open circuit potential (ca. 3.0 V) the $A_{1g}$ band (630 cm$^{-1}$) and a weak shoulder band (577 cm$^{-1}$), which is assigned as $T_{2g}(3)$, are observed. The $A_{1g}$ has a much higher wavenumber value compared to ex situ measurements in chapter 3 were it was observed at 614 cm$^{-1}$, this could arise from laser heating effects [142]. As the cell potential is increased to 4.10 V, the $A_{1g}$ band decreases in prominence. This was in conjunction with an appearance of new bands at ca. 491, 655, 630, 612 and 597 cm$^{-1}$. These bands can be assigned to three $T_2$ and two $A_1$ modes of Li$_{0.5}$Mn$_2$O$_4$ [161].

Above 4.11 V a new band emerged at 589 cm$^{-1}$ and grew in intensity at the expense of the 630 and 655 cm$^{-1}$ bands. This peak can be allocated to the $A_{1g}$ mode of the emerging λ-MnO$_2$ phase. The coexistence of these bands signifies the presence of two or more structural phases for the spinel during the potential range of 4.10 to 4.12 V [141]. Two other bands of this phase are observed either side of the $A_{1g}$ at 491 and 647 cm$^{-1}$ at 4.15 V. These are respectively the $T_{2g}(2)$ and $T_{2g}(3)$ modes. These modes as well as the $A_{1g}$ show a dramatic increase in intensity as the potential reached 4.20 V. The increase in intensity from 4.15 V is due to resonance enhancements effects associated with λ-MnO$_2$ at the excitation laser wavelength of 632.8 nm used [139].

![Figure 5.29](image)

**Figure 5.29:** First de-lithiation curve for lithium manganese oxide (Honeywell). Galvanostatically cycled from 3.0 V to 4.2 V at 20 mA g$^{-1}$ LiMn$_2$O$_4$ in the Raman cell, in 1M LiClO$_4$ 1:1 EC:DMC (Charge rate C/7.5). There is an estimated error of x of 5 %.
**Figure 5.30:** *In situ* Raman spectral series of the first de-lithiation of lithium manganese oxide, LiMn$_2$O$_4$ (Honeywell). Spectra are shifted arbitrarily along the intensity axis (Charge rate C/7.5).

**Table 5.7:** Observed Raman band positions and assignments for LiMn$_2$O$_4$, Li$_{0.5}$Mn$_2$O$_4$ and λ-MnO$_2$ [139, 141, 161].

<table>
<thead>
<tr>
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<th>LiMn$_2$O$_4$</th>
<th>Li$_{0.5}$Mn$_2$O$_4$</th>
<th>λ-MnO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Band position</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>cm$^{-1}$</strong></td>
<td>Symmetry</td>
<td>Band position/ cm$^{-1}$</td>
<td>Symmetry</td>
</tr>
<tr>
<td>568</td>
<td>$T_{2d}(3)$</td>
<td>490</td>
<td>$T_2$</td>
</tr>
<tr>
<td>630</td>
<td>$A_{1g}$</td>
<td>597</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>630</td>
<td>$T_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>655</td>
<td>$A_1$</td>
</tr>
</tbody>
</table>
5.3.3 Positive electrode conclusions

In situ Raman investigations of LiCoO₂ and LiMn₂O₄ performed matched the work of known literature. The structural changes associated with partial de-lithiation of LiCoO₂ and total de-lithiation of LiMn₂O₄ was observed spectroscopically. Improvement in the in situ Raman cell performance is required to obtain enhanced electrochemical curves. It is believed that the internal mechanical pressure on the electrodes within the cell is too low compared to standard test cells. This affects the performance of oxide materials more in the Raman cell as they generally have a lower conductivity than say graphite. For further work on positive electrode materials it is recommended to use a spring loaded current collector, as demonstrated with the three-electrode Raman cell (chapter 2, Figure 2.1). The force created by the spring should be greater than arbitrarily positioning the moveable current collector.

5.4 Electrode materials outlook

Above all else, this work demonstrated the feasibility of measuring various types of negative and positive electrode materials. From the literature many other materials are known as candidates for Raman investigations. These include studies on iron phosphates (including LiFePO₄, NaFePO₄, FePO₄) [236-238], titanium phosphates (LiTi₂(PO₄)₃) [239], vandates (V₂O₅) [240, 241], and mixed oxides such as LiNi₀.₈Co₀.₁₅Al₀.ₐ₅O₂ [242] and LiCoₓMn₂₋ₓO₄ [243]. By carrying out slight improvements of the in situ Raman cell to boost internal mechanical pressure upon the electrodes, work on these and other various oxide materials can be realized.
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6

IN SITU RAMAN MICROSCOPY OF MATERIALS FOR ELECTROCHEMICAL DOUBLE-LAYER CAPACITORS

6.1 Introduction

This chapter will be concerned in answering two questions related to the carbonaceous electrodes present in electrochemical double-layer capacitors (EDLC):

- What is the nature of the reversible Faradaic processes in larger potential windows?
- Do these processes contribute to degradation of the electrodes?

Figure 6.1 illustrates the Franklin model of the structure of activated carbon (a non-graphitising carbon) [244]. It can be seen there are stacked graphite-type regions connected by isolated single graphene sheets. These graphite-type regions have been shown by X-ray diffraction to have a larger interlayer spacing of 3.6 Å (crystalline graphite has a spacing of 3.35 Å). ABAB stacking of these layers is not present. Activated carbons have an open porosity which results in a specific surface area usually exceeding 1000 m² g⁻¹. The pores are typically micro-pores (below 20 Å in diameter). Ion intercalation into these materials, if it occurs at all, has not been studied in any great detail. Indeed one investigation failed to detect any presence of sulphur in graphite oxide formed during electrochemical pre-treatment.
of a glassy carbon in 0.1 M sulphuric acid [245]. However any intercalated HSO$_4^-$ into glassy carbon could have been lost due to lattice damage and oxide formation. Nevertheless recent dilatometry results by Hahn et al. [246] on activated carbon reported significant electrode expansion in EDLC-type aprotic electrolyte solutions. They attributed this to possible insertion reactions when the potential is taken away from standard EDLC potential range. As a consequence, ion intercalation may lead to degradation of the carbon electrodes, which can be anticipated to reduce the lifetime of EDLCs [247-249]. In Chapter 4, Raman microscopy was demonstrated to be a pertinent investigation tool for monitoring intercalation reactions. Consequently this chapter will investigate whether processes other than those related to double-layer effects may readily occur under working conditions. The in situ Raman investigation of capacitors is limited to one notable study by Bonhomme et al. [250], where the observation of concentration change of ionic species during the creation of the double layer at the carbon electrode surface, was reported. Furthermore they measured intensity changes of the carbon electrode which were correlated with carbon electronic conductivity changes [251]. Another spectroelectrochemical study includes an in situ infrared investigation, where spectroscopic measurements showed, under anodic potentials, the formation of an acetonitrile (AN) and BF$_3$ adduct. They suggested this was due to the presence of trace water within the EDLC [252].

*Figure 6.1:* Franklin model for activated carbon (a non-graphitising carbon) [244].
In chapters 4 and 5 the major interest was the insertion and extraction of lithium into and from negative and positive electrodes. In the EDLC systems much larger ions are present in the electrolyte and a size comparison of the electrolyte constituents are shown in Table 6.1.

Table 6.1: Radii and van der Waals volume of selected cations, anions and solvent from crystallographic data [253].

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ionic and molecular radii/ Å</th>
<th>van der Waals volume/ Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>0.76</td>
<td>1.8²</td>
</tr>
<tr>
<td>Et₄N⁺</td>
<td>3.36</td>
<td>159</td>
</tr>
<tr>
<td>EMI⁺</td>
<td>3.65²</td>
<td>200²</td>
</tr>
<tr>
<td>BF₄⁻</td>
<td>2.27</td>
<td>49</td>
</tr>
<tr>
<td>TFSI⁻</td>
<td>3.26</td>
<td>146</td>
</tr>
<tr>
<td>PC</td>
<td>2.76</td>
<td>88¹</td>
</tr>
<tr>
<td>AN</td>
<td>1.91²</td>
<td>29²</td>
</tr>
</tbody>
</table>

¹from MM2 calculations [253].
²Rough estimation from bond length or ionic radii data [253, 254]. A perfect sphere is assumed for van der Waals volume estimation.

The materials chosen to be investigated with in situ Raman microscopy are microcrystalline graphite (KS44), activated carbon (Picactif SC), high surface area graphite (HSAG400) and KOH activated mesophase pitch based coal (AMPC) (Table 6.2).

The following results form the foundation of future investigations of EDLC systems relating to the role of ion intercalation into carbon electrodes with an emphasis on lifetime limitations and optimisation of voltage and storage capacity.
Table 6.2: Summary of material properties [19, 246, 249, 255, 256].

<table>
<thead>
<tr>
<th>Carbon sample</th>
<th>BET/ m² g⁻¹</th>
<th>Total pore volume/ cm³ g⁻¹</th>
<th>Density/ g cm⁻³</th>
<th>d₅₀ / μm</th>
<th>Differential capacitance at zero charge/ F g⁻¹</th>
<th>XRD L₉/ nm</th>
<th>XRD L₉/ nm</th>
<th>Raman L₉/ nm</th>
<th>c/2 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS44</td>
<td>6.2</td>
<td>-</td>
<td>2.26</td>
<td>20.0</td>
<td>-</td>
<td>31</td>
<td>56</td>
<td>39</td>
<td>0.3356</td>
</tr>
<tr>
<td>Picactif</td>
<td>2048</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.36-0.4</td>
</tr>
<tr>
<td>HSAG400</td>
<td>400</td>
<td>0.31</td>
<td>0.8</td>
<td>ca. 6</td>
<td>50</td>
<td>18</td>
<td>-</td>
<td>4</td>
<td>0.336</td>
</tr>
<tr>
<td>KOH activated mesophase pitch based coal</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Before electrochemical activation &lt; 5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>After electrochemical activation ~ 130</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.1.1 Measurement procedure

All measurements in this chapter were carried out with the three electrode in situ Raman cell (chapter 2.4). For each of the following experiments four points were measured on the surface of the electrode. However in all cases all four points measured showed similar spectral trends, suggesting homogeneous behaviour. Therefore, for reasons of clarity, in all subsequent results only one representative point is shown for all experiments.
6.2 Microcrystalline graphite (KS44)

Although microcrystalline graphite is not a suitable material for EDLCs, because of its relatively low surface area, it is potentially a good model material to show that intercalation reactions may occur in “graphitic” regions in activated carbons over a wide potential window. Therefore an initial Raman study on the effects of intercalation for aprotic electrolyte-based electrochemical double layer capacitors (EDLCs) was carried out as the first step in this investigation. Recent measurements in our laboratory with in situ XRD by Ruch et al. [257] also used microcrystalline graphite as a model material to demonstrate ion intercalation in supercapacitor electrolytes.

6.2.1 KS44 in TEABF₄, AN

*In situ* Raman microscopy is first employed in the study of the electrochemical intercalation of tetraethylammonium (Et₄N⁺, TEA) and tetrafluoroborate (BF₄⁻) ions into and out of microcrystalline graphite. Figure 6.2 displays the cyclic voltammogram (CV) of the first cycle of graphite (KS44, Timcal SA, Switzerland) in 1 mol dm⁻³ tetraethylammonium-tetrafluoroborate (TEABF₄) in acetonitrile over the negative (3 - 0.3 V vs. Li/Li⁺) and the positive potential sweep (3 - 5 V). Aluminium current collectors were used in this study instead of copper because of the well documented dissolution of copper in the presence of acetonitrile [258]. CV corresponds to tetraethylammonium (Et₄N⁺) intercalation/extraction (Figure 6.3) and tetrafluoroborate (BF₄⁻) intercalation/extraction (Figure 6.4). For the intercalation of Et₄N⁺ the specific charge capacity is calculated to be 54 Ah kg⁻¹ with a 65 % coulombic efficiency for the extraction. For BF₄⁻ intercalation the specific charge capacity is found to be 63 Ah kg⁻¹ with an efficiency of 36 % during extraction. These low efficiencies probably arise from electrolyte decomposition reactions occurring in the visited potential ranges [259].
Figure 6.2: Graphite (KS44) half cell CV (1st cycle) for the negative (3 - 0.3 V vs. Li/Li⁺) and the positive potential sweep (3 - 5 V) measured from the Raman cell. Open circuit potential was ca. 3 V. Cycled in 1 mol dm⁻³ tetraethylammonium-tetrafluoroborate (TEABF₄) in acetonitrile. Scan rate: 0.5 mV s⁻¹.

The Raman spectral series (Figures 6.3 and 6.4) respectively show the Et₄N⁺ and BF₄⁻ intercalation/extraction into and out of microcrystalline graphite. At 2.53 V (Figure 6.3) and at 3.08 V (Figure 6.4) the typical Raman spectrum of graphite is observed. The spectrum displays the D- and G-bands observed at 1329 cm⁻¹ and 1578 cm⁻¹ [108]. The small D'-band at 1614 cm⁻¹ is again observed [188].

For Et₄N⁺ intercalation the first change is observed at 1.0 V, where a slight shoulder at higher wavenumbers can be observed on the G-band. This shoulder quickly forms a complete band seen at 1599 cm⁻¹ (0.87 V) and overtakes the intensity of the G-band at 0.78 V. For BF₄⁻ this same trend is seen through a potential range of 4.17 to 4.79 V. Additionally in both cases as the potential is swept towards 0.3 or 5 V the D-band intensity diminishes and disappears into the background noise.
As discussed previously in chapter 4, the doublet G-band relates to an ordered distribution of Et₄N⁺ or BF₄⁻ in the staged compound, where these bands can be assigned to the interior $E_{2g2}(i)$ (1578 cm⁻¹) and the bounding $E_{2g2}(b)$ (1600 cm⁻¹) bands respectively [260]. $E_{2g2}(i)$ and $E_{2g2}(b)$ are correspondingly associated with carbon-atom vibrations in interior graphite layers (not adjacent to intercalate layer planes) and in bounding graphite layers (adjacent to intercalate planes) [66, 143]. It can be observed that the $E_{2g2}(b)$ mode is much more intense than $E_{2g2}(i)$. Intercalation compounds possess a lower density than pristine graphite and different optical properties, therefore it can be expected that the sampling depths to be larger. Alsmeyer and McCreery [261] showed that with the intercalation of HSO₄⁻ into HOPG the Raman cross-section for the bounding layer was ca. 2.5 times greater up to and including stage 2 compounds. The stage 1 compound was seen to have a Raman cross-section which was 25 times larger. Therefore for these measurements this evaluation of the cross section ratios will be used to estimate the stage number, n [156]:

$$R = \frac{I_i}{I_b} = \frac{\sigma_i}{\sigma_b} \frac{n-2}{2} \quad (n > 2)$$

(6.1)

where $$\frac{\sigma_i}{\sigma_b} = \frac{1}{2.5}$$

(6.2)

Interestingly there is no initial blue-shift of the G-band before doublet formation, seen previously in chapter 4, during the intercalation of the lithium cation. The shift is assigned to the formation of a dilute stage one graphite intercalation compound (GIC). From this observation it could be deduced that the dilute stage one is not present when either Et₄N⁺ or BF₄⁻ is inserted. In the reverse potential sweeps the opposite trends are seen when Et₄N⁺ and BF₄⁻ are extracted. The $E_{2g2}(b)$ band diminishes and disappears at the expense of the reappearance and growth of the $E_{2g2}(i)$. The D-band also returns, providing the original graphite spectrum back at potentials around 3 V. The major difference is that the D-band now has a much greater intensity, which is also the case for the D'-band.
Figure 6.3: *In situ* Raman spectra series of the first Et$_4$N$^+$ intercalation and de-intercalation into graphite (KS44). Spectra are shifted arbitrarily up the y-axis.
Figure 6.4: *In situ* Raman spectra series of the first BF$_4^-$ intercalation and de-intercalation into graphite (KS44). Spectra are arbitrarily shifted up the y-axis. Measurement follows on from experiment shown in Figure 6.3.

The disappearance of the D-band, as graphite is either intercalated with Et$_4$N$^+$ or BF$_4^-$ and the subsequent removal, giving a more intense reappearance of the peak, will be first examined. Hence the ratio of the G-band and the G-band doublet bands ($E_{2g2}(i)$ and $E_{2g2}(b)$) is plotted against the D-band (Figure 6.5A, the contribution intensity of the D$'$-band to the G-band was subtracted where appropriate). The figure demonstrates that with intercalation the ratio increases, showing the disappearance of the D-band and with extraction a ratio decrease is observed, displaying the re-emergence of the D-band. This trend has been previously
observed and reported by us for Li⁺ intercalation/extraction and discussed previously in chapter 4 [67, 146]. Here the D-band disappearance was linked to intercalation of ions in the surface regions of graphite, which disrupts the Raman activity of this band. The intensity of the $E_{2g2}(i)$ band is therefore linked to the D-band, as its activity depends on lithium free layers and in Figure 6.5B the change in intensity ratio of $I_D$ D-band is shown. For the intercalation of Et₄N⁺ at 1.0 V it can be observed that the ratio decreases sharply. These results show that the intensity of the $E_{2g2}(i)$ decreases at a greater amount than the also weakening D-band. For Et₄N⁺ extraction the ratio is unclear because of the massive enlargement of the D-band once the ions are removed. This also affects the trend for BF₄⁻ intercalation/ de-intercalation. In Figure 6.5C the intensity ratio of the $E_{2g2}(i)$ and $E_{2g2}(b)$ bands ($I_E$ $I_B$) is plotted against potential and shows that staging begins below potentials of 1.0 V and a stage 2 GIC is reached in the case of Et₄N⁺ intercalation at 0.3 V. Similar trends are seen in the Raman spectral series when BF₄⁻ is intercalated into graphite at potentials above 4.3 V. Figure 6.5C shows that the maximum amount of BF₄⁻ intercalated produced a stage 3 GIC at 5 V.
Figure 6.5:  (A) The intensity ratio of contributions from both \((I_i + I_b)\) with the D-band (B) the intensity ratio of just \(I_i\) (G-band) with the D-band and (C) the intensity ratio of the G-band doublet, \(I/I_b\) are plotted over the potential range 0.3 to 5 V vs. Li/Li\(^+\). For (C) the stage number axis from the G-band doublet ratio is also plotted using equation 6.1. Note equation is only valid when there is G-band doublet, therefore for all other potentials, no ions are intercalated and the stage number is therefore infinite. The ratio calculation subtracted, where necessary, contributions from the D'-band.
In relation with this study, the large ensuing D-band could result from the lattice damage once the large ions are removed from the graphite. For cation intercalation, such irreversible changes of the graphite structure are confirmed by scanning electron microscopy (SEM) pictures presented in Figure 6.6. Figure 6.6a displays the uncycled electrode and Figure 6.6b the negatively cycled electrode, where strong roughness on the edge planes and some roughness on the basal planes were observed on a few particles. It should be noted that Raman spectra were also collected at various points on the graphite electrode and they all showed a more intense D-band. Therefore SEM pictures alone are not fully representative, because most of the damage may occur inside the particles and hence will be invisible. Furthermore no exfoliation effects are observed in the SEM.
Figure 6.6: SEM pictures of KS44 graphite electrodes (a) KS44 washed with acetonitrile, unycled and (b) KS44 after Li$_4$N$^+$ intercalation/ de-intercalation, cycled once between open circuit potential (3 V) to 0.3 V and back to 3 V vs. Li/Li$^+$, washed with acetonitrile. Scan rate 0.5 mV s$^{-1}$. Arrows point to areas of roughness observed at the edge and basal planes.
6.2.2 KS44 in TEABF₄, PC

In situ Raman microscopy is next used in the study of the electrochemical intercalation of tetraethylammonium (Et₄N⁺) and tetrafluoroborate (BF₄⁻) ions into and out of microcrystalline graphite. Figure 6.7 displays the cyclic voltammogram (CV) of the first cycle of graphite (KS44) in 1 mol dm⁻³ tetraethylammonium-tetrafluoroborate (TEABF₄) in propylene carbonate (PC) over the negative (3 - 0.3 V vs. Li/Li⁺) and the positive potential sweep (3 - 5 V). The CV is very similar to the CV when acetonitrile (AN) is used as the solvent (Figure 6.2), suggesting the electrochemistry is independent to which solvent is used. The measured charge of 50 Ah kg⁻¹ with a 76 % discharge efficiency for cation insertion is similar to cycling in AN. Anion insertion had a charge of 44 Ah kg⁻¹ with a discharge efficiency of 52 %. These results are similar to in situ XRD cell measurements in our laboratory by Ruch et al. [257].

Figure 6.7: Graphite (KS44) half cell CV (1ˢᵗ cycle) for the negative (3 - 0.3 V vs. Li/Li⁺) and the positive potential sweep (3 - 5 V) measured from the Raman cell. Open circuit potential was ca. 3 V. Cycled in 1 mol dm⁻³ tetraethylammonium-tetrafluoroborate (TEABF₄) in propylene carbonate (PC). Scan rate: 0.5 mV s⁻¹.
The Raman spectral series (Figures 6.8 and 6.9) respectively show the Et₄N⁺ and BF₄⁻ intercalation/extraction into and out of microcrystalline graphite. Again similar spectral features are seen as described previously for TEABF₄ in AN. However the first changes in the spectrum are first observed in a narrower potential range of 1.07 V and 4.23 V, leading to the onset potentials of intercalation to be ca. 1.1 V for Et₄N⁺ and 4.2 V for BF₄⁻. Nevertheless there is one striking difference to be observed in the spectra. On the reverse scan during Et₄N⁺ extraction at potentials greater than 2 V three bands are observed in the G-band region: the $E_{2g2}(i)$, the $D'$ and what seems to be the still present $E_{2g2}(b)$ (Figure 6.10). The growing $D'$-band is coupled with the growing D-band. The spectra suggest that a high staged compound is present at 3 V, which leads to the conclusion that the ions are trapped in the graphite structure or that the graphite structure has been irreversible altered during the intercalation process. This could be the case, as earlier discussed in chapter 4, when PC is used as an electrolyte constituent with highly crystalline graphite; exfoliation of the graphite results [19, 262].
Figure 6.8: *In situ* Raman spectra series of the first Et$_4$N$^+$ intercalation and de-intercalation into graphite (KS44). Spectra are shifted arbitrarily up the y-axis.

Interestingly after BF$_4^-$ extraction the Raman spectrum (Figure 6.9) appears to be identical to the initial graphite spectrum (Figure 6.8). Again the D-band is seen to decrease in intensity with cation insertion and return with greater intensity upon cation extraction. To then subsequently decrease on intercalation of anions and to partially return with their removal.
Figure 6.9: *In situ* Raman spectra series of the first BF$_4^-$ intercalation and de-intercalation into graphite (KS44). Spectra are shifted arbitrarily up the y-axis. Measurement follows on from experiment shown in Figure 6.8.

The spectrum acquired before and after the first Et$_4$N$^+$ insertion/extraction is shown in Figure 6.10. A large increase of the D-band is observed, this maybe due to exfoliation. The D-band position has also blue-shifted from 1335 to 1323 cm$^{-1}$. Before the potential sweep two bands (the G- and D'-bands) at 1581 and 1620 cm$^{-1}$ are respectively observed. Afterwards three bands are seen in this region. The G-band remains at the same position but with greater intensity. The D'-band also has a greater intensity and has slightly shifted position to 1617 cm$^{-1}$. The third band, seen at 1602 cm$^{-1}$ has been cautiously assigned as trapped Et$_4$N$^+$. The $I_d/I_G$ intensity ratio (Figure 6.11) shows that stage 2 GICs were formed at both potential
limits and at 3 - 4 V vs. Li/Li⁺ very dilute staged compounds (stage 17 - 24) are present. The onset potentials for cation and anion intercalation are shown to be 1.1 and 4.2 V respectively. Partial exfoliation of the electrode was confirmed by post mortem SEM, where an expansion of the edge planes due to internal gas formation, is clearly shown (Figure 6.12) [15, 19].

![Graphite spectra before (thick line) and after (thin line) first intercalation/deintercalation of Et₄N⁺ showing G-band, D'-band and the still present E₃c₃(b) at 1602 cm⁻¹.](image)

**Figure 6.10:** Graphite spectra before (thick line) and after (thin line) first intercalation/deintercalation of Et₄N⁺ showing G-band, D'-band and the still present $E_{3c3}(b)$ at 1602 cm⁻¹.
Figure 6.11: Intensity ratio of the G-band doublets, \( I_2 / I_b \) (\( E_{2g}(i)/E_{2g}(b) \)) over the potential range 0.3 to 5 V vs. Li/Li\(^+\). The stage number axis derived from the G-band doublet ratio is also plotted. The ratio calculation subtracted, where necessary, contributions from the D\(^{\prime}\)-band.
Figure 6.12: (a) SEM picture of uncycled KS44 graphite, (b) SEM picture of KS44 graphite electrodes used in the Raman experiment. KS44 washed with propylene carbonate, after Et₄N⁺ and BF₄⁻ intercalation/de-intercalation cycles. Cycled once between open circuit potential (3 V) to 0.3 V and back to 3 V vs. Li/Li⁺. In the positive sweep between 3 V to 5.0 V and back to 3 V. Scan rate 0.5 mV s⁻¹. Arrow points to exfoliated edge planes.
6.2.3 KS44 Ionic Liquid, EMI TFSI

To show that intercalation of large ions is possible without the co-intercalation of the solvent, *in situ* Raman microscopy is used in the study of the electrochemical intercalation in a solvent free electrolyte. The ionic liquid salt 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl) imide (EMI-TFSI) is used as the electrolyte. Figure 6.13 displays the cyclic voltammogram (CV) of the first cycle of graphite (KS44) in over the negative (3 - 0.5 V vs. Li/Li⁺) and the positive potential sweep (3 - 5 V). During EMI⁺ intercalation the specific charge capacity was determined to be 103 Ah kg⁻¹ with a discharge efficiency of 45%. For TFSI⁻ these values were calculated to be 49 Ah kg⁻¹ and 57% respectively.

![Graphite (KS44) half cell CV (1st cycle) for the negative (3 - 0.5 V vs. Li/Li⁺) and the positive potential sweep (3 - 5 V) measured from the Raman cell. Open circuit potential was ca. 3 V. Cycled in 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl) imide (EMI-TFSI). Scan rate: 0.5 mV s⁻¹.](image)

*Figure 6.13:* Graphite (KS44) half cell CV (1st cycle) for the negative (3 - 0.5 V vs. Li/Li⁺) and the positive potential sweep (3 - 5 V) measured from the Raman cell. Open circuit potential was ca. 3 V. Cycled in 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl) imide (EMI-TFSI). Scan rate: 0.5 mV s⁻¹.
The Raman spectral series (Figures 6.14 and 6.15) respectively show EMI⁺ and TFSI⁻ intercalation/extraction into and out of microcrystalline graphite. Once again similar spectral features are seen as described previously for TEABF₄ in AN. For this system the onset potentials are 1.0 V for insertion EMI⁺ and 4.6 V for TFSI⁻ insertion. In this experiment copper was used as the current collector because of the well documented instability of the TFSI⁻ anion with aluminium [18, 263]. These results confirm that large ions can and are intercalating into graphite as bare ions. Therefore the same signal change is seen whether the bare ion is intercalating or when there is co-solvation as in the case of TEA-BF₄ in PC. Nonetheless no difference in the Raman spectrum for both cation and anion intercalation between the two reverse peaks are observed.

Figure 6.14: In situ Raman spectra series of the first EMI⁺ intercalation and de-intercalation into graphite (KS44). Spectra are shifted arbitrarily up the y-axis. The intensity axis is identical for both scans.
**Figure 6.15:** *In situ* Raman spectra series of the first TFSI intercalation and de-intercalation into graphite (KS44). Spectra are shifted arbitrarily up the y-axis. The intensity axes are dissimilar for both scans. Measurement follows on from experiment shown in Figure 6.14.
Figure 6.16 displays the plotted $I/I_b$ intensity ratio against potential and shows that GICs between stage 2 and 3 were formed at the potential limits of 0.5 and 5 V vs. Li/Li$. An onset potential of 1.0 V for EMI$^+$ and 4.7 V for TFSI$^-$ is noted.

Figure 6.16: Intensity ratio of the G-band doublets, $I/I_b$ ($E_{2g}(i)/E_{2g}(b)$) over the potential range 0.5 to 5 V vs. Li/Li$. The stage number axis derived from the G-band doublet ratio is also plotted. The ratio calculation subtracted, where necessary, contributions from the D$^*$-band.
6.3 Activated carbon: Picactif

Activated (or amorphous) carbon refers to carbon which has bonding and structure similar to graphite, except there is no long-range order (Figure 6.1) [101]. The AB stacking order is absent and the layers are not usually flat and X-ray diffraction measurements on this material suggest a layer spacing of the graphitic regions to be ca. 3.6 Å. The structure of Picactif is illustrated in the SEM pictures shown in Figure 6.17. The particles can be seen to be quite irregular both in size and shape with edges of the particles appearing rough.

Figure 6.17: SEM pictures of Picactif (a) overview of particles (b) detailed view of one particle.
It is well understood that the rules of Raman spectra of these carbons are different than microcrystalline graphite, therefore a split of the G-band is not expected, and if it was predicted to occur, it would most likely be unobservable because of the broadness of the band [117]. Apart from the Bonhomme study [250], no other in situ Raman spectra of activated carbons have been reported. Here they described moderate band shifts of the G-band and D-bands with variation of applied potential. The explanation of these peak shifts was related to changes in electronic density variations on the carbon surface accompanied by reversible modifications of the C-C bond length, force constant and polarisability. The resulting spectra will be evaluated to see if similar information can be extracted and if a broader explanation of these peak shifts can be derived with special attention to possible ion insertion.

Picactif has a relatively high surface area of 2048 m$^2$ g$^{-1}$ [255, 256] (Table 6.2), and is an excellent material for EDLCs possessing a capacitance of 81 F g$^{-1}$. Figure 6.18 displays the cyclic voltammogram (CV) of the first cycle of activated carbon (Picactif) in 1 mol dm$^{-3}$ tetraethylammonium-tetrafluoroborate (TEABF$_4$) in acetonitrile over the negative (3 - 0.5 V vs. Li/Li$^+$) and the positive potential sweep (3 - 5 V). As can be seen from the CV small reversible peaks suggest the occurrence of faradaic reactions and therefore possible ion intercalation in the graphitic-type regions.
Figure 6.18: Activated carbon (Picactif) half cell CV (1st cycle) for the negative (3 - 0.5 V vs. Li/Li⁺) and the positive potential sweep (3 - 5 V) measured from the Raman cell. Open circuit potential was ca. 3 V. Cycled in 1 mol dm⁻³ tetraethylammonium-tetrafluoroborate (TEABF₄) in acetonitrile. Scan rate: 0.5 mV s⁻¹.

Figures 6.19 and 6.20 respectively display the Raman spectral series during the negative and positive potential sweeps. The both spectral series show broad G- and D-bands (FWHM of 53 and 118 cm⁻¹ respectively). During the potential sweeps the $I_D/I_G$ ratio remains constant (Figure 6.21a) suggesting there is no degradation of the material during cycling. Moreover no G-band doublet formation is observed. This does not rule out ion intercalation; it only excludes the formation of staged compounds within these graphitic regions. What is observed however, is during the negative potential sweep from 3 - 0.5 V, the G-band red-shifts from 1587 cm⁻¹ to 1569 cm⁻¹ and then the shift is reversed on the return scan from 1569 cm⁻¹ to a higher wavenumber of 1595 cm⁻¹. During the positive potential sweep the G-band remains at this position (Figure 6.21b). The shift of the G-band with potential matches very well to the theoretical study of Chan et al. [264]. In this work the frequency change of the $E_{2g}$ mode was
modelled from separate contributions of charge transfer and also the in-plane lattice constant change during the formation of GIC’s (Figure 6.22). However the $E_{2g2}$ shift trend, due to pure charge transfer, is not seen in GICs because of the presence of the intercalate atoms. When the C atoms vibrate about their equilibrium positions, they squeeze the intercalate atoms or molecules in their immediate vicinity, causing an increase in frequency for both donor and acceptor GIC’s.

![Figure 6.19: In situ Raman spectra series of the first Et,N$^+$ intercalation and de-intercalation into activated carbon (Picactif). Spectra are shifted arbitrarily up the y-axis. Intensity scales are identical for both axes. Arrows indicate direction of scan.](image)
The observed movement of this mode in activated carbon (Picactif) could therefore be explained as a function of charge transfer to or from the graphene sheets. At the Fermi level in graphite, second-neighbour interactions are slightly anti-bonding [265, 266]. Therefore charge transfer to the graphene layer results in occupation of the $\pi^*$ antibonding-band leading to a weakening of the C-C bond, resulting in the elongation of the C-C distance, and subsequent red-shift of the G-band. Charge transfer from the graphene sheet leads to a vacancy at the top of the bonding $\pi$-band; therefore strengthening the intralayer C-C bond; resulting in the contraction of the C-C distance, with slight blue-shift of the G-band. (The charge transfer results from the formation of the double layer along the graphene sheets; with the graphene

Figure 6.20: *In situ* Raman spectra series of the first BF$_4^-$ intercalation and de-intercalation into activated carbon (Picactif). Spectra are arbitrarily shifted up the y-axis. Intensity scales are identical for both axes. Arrows indicate direction of scan. Measurement follows on from experiment shown in Figure 6.19.
sheet either being positively or negatively charged. Hence the red-shift of the G-band cannot substantiate intercalation of ions into graphitic regions). Nevertheless in situ Raman measurements on the lithium insertion into mesocarbon microbeads (MCMBs) \[164\], low-temperature pyrolytic carbon \[165\] and poly(paraphenylene) (PPP) based disordered carbon \[166\] also record this G-band shift, and from these papers all authors conclude that lithium is inserted randomly between the graphene layers without the formation of a staged GIC compound.

Figure 6.21: (a) Intensity ratio of the G-band/D-band and (b) Function of G- and D-band position with potential for activated carbon (Picactif) with potential vs. Li/Li⁺. Peak positions calculated with a two-peak Lorentzian fit.
In situ Raman Microscopy of Materials for EDLCs

Figure 6.22: First-principle calculation of the $E_{2g}$ phonon mode frequency as a function of charge transfer, adapted from C.T. Chan et al. [264].

The D-band position is also seen to shift (Figure 6.21b). At the wide potential limits the D-band blue-shifts from 1315 cm$^{-1}$ to 1345 cm$^{-1}$ (0.5 V) or 1335 cm$^{-1}$ (5 V). The following hypothesis has been considered to explain this phenomenon: In activated carbon it could be assumed that the D-band is made up of two components; ring-breathing in graphitic-type regions and ring breathing in isolated graphene sheets. The wavenumber of the graphitic region D-band is assumed be lower than the isolated regions because some of the energy of this system is consumed by the weak attractive van der Waals forces, whereas isolated sheets have either no or weaker van der Waals interactions. In chapter 4 numerous experiments of lithium intercalation into graphite demonstrated the disappearance of the D-band with intercalation. Furthermore in previous experiments described in this chapter, this event was also observed both for cation and anion insertion into microcrystalline graphite. Therefore it is proposed that the shift of this D-band could result from the disappearance of the lower wavenumber graphitic type component, caused by the intercalation of ions within these graphite-like regions (Figure 6.23).
If intercalation is occurring then the $I_G/I_D$ ratio should increase during the potential extremes as the D-band contribution from graphitic regions become forbidden? Certainly for BF$_4^-$ intercalation the $I_G/I_D$ ratio is seen to increase (Figure 6.21a). For Et$_4$N$^+$ a slight increase is observed, however the G-band peak shift may affect the reliability of the peak-fitting. Moreover these shifts are not due to laser heating, as is the case with some carbonaceous materials, because the shifts measured are reversible, reproducible and are as a function of potential (Figure 6.21b) [126]. No explanation can be proposed for the changes in band intensities during the potential sweeps, apart from changes in the optical skin depth or Raman cross sections.
Figure 6.23: Model for shift of D-band observed in activated carbons (bold line) at 3V vs. Li/Li⁺, (thin line) at 0.5 V vs. Li/Li⁺.
6.4 High surface area graphite (HSAG400)

High surface area graphite (HSAG400, TIMCAL AG, Switzerland) is a promising material for EDLCs. Because of its mesoporous graphite structure, it has a high specific surface area of 280 m$^2$ g$^{-1}$ [246] (Table 6.2). This material sits between both extremes of highly crystalline graphite (K544) and activated carbon (Picactiv). It consists of very small graphitic crystals ($L_\alpha = \text{ca.} 4 \text{ nm}$) but has a significant double-layer charging region because of its high surface area. The structure of HSAG is illustrated in the SEM pictures shown in Figure 6.24. The material consists of a variation of globular sized particles from ca. 5 to 100 μm. Of which each globular consists of a hotchpotch of irregular graphitic crystallites.

Figure 6.24: SEM pictures of HSAG400 (a) overview of particles (b) detailed view of one particle.
This material was investigated with in situ Raman microscopy in order to demonstrate ion intercalation into these small crystallites. Figure 6.19 displays the cyclic voltammogram (CV) of the first cycle of graphite (KS44) over the negative (3 - 0.5 V vs. Li/Li⁺) and the positive potential sweep (3 - 5 V) in 1 mol dm⁻³ tetraethylammonium-tetrafluoroborate (TEABF₄) in acetonitrile. Small reversible peaks on the return scans show that faradaic reactions as well as double layer charging are occurring. The charge consumed for the anodic sweep (143 Ah kg⁻¹) was double the cathodic (78 Ah kg⁻¹), with the discharge efficiencies being low for both processes correspondingly 20 and 58 %.

![Cyclic Voltammogram](image)

**Figure 6.25:** HSAG half cell CV (1ˢᵗ cycle) for the negative (3 - 0.5 V vs. Li/Li⁺) and the positive potential sweep (3 - 5 V) measured from the Raman cell. Open circuit potential was ca. 3 V. Cycled in 1 mol dm⁻³ tetraethylammonium-tetrafluoroborate (TEABF₄) in acetonitrile. Scan rate: 0.5 mV s⁻¹.

It can be seen for both Raman spectral series (Figures 6.25 and 6.26), the G-band doublet is observed, and therefore ion intercalation and staging is taking place. For the negative potential sweep the onset potential of insertion is 1.0 V and the positive 4.3 V. A shift in the D-band is also observed (Figure 6.27a), though it only resembles the shift seen for activated carbon in
In situ Raman Microscopy of Materials for EDLCs

the positive potential range. Using the intensity ratio of the interior and bounding bands of the G-band doublet a stage 2 GIC is calculated for Et$_4$N$^+$ intercalation and stage 4 GIC for BF$_4^-$. The reason for a higher GIC for BF$_4^-$ could be the large amount of solvent decomposition above 4.5 V.

Figure 6.25: In situ Raman spectra series of the first Et$_4$N$^+$ intercalation and de-intercalation into HSAG. Spectra are shifted arbitrarily up the y-axis. Intensity scales are identical for both axes. Arrows indicate direction of scan.
Figure 6.26: *In situ* Raman spectra series of the first BF$_4^-$ intercalation and de-intercalation into HSAG. Spectra are arbitrarily shifted up the y-axis. Intensity scales are identical for both axes. Arrows indicate direction of scan. Measurement follows on from experiment shown in Figure 6.25.
Figure 6.27: (a) Function of D-band position with potential for HSAG (b) Intensity ratio of the G-band doublets, $I_1/I_0$ over the potential range 0.5 to 5 V vs. Li/Li$^+$. The stage number axis derived from the G-band doublet ratio is also plotted (right axis). The ratio calculation subtracted, where necessary, contributions from the D'-band.
6.5 KOH activated mesophase pitch based coal (AMPC)

Mesophase pitch based carbons (MPC) have recently been suggested as high energy density EDLC electrode materials [249]. An activated MPC (AMPC) that was obtained by pyrolysis (800 °C, 2 hours, argon atmosphere) and subsequent activation in a KOH melt (800 °C, 2 hours, Ar, KOH/carbon mass ratio = 4) of a coal-tar-based mesophase pitch, was investigated.

MPC is a graphitisable carbon consisting of relatively well-ordered graphite-like crystallites (with $d_{002} = 0.37$ nm [249, 267]). The cross-linkages between these crystallites are attacked by KOH activation [249], thereby setting up the latent ability of insertion of ions into the material [249]. AMPC is only weakly porous with a Brunauer-Emmett-Teller (BET) surface area of 50 m$^2$ g$^{-1}$ (Table 6.2). This material develops its huge capacity only during first electrochemical charging upon which ions are inserted into the structure. After this electrochemical activation, which is accompanied by a huge swelling of the material [268], a steady state capacitance of ca. 130 F g$^{-1}$ is attained Figure 6.28 shows the SEM images of the material before electrochemical activation. The individual particles are needle shaped with a fine texture on each needle of stacked bundles of jagged graphene sheets, which probably results from the KOH treatment.
Figure 6.28: SEM picture of KOH activated mesophase pitch based coal (AMPC) of (a) overview of needle particles, (b) detailed view of needles particles, (c) enlarged view of one needle particle, before electrochemical activation. The white edges are the SEI layer formed from the KOH/heat treatment.
Figure 6.29 displays the cyclic voltammogram (CV) of the first cycle of AMPC in 1 mol dm$^{-3}$ tetraethylammonium-tetrafluoroborate (TEABF$_4$) in acetonitrile over the negative (3 - 0.5 V vs. Li/Li$^+$) and the positive potential sweep (3 - 5 V). Electrochemical activation of the material takes place at ca. 2 V vs. Li/Li$^+$, where corresponding peak is observed in the CV, indicating initial ion insertion. Again after electrochemical activation, as was previously observed for activated carbon (Picactif), small reversible peaks can be seen from the CV. This may again indicate the occurrence of ion intercalation in the graphitic-type regions in this material.

![Graphical representation of cyclic voltammogram](image)

**Figure 6.29:** AMPC half cell CV (1$^{st}$ cycle) for the negative (3 - 0.5 V vs. Li/Li$^+$) and the positive potential sweep (3 - 5 V) measured from the Raman cell. Open circuit potential was ca. 3 V. Cycled in 1 mol dm$^{-3}$ tetraethylammonium-tetrafluoroborate (TEABF$_4$) in acetonitrile. Scan rate: 0.5 mV s$^{-1}$.

Figures 6.30 and 6.31 demonstrate the Raman spectral series during the first and second negative potential sweep; the spectra taken during the first positive sweep are shown in Figure 6.32. Both spectral series show broad G- and D-bands (FWHM were found to respectively be 90 and 237 cm$^{-1}$). As with activated carbon (Picactif), during the potential sweeps no G-band
doublet formation is observed, instead similar G- and D-band shifts are observed, which correspondingly relate to charge transfer during double-layer charging and ion insertion. The only difference compared to Picactif, is that throughout the negative potential sweep, the D-band does not shift on the forward scan (Figure 6.33B); the shift only resembles activated carbon on the reverse scan where the D-band shifts from 1350 to 1335 cm$^{-1}$. This difference is thought to arise from the electrochemical activation of this material, seen as the current peak at 2.0 V (Figure 6.29). On the second scan (Figure 6.33B) the D-band shift resembles the shift observed for Picactif (Figure 6.21). Again this shift is tentatively assigned as evidence of intercalation of ions within the graphitic regions. The $I_G/I_D$ trend for this material is not very clear (Figure 6.33A), and it does not vary much with cycling, thus demonstrating the stability of this material. However for both negative cycles the $I_G/I_D$ ratio increases below a potential 2 V. This could be related to the electrochemical activation, where the pores within the material are opened up which results in a more ordered arrangement.
Figure 6.30: In situ Raman spectra series of the first Et$_3$N$^+$ intercalation and de-intercalation into AMPC. Spectra are shifted arbitrarily up the y-axis. Intensity scales are identical for both axes. Arrows indicate direction of scan.
Figure 6.31: *In situ* Raman spectra series of the second Et₄N⁺ intercalation and de-intercalation into AMPC. Spectra are shifted arbitrarily up the y-axis. Intensity scales are dissimilar for both axes. Arrows indicate direction of scan. Measurement follows on from experiment shown in Figure 6.31.
Figure 6.32: *In situ* Raman spectra series of the first BF$_4^-$ intercalation and de-intercalation into AMPC. Spectra are arbitrarily shifted up the y-axis. Intensity scales are identical for both axes. Arrows indicate direction of scan. Measurement follows on from experiment shown in Figure 6.32.
Figure 6.33: (a) $I_G/I_D$ ratio for AMPC (b) Function of G and D-band position with potential for AMPC. Peak positions calculated with a two-peak Lorentzian fit. In grey the 2nd insertion/extraction is shown. The second cycle G-band shift is identical to the first cycle shift and is omitted for clarity.
6.6 Summary

Tables 6.3, 6.4, 6.5, and 6.6 display the summary information for the results discussed previously. Table 6.3 shows that the onset potential for cation intercalation in all electrolytes is around 1.0 V. However for TFSI⁻ insertion the onset potential is much higher than BF₄⁻, respectively giving values of 4.7 and 4.3 V. Table 6.4 lists all the \( I_\text{c} / I_\text{D} \) ratios, for the graphitic materials the ratio decreases, indicating more disorder in the graphite whilst the activated carbons the ratio stays constant. The D- and G-band positions (cm⁻¹) and full width at half maximum (FWHM, cm⁻¹) are listed in Tables 6.5 and 6.6. No great variations of peak positions are observed between before and after cycling. The FWHM is seen to decrease dramatically for AMPC, where as for other materials it remains the same.

Table 6.3: Summary of behaviour of the in situ Raman experiments of carbonaceous materials investigated, the onset potential (V) and stage number are derived from the Raman data and the specific charge capacity (Ah kg⁻¹) and discharge efficiency (%) are from the first CV unless indicated.

<table>
<thead>
<tr>
<th>Carbon sample</th>
<th>Electrolyte</th>
<th>Cation insertion</th>
<th>Anion insertion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Onset potential/ V vs. Li/Li⁺</td>
<td>Stage number</td>
</tr>
<tr>
<td>KS44</td>
<td>TEABF₄⁻ AN</td>
<td>1.0</td>
<td>2</td>
</tr>
<tr>
<td>KS44</td>
<td>TEABF₄⁻ PC</td>
<td>1.1</td>
<td>2</td>
</tr>
<tr>
<td>KS44</td>
<td>EMI⁻ TFSI</td>
<td>1.0</td>
<td>2.2</td>
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<tr>
<td>Picactif</td>
<td>TEABF₄⁻ AN</td>
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<td>-</td>
</tr>
<tr>
<td>HSAG400</td>
<td>TEABF₄⁻ AN</td>
<td>1.0</td>
<td>2</td>
</tr>
<tr>
<td>AMPC</td>
<td>TEABF₄⁻ AN</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

ᵃResults from cycle 1 (electrochemical activation)
ᵇResults from cycle 2
### Table 6.4: Summary of $I_d/I_D$.

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<th>Carbon sample</th>
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<th>Anion insertion: $I_d/I_D \pm 0.01$</th>
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<tr>
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<td></td>
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<td>End</td>
</tr>
<tr>
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<td>TEABF$_4$ AN</td>
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<td>0.56</td>
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<tr>
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<td>2.26</td>
<td>0.29</td>
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<tr>
<td>KS44</td>
<td>EMI TFSI</td>
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<td>2.68</td>
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<tr>
<td></td>
<td>TEABF$_4$ AN</td>
<td>1st</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>2nd</td>
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### Table 6.5: Summary of D- and G- band peak positions cm$^{-1}$.

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<th>Carbon sample</th>
<th>Electrolyte</th>
<th>Cation insertion: Peak position / cm$^{-1} \pm 1$</th>
<th>Anion insertion: Peak position / cm$^{-1} \pm 1$</th>
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<td>End</td>
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<tr>
<td></td>
<td></td>
<td>D</td>
<td>G</td>
</tr>
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<td>TEABF$_4$ AN</td>
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<td>1576</td>
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<td>AMPC</td>
<td>TEABF$_4$ AN</td>
<td>1st</td>
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<tr>
<td></td>
<td></td>
<td>2nd</td>
<td>1336</td>
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</table>

### Table 6.6: Summary of D- and G- band FWHM cm$^{-1}$.

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<th>Electrolyte</th>
<th>Cation insertion: FWHM/ cm$^{-1} \pm 1$</th>
<th>Anion insertion: FWHM/ cm$^{-1} \pm 1$</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td>Start</td>
<td>End</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>G</td>
</tr>
<tr>
<td>KS44</td>
<td>TEABF$_4$ AN</td>
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<tr>
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<td>TEABF$_4$ PC</td>
<td>51</td>
<td>18</td>
</tr>
<tr>
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<td>EMI TFSI</td>
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<td>15</td>
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<td>118</td>
<td>53</td>
</tr>
<tr>
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<td>TEABF$_4$ AN</td>
<td>65</td>
<td>29</td>
</tr>
<tr>
<td>AMPC</td>
<td>TEABF$_4$ AN</td>
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<td>237</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2nd</td>
<td>196</td>
</tr>
</tbody>
</table>
6.7 Conclusions

*In situ* Raman measurements of graphitic materials (KS44 and HSAG) evidenced intercalation through the formation of the Raman G-band doublet of both large cations (Et₄N⁺, EMI⁺) and anions (BF₄⁻, TFSI⁻) in super-capacitor type electrolytes. Possible co-intercalation of PC was observed, when it was used as the solvent. Intercalation in AN, PC and ionic liquid containing electrolytes were all detrimental to the graphite structure with an increased D-band observed in all cases after anodic and cathodic cycles.

Possible intercalation of ions in activated carbons was indicated by a blue-shifting D-band. The G-band shift in these materials can be attributed to both charge transfer effects from either formation of the double layer or by intercalation.

Therefore regarding the questions posed in the introduction, it can be concluded:

- **What is the nature of the reversible Faradaic processes in larger potential windows?**
  
  For graphitic materials: intercalation. For activated carbons evidence from *in situ* Raman studies points towards intercalation.

- **Do these processes contribute to degradation of the electrodes?**
  
  For graphitic materials intercalation is seen to degrade the electrodes significantly. For activated carbons the $I_D/I_G$ ratio remains more or less constant, suggesting that these materials are more resistant to degradation caused by possible intercalation.
GENERAL CONCLUSIONS AND OUTLOOK

You see I went on with this research just the way it led me. That is the only way I ever heard of research going. I asked a question, devised some method of getting an answer, and got—a fresh question. Was this possible, or that possible? You cannot imagine what this means to an investigator, what an intellectual passion grows upon him. You cannot imagine the strange colourless delight of these intellectual desires.

H.G. Wells, The Island of Dr. Moreau

The aim of this doctoral work was to broaden the knowledge of the behaviour of insertion electrodes used in lithium-ion batteries and intercalation degradation processes in electrochemical double-layer capacitors (EDLCs) by characterisation with ex situ, and primarily in situ Raman microscopy. In the following, a summary of the outcome will be given.

Ex situ Raman mapping of graphitic carbon electrodes showed that the measurement angle of incidence had a minimal effect on average $L_a$ values calculated from maps of 225 spectra. Large number point mapping of graphite electrode surfaces (2500 – 10000 spectra) showed a correlation between $L_a$ values obtained and electrode morphological features such as crystal edges and defects on individual crystal surfaces. The association of $L_a$ values with the electrode appearance is enhanced, when a confocal resolution approaching (1 μm)$^3$, is used.
For positive electrodes, the ability to map the surface distribution of carbon and oxide particles (specifically either LiCoO₂ or LiMn₂O₄) within a composite electrode was demonstrated.

_In situ_ Raman microscopy carried out over a single point on standard microcrystalline graphite (SFG44) electrode for the first lithiation showed similar spectral features and trends previously published in the literature. Consequently, confirming the acceptable electrochemical performance of the _in situ_ Raman cell and employed experimental method. The D- and D'-bands weaken and disappears between 3 - 0.6 V, and it is believed that this is due to surface intercalation during the formation of the solid electrolyte interphase (SEI). The G-band shifts from 1585 cm⁻¹ to 1595 cm⁻¹ (0.6 - 0.2 V), due to the formation of a dilute stage 1 graphite intercalation compound (GIC). The G-band splits into $E_{2g}(i)$ (1578 cm⁻¹) and $E_{2g}(b)$ (1601 cm⁻¹) bands (0.16 - 0.09 V) showing the formation of stage 4 and 3 GICs. The band at 1850 cm⁻¹, assigned as a carbon-carbon triple bonded species, was observed to appear below 0.12 V, during the first electrochemical lithiation. However another band, which to the best of all knowledge has not been reported, was seen at 1370 cm⁻¹. The origin of this band, at the present time, remains uncertain. For the first time the Raman spectra of the first de-intercalation of lithium from graphite has been shown. Most importantly, a red-shift of a broad band (tentatively assigned as stage 1L phase) at 1540 to 1601 cm⁻¹ to form the $E_{2g}(b)$ of stage 2 GIC (0.16 - 0.17 V), was noted. The reverse spectral trend was seen during the lithium extraction suggesting the reversibility of lithium intercalation/de-intercalation.

It was found that for some graphitic materials, not all points on the electrode behave identically, through visual observation of differently coloured graphite particles. This indicated the co-existence of various staged compounds. Verification by _in situ_ Raman microscopy of four points on a disordered graphite demonstrated that at 0.17 V both stage 4 GIC and dilute stage 1 GICs were present. These local phenomena could be responsible for the uneven performance of the graphitic electrode, which would lead to irreversible capacity loss. However, this heterogeneity was not observed for all graphitic materials, such as SFG44. The necessity of multipoint measurement for all _in situ_ Raman experiments is hence established to achieve more reliable spectra and understanding of the behaviour of the whole electrode.
Investigation of the disappearance of the D-band (1300 cm$^{-1}$) showed that in more disordered graphitic material the D-band remains clearly visible above 0.14 V. Whereas, in more ordered graphitic carbons, the D-band vanishes below the signal-noise below ca. 0.3 V.

Local influence of the $L_a$ value upon the degree of intercalation at a holding potential of 0.17 V is inconclusive. Since the current experimental set-up does not allow for reliable results, because of the long accumulation times required to obtain a single spectrum with an acceptable signal to noise ratio.

On the other hand, the effect of both graphite crystal particle size and rhombohedral fraction can be discounted of having any measurable effect on the Raman spectra, and therefore they do not affect the mechanism of intercalation of lithium into graphite.

The on-set of exfoliation of graphite can be monitored by the appearance of the exfoliation-band or E-band at 1597 cm$^{-1}$ which can be related to the presence of Li(solvent)$_x$ moieties ($x > 0$). The electrochemical cycling of microcrystalline graphite SFG44 in LiClO$_4$, 1:1 ethylene carbonate (EC): propylene carbonate (PC) electrolyte demonstrated the appearance of this band in the Raman spectra. SFG44 exfoliation in EC:PC was substantiated with scanning electron microscopy (SEM). Multipoint mapping of the electrode surface demonstrated the variation in intensity of this band with respect to the unchanged G-band at 1584 cm$^{-1}$. Moreover some points measured did not show the E-band and only contained the G-band at potentials below 0.8 V. The variation of the appearance of the E-band in the Raman spectra was supported by SEM images, which suggest that not all graphite particles exfoliate. Potential stabilisation studies show that the E-band shifts from 1597 to 1607 cm$^{-1}$ when the potential is held at 0.8 then 0.3 V vs. Li/Li$^+$. This is thought to be due to a greater amount of lithium solvent co-intercalation at the surface region of the graphite crystal. SEM images show different stages of exfoliation at these potentials. At 0.8 V exfoliation takes place preferentially on larger particles. However, by 0.6 V full exfoliation on all graphite particles is observable.
The phase change between stage 2L phase and stage 3 and 2 GIC phases was investigated by reversing the temperature between 23 and 0 °C. The Raman spectrum displayed at some points of the graphite electrode, the loss and reappearance of the stage 2L phase at 0.12 V. These results concur with the established phase diagram of Li₄C₆. Mapping the graphite surface at 25 points reveals markedly different spectra according to position, reaffirming the heterogeneous nature of lithium intercalation into this material. Indeed some of the spectra displayed previously unreported bands at 1263 cm⁻¹ and 1429 cm⁻¹, whose assignment is currently unknown.

The first lithiation Raman spectra of nano-silicon vs. Li in situ cell showed the decrease in intensity of the TO silicon band at 520 cm⁻¹, when the potential is reduced from 3 V to 0.005 V. This can be related to either a loss of diamond-like symmetry during lithium insertion or a decrease in the optical skin depth as the conductivity of silicon-lithium alloy increases. The graphitic carbon also employed in the electrode displayed showed that normal lithium intercalation was occurring. The spectra measured during the first de-lithiation shows no reappearance of the silicon band at 520 cm⁻¹. Given that the silicon band vanished quickly, at a low specific charge capacity, it is unlikely that sufficient lithium could be removed to totally restore the silicon structure. Reversible intercalation into graphite is verified by the reappearance of the G-band. Detection of non-contacted particles was also confirmed by Raman spectroscopy.

In situ Raman spectra of the lithiation and de-lithiation into and out of various nano-sized anatase titanium dioxide (TiO₂) showed the biphasic transition from tetragonal TiO₂ to orthorhombic titanate LiₓTiO₂. The phase transition seen by Raman spectra takes place at different lithium contents depending on the crystallite size. Which is seen as x = 0.03 for the TiO₂ sample Prolabo (ca. 80 nm), 0.1 for AK1 (ca. 15 nm) and 0.14 for MTi5 (ca. 8 nm). This is consistent with the extension of the solid solution domain, when particle size is reduced. Additionally, the heterogeneous lithium insertion nature of the larger-sized Prolabo (ca. 80 nm) and the homogenous behaviour of the smaller AK1 (ca. 15 nm) and MTi5 (ca. 8 nm) under electrochemical operation were shown. This can explain the better cyclability observed for smaller nano-scale TiO₂ based electrodes (AK1 and MTi5). The measured steady decrease in band intensity for AK1 and MTi5, when x > 0.3, could be related to an increase in conductivity of the lithiated TiO₂ anatase, which causes a lowering of the optical skin depth.
In situ Raman investigations of lithium cobalt oxide (LiCoO₂) and lithium manganese oxide (LiMn₂O₄) were in line with the work of known literature. The structural changes associated with partial de-lithiation of LiCoO₂ and total de-lithiation of LiMn₂O₄ was monitored spectroscopically.

In situ Raman measurements of commercially available graphitic materials (KS44 and HSAG, TIMCAL AG) demonstrated intercalation, through the formation of the Raman G-band doublet of both large cations (Et₄N⁺, EMI⁺) and anions (BF₄⁻, TFSI⁻) in super-capacitor type electrolytes. Possible co-intercalation of PC was observed, when it was used as the solvent. Intercalation in AN, PC and ionic liquid containing electrolytes were all damaging to the graphite structure, with an increased D-band seen for all carbonaceous materials, after anodic and cathodic cycles.

Possible intercalation of large ions from the electrolyte into activated carbons was indicated by a blue-shifting D-band. The G-band shift in activated carbons can be credited to both charge transfer effects from either formation of the double layer or by intercalation.

Outlook

This thesis focussed heavily on the study with in situ Raman microscopy of negative electrode materials of the lithium-ion battery; most especially the graphitic electrode. The main opportunity for further work can thus be suggested to take place using positive electrode materials. However, for successful in situ Raman measurements, care must be taken to ensure a high internal mechanical pressure upon the electrode. Some positive electrode materials have a lower conductivity than graphite, therefore high-quality electrode production and good Raman cell construction remain key factors to reduce the cells internal resistance and thus keep the overpotential to a minimum. Though as with graphite, slow C-rates and low currents can reduce this problem.
In the near future it is likely that mixed metal alloys will replace the present graphitic negative electrode for commercial lithium-ion batteries. Therefore relevant use of Raman microscopy is limited, as demonstrated in this thesis with nano silicon, to the monitoring of the carbon used in the composite electrode. In general, highly conductive metallic materials do not possess a Raman spectrum.

However from studies carried out in this dissertation with graphite, some further avenues of investigation remain.

For Raman spectra of graphite during lithium intercalation:

- The determination of the origin of 1380 cm\(^{-1}\) band below 0.12 V
- Confirmation and identification of the 1263 cm\(^{-1}\) and 1429 cm\(^{-1}\) bands at 0.12 V
- Determine relationship between \(I_C/I_D\) (3.0 V) and \(E_{2g2(i)}/E_{2g2(h)}\) (0.17 V)
- The measurement of stronger spectral evidence of a phase change of stage 2L to stage 3 or 2 GIC below 10 °C

For the monitoring of the exfoliation or E-band:

- It is known that graphite SLX50-HT exfoliates even in EC at ca. 0.55 V. This would be an interesting system to monitor the possible occurrence of the E-band. Because EC co-intercalation has not yet been confirmed spectroscopically
- For graphite SFG44 in PC, it could be possible to observe the reversible appearance/disappearance of E-band by using cyclic voltammetry down to reduce the potential to 0.85 V and back to 1.5 V
- High number point mapping of SFG44 in PC at open circuit potential (OCP) and at 0.8 V determine a possible relationship between \(I_C/I_D\) and \(I_C/I_E\). This could be a crucial experiment to show the effect of local surface disorder on electrochemical behaviour
As stated earlier, for the monitoring with *in situ* Raman microscopy of the effect of lithium intercalation into positive electrode materials, possible research could be focused on the following:

- To understand possible lifetime and degradation phenomenon, observation of either BF$_4^-$, ClO$_4^-$, or PF$_6^-$ intercalation into carbon additives at potentials above 4.2 V in positive electrode materials, could be undertaken by the detection of the G-band doublet.
- *Ex situ* mapping of fresh, multi-cycled, aged, failed positive electrodes could determine the surface distribution of active material and carbon in the composite electrode.
- The lithium-air battery may provide a system which has higher energy and power densities than current lithium-ion batteries. Monitoring Li-O band loss in Li$_2$O$_2$ would evidence the reaction: Li$_2$O$_2$ → 2Li + O$_2$.
- If successful, this measurement could also be implemented in the sodium- or potassium-air battery by following the loss Na-O or K-O bonds in Na$_2$O$_2$ or K$_2$O$_2$.
- Monitoring of lithium extraction/intercalation into/from mixed layered oxides, for example LiCo$_{0.33}$Ni$_{0.33}$Mn$_{0.33}$O$_2$ or LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$.

Lithium iron phosphate (LiFePO$_4$) is a candidate material to replace the current positive electrode LiCoO$_2$ in commercial lithium-ion batteries. This material has been studied with both *in situ* Raman and infrared (IR). Because of this material's poor conductivity, it has to be carbon-coated to achieve good electrochemical behaviour. This therefore makes the study of LiFePO$_4$ with Raman spectroscopy problematic, as the carbon signal will only be detectable. It is therefore recommended to develop *in situ* IR as a complementary analytical method.

Further Raman studies on alternative negative electrodes can be suggested:

- For nano silicon/graphite composite electrodes it possible work could include the *ex situ* mapping of fresh and cycled electrodes. This would be to identical number and distribution of non-contacted particles. It would be advised to cycle the electrodes in standard measurement cells before transferring them to the *in situ* cell in order to measure without contact to air and moisture.
• Further work remains for titanium dioxide anatase (TiO$_2$). The assignment of the bands for Li$_x$TiO$_2$ orthorhombic Raman spectrum and understanding of the structural evolution is not yet complete
• As with TiO$_2$, it maybe possible to monitor the effect of particle size on lithium intercalation into $\alpha$-Fe$_2$O$_3$

As shown in this work, *in situ* Raman microscopy can also be an important method in other electrochemical systems, such as electrochemical double layer capacitors (EDLCs). Further work in this direction would include:

• A comparison of graphite in a PC containing electrolyte just after a positive potential sweep with both *in situ* Raman and scanning electron microscopy (SEM)
• It would also be prudent to repeat all measurements in chapter 6, with just running a positive potential sweep
• Investigation of ion insertion into various carbon systems such as carbon nanotubes (SWNT, DWNT, MWNT), carbon nanobeads, carbon fibres
• Ion insertion in aqueous systems (H$_2$SO$_4$ (aq)) into carbon materials (nanotubes), relating to actuators
• Galvanostatic investigation of the two reduction and oxidation peaks in microcrystalline graphite in 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl) imide (EMI-TFSI) to determine more precisely the stage compounds formed during both anodic and cathodic cycling
• Compare the intercalation of EMI$^+$ into graphite in a vinylene carbonate (VC) containing electrolyte. SEI formation from the decomposition of VC on the graphite surface should prevent solvent anions from entering graphite. Therefore no G-band doublet peak should be observed
• Degradation of carbon used in fuel cell systems could be examined
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Electrochemical lithium insertion into TiO$_2$ anatase materials: An *in situ* Raman microscopy investigation


Behaviour of highly crystalline graphites in lithium-ion cells with propylene carbonate containing electrolytes: An *in situ* Raman and SEM study

L. J. Hardwick, H. Buqa, M. Holzapfel, W. Scheifele, F. Krumeich, P. Novák,

Raman spectroscopic investigation of lithium coordination in the EMI-TFSI ionic liquid system


An *in situ* Raman study of the intercalation of supercapacitor-type electrolyte into microcrystalline graphite


Graphite surface disorder detection using *in situ* Raman microscopy

Nano silicon for lithium-ion batteries

Surface reactivity of graphite materials and their surface passivation during the first electrochemical lithium insertion

Advanced in situ characterization methods applied to carbonaceous materials

Behaviour of highly crystalline graphites in lithium-ion cells with propylene carbonate containing electrolytes

Raman spectroscopic and structural studies of heat-treated graphites for lithium-ion batteries
CONFERENCE CONTRIBUTIONS

TALKS

An \textit{in situ} Raman Microscopic Study of Electrochemical Lithium Insertion into TiO$_2$ Anatase
Laurence J. Hardwick, Michael Holzapfel, Alexander Wokaun, Petr Novák
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Graphite surface disorder detection using Raman microscopy
Laurence J. Hardwick, Hilmi Buqa, Petr Novák
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Detection of surface disorder on graphite electrodes using Raman microscopy
Laurence J. Hardwick, Petr Novák
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Raman study of lithium intercalation into graphite
Laurence J. Hardwick, Hilmi Buqa, Alexander Wokaun, Petr Novák
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CURRICULUM VITAE

Laurence James Hardwick

Personal

Date of Birth: 17\textsuperscript{th} February 1981
Place of Birth: Bury St Edmunds, United Kingdom
Nationality: British

Education

1985-1990  Westgate County Primary School, Bury St Edmunds, England
1990-1994  Horringer Court Middle School, Bury St Edmunds, England
1994-1999  King Edward VI Upper School, Bury St Edmunds, England
1999-2003  Master of Chemistry (MChem), University of Southampton, England
2003-2006  Ph.D thesis under the supervision of Prof. Dr. A Wokaun,
            Swiss Federal Institute of Technology, ETH-Zurich and Paul Scherrer Institut,
            Villigen, Switzerland