Surface Phenomena in Li-Ion Batteries

BY

ANNA ANDERSSON

ABSTRACT

The formation of surface films on electrodes in contact with non-aqueous electrolytes in lithium-ion batteries has a vital impact on battery performance. A basic understanding of such films is essential to the development of next-generation power sources. The surface chemistry, morphology and thermal stability of two typical anode and cathode materials, graphite and LiNi₀.₈Co₀.₂O₂, have here been evaluated by X-ray photoelectron spectroscopy (XPS), X-ray diffraction, scanning electron microscopy and differential scanning calorimetry, and placed in relation to the electrochemical performance of the electrodes.

Chemical and morphological information on electrochemically formed graphite surface films has been obtained accurately by combining XPS measurements with Ar⁺ ion etching. An improved picture of the spatial organisation, including thickness determination of the surface film and characterisation of individual component species, has been established by a novel sputtering calibration procedure. The stability of the surface films has been shown to depend strongly on temperature and choice of lithium salt. Decomposition products from elevated-temperature storage in different electrolyte systems were identified and coupled to effects such as capacity loss and increase in electrode resistance. Different decomposition mechanisms are proposed for surface films formed in electrolytes containing LiBF₄, LiPF₆, LiN(SO₂CF₃)₂ and LiCF₃SO₃ salts.

Surface film formation due to electrolyte decomposition has been confirmed on LiNi₀.₈Co₀.₂O₂ positive electrodes. An overall surface-layer increase with temperature has been identified and provides an explanation for the impedance increase the material experiences on elevated-temperature storage.

Surface phenomena are clearly major factors to consider in selecting materials for practical Li-ion batteries.

Key words: Li-ion batteries, graphite, surface films, non-aqueous electrolytes, thermal stability, salt dependence.

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PREFACE

This thesis comprises a summary based on the following papers, which are referred to in the text by their Roman numerals, I-V.

I. Electrochemically Lithiated Graphite Characterised by Photoelectron Spectroscopy,
   A.M. Andersson, A. Heningsson, H. Siegbahn, U. Jansson and K. Edström,

II. Chemical Composition and Morphology of the Elevated Temperature SEI on Graphite,
    A.M. Andersson and K. Edström,

III. A Furnace for in situ X-ray Diffraction Studies of Insertion Processes in Electrode Materials at Elevated Temperatures,
     T. Ericsson, A.M. Andersson, Ö. Bergström, K. Edström, T. Gustafsson and J.O. Thomas,

IV. The Influence of Lithium Salt on the Interfacial Reactions Controlling the Thermal Stability of Graphite Anodes,
    A.M. Andersson, M. Herstedt, A. Bishop and K. Edström,

V. Surface Characterization of Electrodes from High-Power Lithium-Ion Batteries,
   A.M. Andersson, D.P. Abraham, R. Haasch, S. MacLaren, J. Liu, K. Edström and K. Amine,
   in manuscript.
Papers not included in this thesis:


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1 INTRODUCTION

It has become increasingly important in today’s society to have ready access to energy in different forms. Rechargeable batteries are therefore becoming immensely important, by virtue of their ability to store electricity and make energy mobile [1].

New markets are being created for these batteries, notably for the purpose of powering portable electronics, especially the 3C’s: Camcorders, Cellular phones and portable Computers. Alternative power sources for transportation is another topic of high current interest. Combustion engines are emitting green-house gases, which will have a serious influence on the future climate. The State of California (USA) has, in a radical effort to reduce exhausts gases, demanded a shift from combustion-engine vehicles to zero-emission-vehicles (ZEV’s) [2]. This has spurred the development of electric vehicles (EV’s) driven by rechargeable batteries. Thusfar, battery technology has been inadequate for the commercialisation of EV’s. However, it has proven sufficient for use in hybrid electric vehicles (HEV’s), which use batteries in conjunction with a small, fuel-efficient engine.

The lithium ion (Li-ion) battery fulfils many of the demands made within the areas of portable electronics and EV/HEV’s, and is superior in many ways to the more common nickel-cadmium (Ni-Cd) and nickel-metal hydride (Ni-MH) batteries [1, 3]. Its superiority lies in the use of lithium with its large negative electrode potential (-3.04 V vs. SHE\(^1\)) and high energy density, and in the development of intercalation\(^2\) electrodes that can repeatedly accept and release \(\text{Li}^+\) ions on charge and discharge [4]. On reduction of such an electrode material, \(\text{Li}^+\) ions are inserted from the electrolyte into available sites in the host-structure framework, and electrons fill the conduction band in the electronic structure of the host.

The first reports came in the early 70’s of the potential use of intercalation compounds as cathode material in secondary (rechargeable) batteries. These cells contained a lithium-metal anode and a transition-metal oxide (TMO) or chalcogenide cathode, e.g. \(\text{TiS}_2\), \(\text{TiO}_2\), \(\text{MnO}_2\), \(\text{V}_2\text{O}_5\) and \(\text{V}_6\text{O}_{13}\). In 1989, Moli Energy Ltd. (British Columbia, Canada) went into large-scale production of such a system containing a \(\text{MoS}_2\) host material. However, some serious accidents caused these cells to be quickly withdrawn from the market [5]. The difficulties encountered were all associated with the use of highly reactive lithium metal as anode material. A dramatic increase of the lithium surface area with lithium dendrite formation during cycling was the origin of short-circuiting and thermal runaway [6].

---

1 Standard Hydrogen Electrode

2 Intercalation derives from the term used to describe the process of inserting an extra day (the 29th of February) into the calendar to maintain the synchrony between the calendar year and the solar year. In Chemistry, intercalation is thus strictly the term used to describe the insertion of a guest atom or ion into a planar crystalline host without losing the structural integrity of the host.
The solution to the dendrite problem came when lithium-metal was replaced by a second intercalation compound that could host Li$^+$ ions at a low potential vs. the Li/Li$^+$ redox couple [7]. This so-called Li-ion battery thus consists of two intercalation electrodes that can both host lithium ions as they are transferred on charge and discharge (see Fig. 1). Since no metallic lithium is present, the safety of the cells is immensely improved. The Li$^+$ ions are usually supplied by some lithium-containing TMO cathode\(^3\) material (LiMO\(_x\)), such as LiCoO\(_2\), LiNiO\(_2\) or LiMn\(_2\)O\(_4\). Carbonaceous materials have been shown to make the most appropriate anodes. In 1991, Sony made the first commercial Li-ion battery [8] and, today, more than ten companies are producing these batteries—almost all in Japan [9].

However, these batteries still have serious drawbacks. Effects of prolonged cycling (repeated charge and discharge) or prolonged storage push them away from their theoretical and initially excellent performance [10-12]. These effects are typically capacity loss, poor cyclability, power-fade and self-discharge.

Many of the problems can be related to surface phenomena occurring on the anodes and cathodes. The main goal of this thesis is therefore to shed light on some of the unwanted processes that can have a detrimental effect on battery performance in one way or another. Two typical anode and cathode materials, graphite and LiNi\(_{0.8}\)Co\(_{0.2}\)O\(_2\), have been studied in this context. Their surface chemistry has been evaluated and placed in relation to their electrochemical performance. It is essential to address these issues to better understand the gradual deterioration of the active materials, and hence find solutions to the problems that remain.

\(^3\)“Cathode” is used throughout this thesis in referring to the electrode which is positive on discharge in a Li-ion battery; likewise, the term “anode” for the negative electrode.
2 BATTERY MATERIALS

2.1 CARBON-BASED ANODE MATERIALS

2.1.1 Basic structure of carbon materials

Ever since the pioneering work of Herold in the mid 50’s, graphitic carbon materials have been known to intercalate lithium [13]. More recently came the discovery that the insertion could be made electrochemically at a very low potential \( \text{vs. Li/Li}^+ \) [14], and that carbon therefore could be used for battery application as a replacements for the hazardous lithium metal [8, 15]. Carbon exhibits both electronic and ionic conductivity and can incorporate a large number of lithium ions. Their low cost, availability, low intercalation potential and good cycling properties has made them, so far, the most attractive anode choice for practical Li-ion cells.

Carbons show an almost infinitely large amount of structural modifications, ranging from highly crystalline graphites to highly disordered amorphous carbons. They all exhibit different electrochemical properties. The extent of lithium intercalation and the reversibility of the intercalation process both depend on the structure, morphology, texture, grain-size, grain-shape and crystallinity of the carbonaceous host material [6, 16, 17].

The basic structure of graphitic carbon materials comprises extended sheets of sp\(^2\)-hybridized carbon atoms arranged in hexagonal rings extended in two dimensions, sometimes referred to as graphene sheets. These sheets are usually stacked in an ABAB… pattern (hexagonal graphite), but can also be arranged in a more unusual ABCABC… stacking (rhombohedral graphite). The ideal structure of graphite is never obtained in practise, due to the ever-present high density of stacking faults and structural defects. The graphites are therefore usually characterized by the size/extension of isolated, perfectly stacked regions, so-called crystallites. The extension of the crystallites in the crystallographic a and c directions can vary from nanometers to several micrometers. The crystallites are separated by more disordered carbon regions, which dominate structures referred to as non-graphitic carbons. These also comprise segments of hexagonal sheets, but no planar ordering occurs in the c-direction, \( i.e. \), the planes are not stacked.

2.1.2 Lithium intercalation

Lithium can be intercalated electrochemically into highly crystalline graphite on charging a lithium-ion battery, as described by the electrode reaction:

\[
\text{C}_n + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C}_n
\]
The electrode potential is very close to that of the Li/Li⁺ redox couple (~0.2-0.05 V). Under ambient conditions, a maximum of one lithium per six carbons (LiC₆) is expected to be intercalated in the Van der Waals gaps above and below a carbon hexagon. This corresponds to a specific theoretical capacity of 372 mAh/g. On intercalation, the graphite structure shifts to an AA… stacking type. The structure of the fully lithiated graphite is shown in Fig. 2a. During the formation of this compound, graphite passes through a number of characteristic staged phases, as the amount of lithium increases [13, 18, 19]. In this staging process, lithium fills one interplanar gap before filling neighbouring gaps. This is a thermodynamic consequence of the smaller coulombic energy associated with lithium-ions interacting than the energy required to open the gap between two adjacent layers to accommodate the lithium. The different staged phases are usually referred to as stage I, stage II, stage III and stage IV etc., where the figures indicate the number of graphite sheets that separate two nearest-neighbour lithium layers. The Li-graphite intercalation phases are formed sequentially through first-order phase transitions. For two LiₓC₆ phases to coexist at equilibrium within an electrode, the chemical potential of lithium, μₗi, in each stage must be equal [20]. The electrode potential will therefore be constant throughout a phase transition from one stage to another, according to the relation E = -μₗi/F (F, Faraday’s constant). As a consequence, the potential profile of lithium intercalation into graphite shows a number of steps, where horizontal regions (E constant) correspond to two-phase coexistence and vertical regions to single phases. The staging process and the corresponding potential response are schematically pictured in Fig. 2b.

Figure 2 Lithium-graphite intercalation compounds: a) structure of LiC₆ and b) schematic potential profile of stage (S) formation during electrochemical lithium intercalation in graphite. (Adapted from [4]).
In reality, the intercalation mechanism is complicated and goes through a number of intermediate phases. For example, a stage II L, which is a less dense, “liquid-like”, stage II phase [19]. There are still some ambiguities regarding the complete staging process, especially for stages greater than IV, and work continues to achieve a more complete description of the intercalation mechanism. However, for most purposes, the more simplistic “staging” representation is adequate (Fig. 2b).

Most studies of carbon electrodes in this thesis were conducted on synthetic KS6 graphite from Timcal Corp. (Switzerland) (Papers I, II, III and IV). This graphite has a high degree of crystallinity, with an $L_c$ value (planar stacking in the c-direction) of $>100$ nm. The relatively high capacity and the good reversibility of the intercalation process make this material a good candidate for practical Li-ion batteries.

2.2 TRANSITION-METAL OXIDE CATHODE MATERIALS

LiCoO$_2$ is the most commonly used cathode material in commercial Li-ion batteries today by virtue of its high working voltage, structural stability and long cycle life [4]. However, Co is an expensive metal and much effort has been made in recent years been to find a cheaper alternative. LiNiO$_2$ (isostructural with LiCoO$_2$) and spinel type LiMn$_2$O$_4$ are promising materials in this respect, with LiNiO$_2$ the more attractive alternative because of its high specific capacity and better elevated-temperature performance. However, LiNiO$_2$ has not been commercialised successfully for several reasons: i) difficult synthesis conditions [21], ii) poor structural stability on cycling [22], and iii) poor thermal stability in the delithiated state as a result of the unstable Ni$^{4+}$ ion [23]. One way to circumvent these problems is to partially substitute nickel by other cations. Many recent studies focus on substituted compounds of this general type.

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>LiCoO$_2$</th>
<th>LiNiO$_2$</th>
<th>LiNi$<em>{0.8}$Co$</em>{0.2}$O$_2$</th>
<th>LiMn$_2$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Practical capacity</td>
<td>150 Ah/kg</td>
<td>170 Ah/kg</td>
<td>180 Ah/kg</td>
<td>120 Ah/kg</td>
</tr>
<tr>
<td>Cycling stability</td>
<td>good</td>
<td>good$^a$</td>
<td>good</td>
<td>poor</td>
</tr>
<tr>
<td>High-T stability</td>
<td>good</td>
<td>good$^a$</td>
<td>good</td>
<td>poor</td>
</tr>
<tr>
<td>Power capability</td>
<td>best</td>
<td>good</td>
<td>good</td>
<td>average</td>
</tr>
<tr>
<td>Safety</td>
<td>good</td>
<td>poor</td>
<td>unclear</td>
<td>best</td>
</tr>
<tr>
<td>Toxicity</td>
<td>poor</td>
<td>poor</td>
<td>poor</td>
<td>best</td>
</tr>
<tr>
<td>Material cost</td>
<td>high</td>
<td>acceptable</td>
<td>acceptable</td>
<td>best</td>
</tr>
</tbody>
</table>

$^a$ Under optimised conditions

Co substituted LiNiO$_2$, LiNi$_{1-x}$Co$_x$O$_2$ (V), has the advantage of combining the favourable properties of LiNiO$_2$ and LiCoO$_2$. LiNi$_{1-x}$Co$_x$O$_2$ is known to have much...
higher structural stability than pure nickel oxide and, combined with its potentially lower cost than LiCoO$_2$, is highly promising material for practical application [24, 25].

Specifically, the Advanced Technology Development (ATD) program in USA has chosen LiNi$_{0.8}$Co$_{0.2}$O$_2$ as cathode material in their first-generation Li-ion batteries for EV and HEV applications. This program was initiated by the PNGV (Partnership for a New Generation Vehicles) to supply the American car industry with new EV and HEV battery solutions. The LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode material has here been studied in collaboration with Argonne National Laboratory, Illinois, USA. Argonne’s battery research group fabricates and evaluates high-power lithium-ion batteries for the ATD program; they have supplied the sample materials for this work from their high-power cells. Some of the LiNi$_{0.8}$Co$_{0.2}$O$_2$ material properties are shown in Table 1. LiNiO$_2$, LiCoO$_2$ and LiMn$_2$O$_4$ are included for comparison.

![Crystal structure of layered Li(Ni,Co)O$_2$](image)

**Figure 3** *The crystal structure of layered Li(Ni,Co)O$_2$ viewed in two different ways.*

LiNiO$_2$, LiCoO$_2$ and their substituted versions adapt the $\alpha$-NaFeO$_2$-type structure (space group $\overline{R}3m$), which is a layered, rhombohedral structure in which the lithium ions can move quite freely in the two-dimensional planes perpendicular to the c-axis (Fig. 4). The $\text{O}^{2-}$ ions form a close-packed face-centred cubic (fcc) structure, and the Ni$^{3+}$ and Li$^+$ ions occupy the octahedral voids on alternating (111) planes. In this structure, ~0.7 Li can be extracted and inserted during the charge and discharge cycles, corresponding to a capacity of ~190 mAh/g. Further extraction leads to irreversible collapse of the structural framework [26, 27]. The electrochemical charging process is described by the electrode reaction:

\[
\text{Li(Ni,Co)O}_2 \rightarrow \text{Li}_{1-x}(\text{Ni,Co})\text{O}_2 + x \text{ Li}^+ + x \text{ e}^-
\]  

(2)
2.3 NON-AQUEOUS ELECTROLYTES
Because of the strong reducing power of Li, the working potential for Li-ion cells lies commonly around 4V, but can be as high as 5V in some cases. The main requirement for the electrolyte is therefore that it must have a wide electrochemical stability window. Aqueous electrolytes therefore cannot be used. Only a few aprotic, non-aqueous alternatives can be used successfully in practical cells. These include liquid, solid and polymeric electrolytes; liquid alternatives are those most commonly exploited so far because of their superior ionic conductivity at ambient temperature. See an extensive review in [28].

### Table 2 Structure and properties of some solvents used for lithium battery electrolytes [3, 28].

<table>
<thead>
<tr>
<th>Solvent name and abbrev.</th>
<th>Structural formula</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Dielectric constant, $\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene carbonate, EC</td>
<td>[O:O]</td>
<td>39-40</td>
<td>248</td>
<td>89.6 (40°C)</td>
</tr>
<tr>
<td>Propylene carbonate, PC</td>
<td>[O:CH$_3$:O]</td>
<td>-49</td>
<td>240</td>
<td>64.4</td>
</tr>
<tr>
<td>Dimethyl carbonate, DMC</td>
<td>[H$_2$C:O:O:CH$_3$]</td>
<td>4.6</td>
<td>91</td>
<td>3.12</td>
</tr>
<tr>
<td>Diethyl carbonate, DEC</td>
<td>[H$_6$C$_2$:O:O:C$_2$H$_5$]</td>
<td>-43</td>
<td>126</td>
<td>2.82</td>
</tr>
<tr>
<td>2-Methyl-tetrahydrofuran, 2Me-THF</td>
<td>[O:CH$_3$]</td>
<td>-137</td>
<td>79</td>
<td>6.29</td>
</tr>
<tr>
<td>Dimethoxyethane, DME</td>
<td>[H$_3$C:O:O:CH$_3$]</td>
<td>-58</td>
<td>85</td>
<td>7.20</td>
</tr>
<tr>
<td>$\gamma$-Butyrolactone, $\gamma$-BL</td>
<td>[O:O]</td>
<td>-43</td>
<td>204</td>
<td>39.1</td>
</tr>
</tbody>
</table>

2.3.1 Solvents
Liquid solvents that fulfil the dual requirements of a high lithium ion conductivity (>10$^{-3}$ S/cm), and a broad electrochemical stability window are mainly carbonates, ethers and esters of various kinds. Those most widely used are presented in Table 2. Of these, the carbonates are by far the most common choice under ambient conditions, because of
their superior cycling behaviour. Ethylene carbonate (EC) and propylene carbonate (PC) provide a sufficient high conductivity and broad stability window. PC causes severe exfoliation of graphitic carbon electrodes, due to extensive co-intercalation during charging [29-31]. EC is the preferred solvent in that context but is a solid at room temperature (RT). It is therefore common to mix these with other solvents with less conductivity to obtain a working electrolyte over a wider temperature interval.

Mixtures of EC with dimethyl carbonate (DMC) or diethyl carbonate (DEC) were used exclusively in this thesis.

2.3.2 Lithium salts
Soluble lithium salts are added to the solvents to act as charge carries of the current passed in the cell during the electrochemical process. Good solubility and charge separation of anion and cation are needed to obtain this high conductivity. This is normally achieved by choosing bulky anions with low negative charge density [28]. Examples of salts used are LiClO₄, LiAsF₆, LiPF₆, LiBF₄, LiCF₃SO₃ and LiN(SO₂CF₃)₂, were LiClO₄ and LiAsF₆ are not realistic for use in commercial cells because of the explosion risk of the ClO₄⁻ anion, and the high toxicity of the AsF₆⁻ anion and its degradation products. The other salts are currently used or considered for use in practical cells, and have been explored during the course of this work.

The salt most commonly used in studies of these systems and in commercial cells is lithium hexafluorophosphate, LiPF₆. It gives high ionic conductivities in carbonate-based solutions, and shows excellent cycling properties at room temperature. It is known, however, to show poor thermal stability [32-35] and bad cycling behaviour for some electrode materials at slightly elevated temperature [33, 36], and is highly sensitive to hydrolysis by trace water. LiBF₄ is very similar to LiPF₆, but is less hygroscopic [33, 37]. It is also interesting from a cost perspective, since it is about one third of the price of LiPF₆.

Li trifluoromethane sulfonate (LiCF₃SO₃, LiTf) and Li bis-(trifluoromethane sulfone) imide (LiN(SO₂CF₃)₂, LiTFSI) have been designed specifically for use in polymer electrolytes. The anions are very bulky with a partly delocalised charge, which reduces the formation of ion pairs drastically and hence increases the transference number (T) and conductivity of the lithium ion, especially in polymer electrolyte. They are, however, also highly interesting for use in liquid electrolytes, mainly because of their superior chemical and thermal stability compared to the LiPF₆ and LiBF₄ alternatives. The main disadvantage of these salts is that they corrode the Al current collector used on the cathode side of Li-ion cells at high potentials [32, 38].
3 SURFACE PHENOMENA IN Li-ION BATTERIES

3.1 CARBON ELECTRODES
Li-ion batteries are assembled in their discharged state, with all lithium present in the positive electrode. During the first charge, carbonate-based electrolytes (solvents and salts) are reduced at the negative electrode (i.e. the carbon electrode) at a potential between ca. 1.5-0.7 V vs. Li/Li⁺ (i.e. prior to any lithium intercalation), depending on the composition of the electrolyte [39]. As a result, a surface film is formed consisting of a variety of solvent and salt reduction products. This film functions as an ionic conductor that allows Li⁺ ions to be transported through the film during the subsequent intercalation and deintercalation processes. The film is also an electronic insulator, which will prevent the continuous reduction of electrolyte as the film thickness reaches a certain limit. This limit has been defined intuitively as the thickness at which electron tunnelling from the graphite surface to the electrolyte is prevented (a few nm) [40]. The film then functions as a passivating layer on the graphite surface. It is most often referred to as a Solid Electrolyte Interphase (SEI). Emanuel Peled was the first to introduce the concept of an SEI, which provided an explanation for why highly reductive lithium metal is stable in certain electrolyte systems, although the system should be thermodynamically unstable (also [40]). Surface films formed on lithium metal and carbon electrodes are very similar [41].

![Figure 4](image-url)

**Figure 4** The first charge/discharge cycle of a graphite electrode in a 1 M LiBF₄, EC/DMC electrolyte.

The potential profile of graphite vs. Li/Li⁺ during the first reduction and subsequent oxidation, i.e. one charge/discharge cycle, is shown in Fig. 4. The plateau near 0.7 V corresponds to the reduction of electrolyte, followed by the characteristic intercalation
plateaux around 0.1 V. The electrolyte reduction is an irreversible process, and no corresponding oxidation plateau is observed in the potential profile. The charge loss, or irreversible capacity, \( C_{irr} \), is usually between 10-30% depending on such aspects as carbon (surface) structure [42], surface area [7, 42]. The irreversible consumption of lithium, must be compensated by additional cathode material, thus reducing the energy density of the entire cell. One of the most important research missions in the Li-ion battery field is therefore to minimise the extent of this electrolyte reduction. However, the formation of a thin but stable film is necessary to maintain passivation of the negative electrode and thus prevent further electrolyte reduction. The film must also protect the graphite from solvent co-intercalation which, for some solvents (e.g. PC), causes detrimental exfoliation of the graphite.

The choice of electrolyte is naturally one of the most important factors governing SEI layer formation, since different electrolyte species will be reduced to form different surface-film products. The primary requirements of the reduction products in a functional SEI layer are Li\(^+\) ion conductivity and electronic insulation. This is one of the major reasons why alkyl carbonates are the preferred choice of solvent. Their reduction products are mainly inorganic or semi-organic lithium carbonates. This superiority, as suggested by Gan et al., may be due to orbital interaction and conjugated charges in the CO\(_3^−\) group, which will provide an efficient mechanism for Li\(^+\) ion conduction through the SEI [49]. The reduction of the most commonly used carbonate-based solvents has been studied extensively [41, 50]. A possible reduction mechanism for EC is shown in Fig. 5.

![Figure 5](image-url)  
*Figure 5 A possible reduction mechanism for EC (based on Ref. [50]).*

The one-electron reduction leads to the formation of a semi-organic lithium alkyl carbonate, \((\text{CH}_2\text{OCO}_2\text{Li})_2\) a so-called semicarbonate. Similar compounds are formed for other carbonate solvents; these are usually abbreviated to ROCO\(_2\)Li. Inorganic Li\(_2\)CO\(_3\) forms if further reduction occurs. Other reduction products, such as lithium alkoxides, have been proposed, but these are believed to be minor surface components [41]. The
proposed major reduction paths of the solvents used in this thesis are summarised in Reaction scheme 1.

Electrolyte salts are also reduced to some extent during charging, giving inorganic products such as LiF, Li₂SO₃, Li₃N etc. [28]. The reduction paths are not uniquely defined, however; the reactions are usually expressed in general formulae not taking into account charge or elemental balance. The reduction reactions for LiPF₆, LiBF₄, LiCF₃SO₃ and LiN(SO₂CF₃)₂ are usually presented as in Reaction scheme 2.

The SEI layer composition is also highly dependent on impurities in the cells. Especially, the amount of H₂O plays a crucial rôle, and its influence has been investigated by numerous researchers [44, 47]. For example, lithium alkyl carbonates are unstable in aqueous environments and transform to Li₂CO₃ and hydroxyls. Most lithium salts are also highly hygroscopic. This is especially crucial in the case of LiPF₆, which is readily decomposed in the presence of water and hydrolyses to form hydrofluoric acid, HF, another highly reactive impurity, that reacts readily with surface species such as carbonates [28, 45, 46]. HF impurities are known to form in small amounts in LiBF₄ electrolytes, although the salt is quite stable in water [33]. Important reactions involving H₂O and HF are shown in Reaction scheme 3. LiF is major reaction product from the reactions in scheme 2 and 3. LiF is, contrary to lithium carbonates, an unwanted SEI component, because of its low permeability for Li⁺ ions.

**Reaction scheme 1 Reduction reactions of alkyl carbonates [28, 43, 44].**

\[
\begin{align*}
EC & \quad 2(CH_2O)_2CO + 2e^- + 2 Li^+ \rightarrow (CH_2OCO_2Li)_2 \downarrow + C_2H_4 \uparrow \\
& \quad (CH_2O)_2CO + 2e^- + 2Li^+ \rightarrow Li_2CO_3 \downarrow + C_2H_4 \uparrow \\
\text{DMC} & \quad CH_3OCO_2CH_3 + e^- + Li^+ \rightarrow CH_3OCO_2Li \downarrow + CH_3\cdot \\
& \quad CH_3OCO_2CH_3 + e^- + Li^+ \rightarrow CH_3OLi \downarrow + CH_3CO_2\cdot \\
\text{DEC} & \quad CH_3CH(OOC)CH_3CH_3 + e^- + Li^+ \rightarrow CH_3CH(OOC)CH_3Li \downarrow + CH_3CH_2\cdot \\
& \quad CH_3CH(OOC)CH_3CH_3 + e^- + Li^+ \rightarrow CH_3CH_2OLi \downarrow + CH_3CH_2CO_2\cdot 
\end{align*}
\]

\(^{5}\) The arrow notation in the reaction schemes refers to solid products that become part of the SEI layer (\(\downarrow\)), and to gaseous products removed from the surface (\(\uparrow\)).
**Reaction scheme 2** *Schematic reduction reactions of some Li salts* [28, 45, 46].

\[
\begin{align*}
\text{LiPF}_6 + ne^- + n\text{Li}^+ & \rightarrow \text{LiF} \downarrow + \text{Li}_x\text{PF}_y \downarrow \\
\text{LiBF}_4 + ne^- + n\text{Li}^+ & \rightarrow \text{LiF} \downarrow + \text{Li}_x\text{BF}_y \downarrow \\
2\text{LiCF}_3\text{SO}_3 + 2e^- + 2\text{Li}^+ & \rightarrow 2\text{Li}_2\text{SO}_3 \downarrow + \text{C}_2\text{F}_6 \uparrow \\
\text{C}_2\text{F}_6 + 2e^- + 2\text{Li}^+ & \rightarrow \text{CF}_3\text{CF}_2\text{Li} + \text{LiF} \downarrow \\
\text{Li}_2\text{SO}_3 + 6e^- + 6\text{Li}^+ & \rightarrow \text{Li}_2\text{S} \downarrow + 3\text{Li}_2\text{O} \downarrow \\
\text{LiN(CF}_3\text{SO}_2)\text{Li}_2 + 4e^- + 4\text{Li}^+ & \rightarrow \text{Li}_3\text{N} \downarrow + 2\text{CF}_3\text{SO}_2\text{Li} \downarrow \\
2\text{CF}_3\text{SO}_2\text{Li} + ne^- + n\text{Li}^+ & \rightarrow \text{Li}_2\text{S}_2\text{O}_4 \downarrow + \text{C}_2\text{F}_6\text{Li}_x + \text{LiF} \downarrow \\
\text{Li}_2\text{S}_2\text{O}_4 + 6e^- + 6\text{Li}^+ & \rightarrow 2\text{Li}_2\text{S} \downarrow + 4\text{Li}_2\text{O} \downarrow 
\end{align*}
\]

**Reaction scheme 3** *Reactions of electrolyte and SEI components with H\textsubscript{2}O and HF impurities* [44, 47, 48].

\[
\begin{align*}
\text{H}_2\text{O} + \text{ROCO}_2\text{Li} \downarrow \rightarrow \text{Li}_2\text{CO}_3 \downarrow + \text{CO}_2 \uparrow + \text{ROH} \\
\text{H}_2\text{O} + x\text{Li}^+ + x\text{e}^- \rightarrow \text{LiOH}/\text{Li}_2\text{O} \downarrow + \text{H}_2 \uparrow \\
\text{H}_2\text{O} + \text{LiPF}_6 \rightarrow \text{LiF} \downarrow + \text{POF}_3 \uparrow + 2\text{HF} \\
\text{H}_2\text{O} + \text{LiBF}_4 \rightarrow \text{LiF} \downarrow + \text{BOF} \uparrow + 2\text{HF} \\
\text{HF} + \text{ROCO}_2\text{Li} \downarrow \rightarrow \text{LiF} \downarrow + \text{ROCO}_2\text{H} \\
2\text{HF} + \text{Li}_2\text{CO}_3 \downarrow \rightarrow 2\text{LiF} \downarrow + \text{H}_2\text{CO}_3 \\
2\text{HF} + \text{Li}_2\text{O} \downarrow \rightarrow 2\text{LiF} \downarrow + \text{H}_2\text{O} \\
2\text{HF} + \text{LiOH} \downarrow \rightarrow 2\text{LiF} \downarrow + \text{H}_2\text{O}
\end{align*}
\]

The formation of polymers on the electrode surface is a somewhat more controversial issue, since they have been difficult to identify with standard FT-IR spectroscopy techniques. However, the positive identification of extended hydrocarbon chains on the surface has recently been proved possible using Secondary Ion Mass Spectrometry (SIMS) [51, 52]. These may be produced as a consequence of the formation of C\textsubscript{2}H\textsubscript{4} and radicals during carbonate reduction (*Reaction scheme 1*). Polycarbonates (-\((\text{CH}_2\text{CH}_2\text{OCO}_2)\text{y}\)-) and poly(ethylene oxide) -\((\text{CH}_2\text{CH}_2\text{O})\text{x}\)- has also been identified as EC polymerisation products [53] according to:
(25)

\[ n(x+y) \text{(CH}_2\text{O})_2\text{CO} \rightarrow \text{-[(CH}_2\text{CH}_2\text{O})_x/-(\text{CH}_2\text{CH}_2\text{OCO}_2)_y]}_{\text{n-}} + nx \text{ CO}_2 \]

However, the formation mechanisms for these compounds have not been established.

The intuitive notion of the SEI components, formed on carbon electrodes according to the above reactions, as being arranged in one thin layer is oversimplified. Several models based on a variety of different experimental techniques have been proposed, ranging from single-layer [40] to multi-layer [43, 54] to more complicated “polyhetero microphase” surface structures [51, 55]. There are still ambiguities regarding these phenomena and no unified picture of the chemical and morphological characteristics of the surface films has so far been provided. It is generally accepted that fully reduced, inorganic components such as LiF, Li$_2$O and Li$_2$CO$_3$ are formed close to the graphite surface, and incompletely reduced materials, ROCO$_2$Li and organic species (polymers), are formed further out towards the electrolyte.

The stability of the SEI layer is crucial for maintaining its passivating effect on the carbon anodes at low potential. It is important to obtain a thin but stable surface layer that does not deteriorate or change its composition or morphology with time and temperature during extended cycling and storage. The SEI layer will then lose its passivating property and cause additional reduction of electrolyte. This can lead to loss of capacity, increased kinetic barrier, poor cyclability, self-discharge, etc. [56-58].

Since the performance of Li-ion batteries at elevated temperature is of ultimate relevance to their safe use in most applications, temperature is the most critical parameter to study in this respect. Elevated temperatures can accelerate the degradation of battery materials causing a decline in capacity and premature cell-death. Raising the temperature can also provoke the onset of thermal runaway, where the cell temperature increases uncontrollably as a result of some exothermic side-reactions. This is especially relevant for the SEI-layer component, as it must also retain its passivating function for the carbon electrode at higher temperatures.

Understanding the formation, stability and functionality of the SEI is one of the most important issues for Li-ion battery researchers, as it has implications for safety and other important properties. The focus in present thesis is i) to provide a better representation of the original SEI layer formed on graphite electrodes (Papers I, III and IV), ii) to investigate the stability of the SEI on graphite at ambient and elevated temperatures (Papers II, III and IV), and iii) to understand the implications of SEI stability for electrochemical performance (Papers II and III).

3.2 LiMO$_x$ Cathodes

Surface phenomena on positive electrodes in Li-ion batteries are studied much less frequently than they are on negative electrodes. This does not mean they are of less
importance. Impedance increase due to surface film formation on LiMO_x electrodes during cycling and storage has been identified by Electrochemical Impedance Spectroscopy (EIS) [59-61]. This means that the Li^+ ions must travel through an extra phase; a step which might even be rate-limiting if the surface species formed are poor Li^+ ion conductors and diffusion through the electrolyte and bulk electrode material is fast.

Electrolyte oxidation has been one of the reasons proposed for film formation, which would be driven mainly by the reduction of unstable M^{4+} ions in the active electrode material. LiMn_2O_4 is a special case in this respect, since corrosion of the oxide leading to dissolution of Mn^{2+} ions may further feed electrolyte oxidation [62].

High-voltage electrolyte oxidation processes have been studied electrochemically, and insoluble reaction products have been shown to form [63]. However, the identification of the oxidation products has not been successful, and the reaction mechanisms are still not clear. The formation of polymers and lithium alkyl carbonates has also been suggested, [64].

Li_2CO_3 is known to be present initially on LiNiO_2 and LiCoO_2, which may be a target for reactions with HF and the subsequent formation of LiF on the surface, in accordance with reaction (22).

Preliminary surface studies have been conducted on LiNi_{0.8}Co_{0.2}O_2 electrodes. ^7Li and ^19F nuclear magnetic resonance (NMR) studies have confirmed the presence of a surface layer on cathode samples [65]. Soft X-ray absorption spectroscopy studies have shown that LiF was present on the cathode surfaces [66]. Zhang et al. reported infrared, Raman and atomic force microscopy results, which confirm the presence of surface layers on the cathode samples [35].

The surface investigation of LiNi_{0.8}Co_{0.2}O_2-based electrodes is here continued in an attempt to better determine the surface chemistry, how it changes with time and temperature, and what impact it might have on electrochemistry (Paper V).
4 EXPERIMENTAL TECHNIQUES

4.1 ELECTROCHEMICAL METHODS

Galvanostatic cycling (or cyclic chronopotentiometry [67]) is an important method for electrochemical evaluation of battery materials. A constant current (I) is here applied to the cell, and the potential is monitored as a function of time (t). The total amount of charge passed per unit mass of electrode material, *i.e.* the specific capacity \( C \), during complete discharge (or charge) is given by:

\[
C = \frac{I \cdot t}{m} \quad \text{Eq. [1]}
\]

Data from galvanostatic measurements are often displayed as cell voltage \( E \) as a function of \( C \) (*e.g.* Fig. 4). The cyclability of the material is usually presented as the total charge or discharge capacity, \( C \), as a function of cycle number. \( C \) will sometimes contain both irreversible, \( C_{\text{irr}} \), and reversible, \( C_{\text{rev}} \), components, where \( C_{\text{irr}} \) is obtained from the discharge and charge capacity difference \( |C_{\text{dch}} - C_{\text{cha}}| \) (see Fig. 4). The cycling rate is usually given as \( C/N \), where \( N \) is the time in hours for a full discharge or charge.

Pulsed galvanostatic techniques can be useful for determining kinetic (and thereby power) characteristics of an electrode material or an entire battery. Here, a short current pulse between \( t_0 \) and \( t_1 \) is applied and the potential response is monitored. This is shown schematically in Fig. 6.

![Figure 6](image_url)  
*Figure 6* Schematic representation of the potential response to a current pulse.

From the potential response, a cell resistance (R) can be obtained according to:

\[
R = \frac{(V_{t0} - V_{t1})}{(I_{t0} - I_{t1})} \quad \text{Eq. [2]}
\]

The area dependent resistance (ASI, Area Specific Impedance) is a better unit for comparison between cells and electrode materials [68].
ASI = R \cdot \text{Material Area (cm}^2) \quad \text{Eq. [3]}

R and ASI represent an overall cell impedance with the major contributions coming from: i) electron transfer from the cell terminals to the reaction sites, ii) electrode reactions involving active material and electrons, and iii) charge and mass transport in the electrolyte and electrodes via ions and reactant molecules. The separation of various impedance components is a complicated matter and alternating current (AC) methods are needed (EIS). This technique has not been used in this study.

The electrochemical testing was, for most part, carried out on a Digatron MBT small battery tester, or a Bio-Logic MacPile II potentiostat/galvanostat.

4.2 X-RAY PHOTOELECTRON SPECTROSCOPY

There has been many publications during the last two decades on the topic of SEI layers formed on various electrode materials. The techniques employed for studying the chemical composition include nuclear magnetic resonance (NMR) spectroscopy [65, 69], Raman spectroscopy [70, 71], electron spin resonance (ESR) spectroscopy [72] and FT-IR spectroscopy [41, 53, 63, 73, 74]. Among these, FT-IR spectroscopy has been the most extensively used technique. Although improvements have been made in recent years in the surface sensitivity of infrared spectroscopy, it cannot match the sensitivity provided by X-ray Photoelectron spectroscopy (XPS). XPS has here been used in Papers I, II, IV and V as the main analysis technique for investigating different aspects of surface-film formation on anode and cathode materials. Conventional monochromatic XPS measurements have been carried out either on a PHI 5500 spectrometer [I], [II], [IV], [V] or a Kratos Axis ULTRA X-ray Photoelectron Spectrometer [V]. Measurements using synchrotron radiation were also carried out in Paper I at beam line 411 at the Swedish National Synchrotron Radiation Laboratory, MAX.

In XPS, a sample is irradiated with a specific photon energy, $h\nu$, causing the ejection of photoelectrons from occupied energy levels, provided that $h\nu$ is larger than the binding energy, $E_B$, of a certain state. The ejected electrons will have a kinetic energy, $E_k$. The process can be described by the relation:

$$E_B = h\nu - E_k - \phi \quad \text{Eq. [4]}$$

$\phi$ is the work function, which is defined as the potential difference between the Fermi level of the sample and the vacuum level, and hence depends on both sample and spectrometer. Equation [4] is a consequence of the photoelectric effect [75]. The principal process of XPS and corresponding energy level diagram are depicted in Fig. 7.
In an XPS measurement the number of photoelectrons are recorded as a function of binding energy. Core-electron binding energies, which have been studied here, are unique to each element and can therefore be used as a fingerprint of the elemental composition of a surface. Changes in chemical environment and oxidation state of a certain atom cause small changes in these core-binding energies (chemical shifts) [76]. This occurs even though the core orbitals are not participating in any bonding. The chemical shifts can, in simple terms, be viewed as the effect a change of the electron density of the valence orbitals has on the emitted photoelectron. For instance, a carbon atom bonded to three oxygens in a carbonate functional group has a low electron density in the valence orbitals because of the electron-withdrawing power of the oxygens. This results in a partial positive charge on the carbon, and hence an increase in the core-orbital binding energy.

The photoionization process is followed by a decay of the excited state to a final-state configuration. There can be several possible final-state configurations with different energies. The ejected photoelectrons will lose part of their energy to these transitions, thus giving rise to discrete satellite peaks on the high binding energy side of the main photoelectron peak. The interactions can either result in an excitation of a second electron to an empty orbital (shake-up), or to the complete emission of that electron (shake-off). The energy released from a decay process can be enough to emit either photons or secondary electrons (Auger electrons). Auger electrons also add lines to the photoelectron spectrum.

XPS is a highly surface sensitive technique, where the analysis depth is limited by the shallow escape depth of the ejected photoelectrons (<50 Å). The escape depth of the photoelectrons can be estimated from the quantity $\lambda_M \cos \theta$, where $\lambda_M$ is the inelastic mean-free-path of an electron with kinetic energy $E_k$, and $\theta$ is the angle of emission of the electron from the surface normal; $\lambda_M$ depends both on $E_k$ and on the matrix within.
which the photoelectron travels, and can be estimated for inorganic compounds from the empirical relationship proposed by Seah and Dench [76, 77]:

$$\lambda_M = 2170aE_k^{-2} + 0.72a^{3/2}E_k^{1/2}$$  
Eq. [5]

where $a$ is the “atom size” of the matrix defined by:

$$a^3 = 10^{24}A / \rho N_a1000$$  
Eq. [6]

Here, $\rho$ is the bulk density, $A$ is the mean atomic or molecular weight, and $N_a$ is Avogadro’s number. Since $E_k$ depends on the X-ray energy through Eq. [4], it is possible to tune the escape depth by changing the X-ray energy using a synchrotron X-ray source [78]. Eq. [5] and [6] are used in Paper I, where the thickness of the SEI layer has been estimated from escape depth calculations.

Quantitative information of the surface can, within a reasonable error (a few %), be obtained from XPS. The quantitative determination of the atomic fraction of a specific element ($C_x$) can be expressed by the generalised formula [79]:

$$C_x = \frac{\sum n_x}{\sum n_x} = \frac{I_x}{I_x}$$  
Eq. [7]

where $S$ is the atomic sensitivity factor, a factor dependent on the element, the elemental environment and the instrumental set-up; $n$ is the number of atoms of the element per cm$^3$ of the sample; $I$ is the number of photoelectrons per second in a specific spectral peak.

Depth profiling of the sample surface can provide useful information on the morphological features of the surface. This can be achieved by Ar$^+$-ion etching (sputtering) of the surface, followed by XPS analysis. Calibration of both the analysis signal and the sputtering rate is required, however, to obtain a reliable depth scale [80]. The topography and changes of surface composition due to ion-beam-induced damages must also be taken into account in the depth profile calibration. This was done for the analysis of SEI layers in Paper I.

4.3 X-RAY DIFFRACTION

X-ray diffraction (XRD) is the most effective and widely used method for obtaining structural information in the bulk of crystalline materials [81]. Through constructive interference, incident X-rays are diffracted from various crystal planes, with Miller indices, hkl, at a certain angle ($\theta$) with respect to the incident beam:

$$n\lambda = 2d_{hkl}\sin\theta$$  
Eq. [8]
XRD in conjunction with electrochemical cycling, \textit{in situ} XRD, has been shown to be particularly suitable for studying ion-insertion and -extraction processes \cite{19, 26, 82}. The combination of the two techniques provides valuable information, inaccessible to \textit{ex situ} experiments, on the relationship between structure and electrochemical properties. A high-temperature device was constructed for \textit{in situ} XRD studies in transmission mode on battery materials at elevated temperatures \cite{III}. The furnace was developed specifically as an attachment for the Stoe STADI Position Sensitive Detector (PSD) X-ray powder diffractometer.

4.4 \textbf{DIFFERENTIAL SCANNING CALORIMETRY}

Differential scanning calorimetry (DSC) is a useful method for studying the thermal stability of battery materials. In the measurements, the temperature and heat-flow of a sample relative to a reference is detected \cite{83}.

In a DSC run, thermal transitions are detected as positive or negative peaks, which represent exothermic and endothermic reactions respectively. Exothermic reactions of materials for battery applications can be crucial since they can cause thermal runaway in the cell and thereby constitute a safety hazard.

DSC has been used in this work for studying the thermal stability of electrochemically lithiated graphite in contact with electrolyte. The methodology and experimental conditions are described in detail in Paper IV. All measurements were carried out on a Mettler DSC 30 Calorimeter.

4.5 \textbf{SCANNING ELECTRON MICROSCOPY}

In scanning electron microscopy (SEM), electrons of a certain energy are focused on and scanned over a surface. The electrons emitted from the surface can be used to create a surface image. In this work, SEM micrographs on electrode samples have been obtained using either JEOL JSM-25D or Hitachi S-4700 high-resolution microscopes.
SURFACE PHENOMENA IN Li-ION BATTERIES

5 SAMPLE PREPARATIONS

For most of the studies conducted on SEI layers formed on graphite electrodes, half-cells were prepared with a graphite-containing working electrode and lithium-metal foil as the counter electrode. The electrodes were laminates consisting of a mixture of 80 wt% synthetic graphite powder (typically KS6, Timcal), 10 wt% high surface area carbon-black powder for conduction, and 10 wt% ethylene propylene dien copolymer (EPDM) as a binder, coated on a Cu foil current collector. The EPDM binder was preferred to the more common PVdF (polyvinylidene fluoride) binder because it did not give interfering peaks in the C1s and F1s spectra in XPS measurements. Electrolytes were prepared as mixtures of EC and DMC in the volume ratio 2:1 and 1 M of a lithium salt (LiBF₄, LiPF₆, LiCF₃SO₃ or LiN(SO₂CF₃)₂). The electrolytes were analysed for water content by Karl Fisher titration, and it was found to be <30 ppm in all cases. The laminate and cell preparations are described in detail in Papers I, II, and IV.

Argonne National Laboratory supplied anode and cathode laminates obtained from practical 1 Ah 18650-type (18 mm diam., 65 mm long) lithium-ion cells (Paper V). These were fabricated and assembled by Polystor, Inc. The cathode laminates comprised a ~40 µm coating containing 84 wt% LiNi₀.₈Co₀.₂O₂ (Sumitomo), 4 wt% graphite (Timcal, SFG-6), 4 wt% acetylene black and 8 wt% PVdF (Kureha 1100) binder on a 20 µm thick Al foil. The anode laminates comprised a ~40 µm coating containing 75 wt% mesocarbon microbead (MCMB) graphite, 17 wt% SFG-6 graphite and 8 wt% PVdF (Kureha C) binder on a 12 µm thick Cu foil. The electrolyte used in the cell was an EC/DEC (1:1), 1 M LiPF₆ mixture.

All cells, regardless of origin, were subjected to various pre-treatments. Most cells were galvanostatically charged and discharged in a few (3-5) formation cycles. Some cells were stored (calendar-life tested) after the pre-cycling step at different temperatures and different states of charge (SOC). The exact conditions for the various tests are elaborated upon in the Experimental sections of the corresponding papers. The electrode samples were extracted form the cells after completion of the tests, and then prepared for the various diagnostic analyses. All cell disassembly was conducted in Ar-filled glove boxes in which water and oxygen content was kept to a minimum (<5ppm H₂O and O₂).

Samples for XPS analysis were mounted on sample holders and transported from the glove box to the analysis chamber in a specially designed chamber to prevent any contact with air. Measurements were also conducted on relevant reference compounds for peak assignment purposes. The peak assignment procedure and the underlying logic for the analysed samples are described in detail in the corresponding papers [I], [II], [IV], [V], and will not be repeated in following summary of results.
DSC samples were prepared from small pieces of the pre-treated electrodes and sealed into standard Al crucibles. The measurements were carried out using a heating rate set at 5°C/min in the temperature range 30-400°C.

SEM measurements were performed on treated electrode samples. These samples were exposed briefly to air before insertion into the analysis chamber.
The results from Papers I, II, III, IV and V are summarised in the following two chapters (6 and 7), and the essential results discussed.

6 SURFACE REACTIONS ON GRAPHITE ANODES

6.1 SEI LAYER CHARACTERISATION
The chemistry and morphology of the SEI layer formed on a graphite electrode in EC/DMC (2:1), 1M LiBF$_4$ after three formation cycles at C/5 rate was characterised in detail by XPS [I].

6.1.1 Chemical composition
The chemical composition of SEI layer was seen to consist of solvent reduction products (mainly ROCO$_2$Li, but possibly also Li$_2$CO$_3$), polymeric species (hydrocarbons and possibly poly(ethylene oxide)) and LiBF$_4$ reduction or decomposition products (LiF and Li$_x$BO$_y$F$_z$). This corresponds well with previous results obtained by FT-IR spectroscopy on carbon electrodes in present the electrolyte system [41], and is in line with the reaction pathways given in Reaction schemes 1, 2 and 3. Fig. 8 shows the corresponding F1s, B1s, Li1s, C1s and O1s XPS spectra for the electrode.

Figure 8 F1s, B1s, Li1s, C1s and O1s XPS spectra of a graphite electrode after 2 cycles in EC/DMC, 1M LiBF$_4$. Binding energy positions from reference compound measurements are marked in the figures.
6.1.2 Morphology

The morphology of the SEI layer was analysed by sequential Ar⁺ ion sputtering and conventional monochromatic XPS measurements. A novel approach for these systems was used for the interpretation of the sputtering results, involving a careful sputtering calibration [I]. The SEI layers are multi-component systems, with each component having its own response to the abrasive sputtering process in which energy is transferred inelastically from the Ar⁺ ion beam to the surface. The effect of sputtering has previously not been investigated for these systems. In the sputtering calibration, the various components on the surface are dealt with separately. Reference samples of compounds known to be present on the surface were analysed. Both sputtering-induced decomposition and variations in sputtering rate were observed. The results are summarised in Table 3.

### Table 3 Summary of sputtering effects seen for surface species on cycled graphite electrodes.

<table>
<thead>
<tr>
<th>Reference compound</th>
<th>Graphite</th>
<th>Lithiated graphite (LiC₆)</th>
<th>Li₂CO₃</th>
<th>LiBF₄</th>
<th>Polyethylene (PE)</th>
<th>LiF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtering rate (Å/min)</td>
<td>27 ± 8</td>
<td>-</td>
<td>20 ± 9</td>
<td>-</td>
<td>25 ± 3</td>
<td>17 ± 3</td>
</tr>
<tr>
<td>Sputtering induced reactions</td>
<td>Increase in LiC₆ deinsertion, formation of LiOH</td>
<td>Li₂CO₃ → Li₂O + CO₂</td>
<td>LiBF₄ → LiF + BF₃</td>
<td>None</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Preferential removal of certain elements</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

a 4 keV accelerating voltage

b FWHM = full-width at half-maximum

Some important conclusions could be drawn from these calibrated sputtering measurements made on the cycled electrodes. The solvent reduction products, i.e. carbonates, were present as a thin surface layer of less than 20 Å. The polymeric phase was present at the surface as a porous matrix upto 900 Å thick. Large crystals of LiF were formed on the surface, with sizes up to 0.2 µm, indicating that other types of reaction occur than charge-transfer at the graphite surface.

Synchrotron XPS with variable X-ray energy was also used as a complement to the morphology interpretation, and showed that the SEI layer indeed completely covered the graphite surface. These measurements also showed that the surface-film thickness was not more than 15 Å at its thinnest point. This number was estimated from the escape depth of a carbon 1s electron travelling through an SEI layer, in which the various components are of similar density and atomic weight (Eqns. [5] and [6]). This is an important result because it is based upon a direct analysis method, which is invariant to the porous surface structure of the powder electrode (including the SEI layer). Thickness
determinations from, for example, EIS (Electrochemical Impedance Spectroscopy) measurements and ellipsometry rely heavily on the assumption that the surface film is homogeneous and dense. Thickness determinations from ellipsometry and AFM (atomic force microscopy) measurements also require a flat analysis surface.

The various thicknesses obtained here are in line with the assumption that the SEI layer is not uniform but can be highly irregular and porous. Moreover, the results provide an explanation to the variety of different SEI-layer thicknesses reported in the literature. Modelling of the total film thickness from EIS measurements using impedance data has given values from 10-50 Å [54]. In situ ellipsometry measurements on a highly oriented pyrolytic graphite (HOPG) crystal gave an SEI thickness of 40 Å [84], and studies by in situ electrochemical atomic force microscopy (ECAFM) have suggested that surface deposits were of the order of 250 Å to several thousand Å thick [85-87]. Here, a separation of the various phases and thicknesses is obtained by one single analysis technique. It can naturally be applied to any electrode and electrolyte system.

6.2 SEI LAYER STABILITY
The stability of the SEI formed on graphite in the EC/DMC-based electrolyte with time and temperature was investigated using different techniques in Papers II, III, IV.

Electrochemical investigations were conducted for electrolyte systems containing LiPF$_6$ and LiBF$_4$. The stability test was made in a three-step process [II]. Equivalent half-cells were cycled galvanostatically at room temperature for three cycles at C/5 rate. They were then stored at 0% SOC$^6$ (delithiated state) or 100% SOC (fully lithiated state) at room temperature (RT), 40°C, 50°C and 60°C for 7 days. The cycling was continued after storage either at the corresponding storage temperatures or at RT, starting with a reduction current. The results for the samples stored in delithiated state, presented as total reduction charge vs. cycle number from 0% SOC samples, are shown in Fig. 9.

The graphite electrodes were unaffected by storage at RT. These cells cycled with retained intercalation capacity after the storage period (Fig. 9). Storage above RT, on the other hand, caused additional reduction charge ($\text{C}_{\text{irr}}$) for both salts, showing that secondary reactions were occurring besides lithium intercalation. The extra charge in the fourth cycle was attributed to additional electrolyte reduction at $\sim$0.8 V, leading to the formation of new SEI components on the graphite surface. This must be a consequence of the rearrangement of the original SEI layer during storage, so that additional electrolyte reduction can occur. This may include dissolution or decomposition of surface species to create a porous SEI structure. It has been shown that some SEI species may be soluble in their mother solvents [88]. It has also been suggested that ROCO$_2$Li compounds are metastable and decompose at elevated temperature to Li$_2$CO$_3$ [97]. Either way, this would lead to a contraction of the SEI layer and enable electrolyte reduction.

$^6$ SOC = State Of Charge
Figure 9  Total reduction charge vs. cycle number for Li/graphite half-cells containing two different electrolytes. The cells were pre-cycled three times at RT (cycles 1-3) prior to storage at different temperatures in a deintercalated state, followed by continued cycling at the respective storage temperatures (top row), and at RT (bottom row).

LiBF₄-based cells stored at RT, 40°C and 50°C, and LiPF₆-based cells stored up to 80°C could all cycle continuously both at RT and elevated temperature after storage (Fig. 9). This shows that, in the competing processes of SEI decomposition and reconstruction, a functional SEI layer is maintained. This was not the case for LiBF₄-based cells stored at 60°C, where parasitic reactions (electrolyte reduction, possibly in combination with other effects, such as graphite exfoliation) were completely dominating in the fourth cycle. In subsequent cycles, the consumed charge decreased rapidly, indicating a blocking of the electrode. This effect was also seen for the cell cycled at RT after storage. These results suggest that the SEI decomposes into a highly resistive surface film at 60°C. Fig. 10 shows the measured resistance (Section 4.1) at the end of each charge sweep for the LiBF₄ cells. These results confirm that the resistance of the heat-treated samples in general increase after storage, and become more than three times larger for the 60°C cell.
Studies on cells stored in their fully charged (lithiated) state also showed that part of the extra charge consumed after storage ($C_{\text{irr}}$) could be attributed to deintercalation of lithium from the graphite bulk and its subsequent reaction with electrolyte.

This phenomenon was further explored for the LiBF$_4$ system with the new set-up for \textit{in situ} X-ray diffraction at elevated temperature \cite{III} (and \cite{II}). Spontaneous oxidation, \textit{i.e.} self-discharge, occurred for a half-cell stored at 70°C in a fully intercalated state. The OCV monitored during storage (Fig. 11) revealed a stepwise increase in potential, characteristic for the formation of different staged phases of the Li-graphite intercalation system. Simultaneous X-ray diffraction monitoring of the LiC$_6$ (001) peak were consistent with the OCV curve, in that higher stages of intercalation compounds were formed during storage, ending in the complete removal of lithium from the surface within 30 h (Fig. 12). The removal of all lithium from the graphite bulk shows that the reaction of lithium with electrolyte does not create a new stable SEI layer, but that the reaction products decompose continuously into a less passivating film. The cell was significantly polarised on continued cycling, and only a minor amount of Li$^+$ ions could be reinserted at a slow C/10 rate (0.255 mA/cm$^2$), in agreement with Fig. 9. In a corresponding experiment using LiPF$_6$, delithiation occurred only at the beginning of the storage period, but then levelled off, probably through the formation of a new functional SEI layer \cite{II} \cite{90}.

The general consensus from the electrochemical and \textit{in situ} diffraction measurements is that the SEI layers formed in these two electrolyte systems are not stable, but change their structure at elevated temperature, and thereby lose their passivating effect. However, more severe rearrangements of the surface structure occur exclusively at 60°C for the LiBF$_4$ case and not for LiPF$_6$. 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{Resistance (R) at the end of charge plotted as a function of cycle number and storage temperature for graphite/1M LiBF$_4$, EC:DMC (2:1)/Li half-cells \cite{89}.}
\end{figure}
Figure 11  The spontaneous potential changes occurring during storage of a graphite/1M LiBF₄, EC:DMC (2:1)/Li half-cell at 70°C in a fully lithiated state. Figures mark the time intervals at which X-ray scans were made.

Figure 12  In situ X-ray diffractograms of the (001) reflection of LiC₆ during the spontaneous oxidation shown in Fig. 11: A. 0-2 h; B. 2-10 h; C. 10-18 h; D. 18-26 h.
The compositional and morphological changes in the surface films after storage at 60°C were studied by XPS, to further investigate the SEI destruction processes [II]. The results provide experimental evidence that lithium carbonates are indeed removed on storage, either through dissolution or decomposition. As a consequence, the graphite surface is partially exposed. This may thus be the reason for loss of charge on continued cycling, as electrolyte may come in contact with the graphite surface. Sputtering experiments show that the amount of LiF, on the other hand, increases drastically in relation to graphite for both electrolyte systems. An increase in polymeric species within the surface layer is observed relative to graphite after storage; mostly hydrocarbon species but the results also indicated formation of PEO and possibly polycarbonate species. The qualitative and quantitative results are summarised in plots showing the relative concentrations of the major groups of surface species i.e. graphite, LiF and solvent-based products (SBP’s) (mainly carbonates and polymers), as a function of sputtering time (Fig. 13).

![Graph showing molar fractions of LiF, graphite, solvent-based product (SBP) and electrolyte salt found on the graphite electrode surface as a function of sputtering time.](image)

**Figure 13** Molar fractions of LiF, graphite, solvent-based product (SBP) and electrolyte salt found on the graphite electrode surface as a function of sputtering time. The electrodes were (a and c) only pre-cycled, or (b and d) pre-cycled and stored at 60°C. 1 M LiPF₆ in EC/DMC (2:1) (a and b); 1 M LiBF₄ in EC/DMC (2:1) (c and d).

From the shapes of the sputtering curves together with SEM images of the electrodes stored at 60°C [II], it is concluded that larger LiF crystals (up to 0.5 µm) are formed in the case of LiBF₄ (slow removal of LiF on sputtering in Fig. 13d), while the crystals
formed in the LiPF$_6$ case are smaller but cover a larger surface area (fast removal on sputtering but with a high maximum value, Fig. 13b). The LiBF$_4$ system contains a larger overall LiF content. The LiF increase was considered to be the main cause of impedance increase in the cells and, in the case of LiBF$_4$, the cause of cell failure after storage at 60°C.

It is often discussed that an excess of LiF on electrode surfaces in LiBF$_4$- and LiPF$_6$-based electrolytes is due to the reactions between trace amounts HF or H$_2$O with electrolyte and SEI layer components (Reaction scheme 3). This may indeed be true for LiPF$_6$, which reacts readily with water to form LiF and HF at ambient conditions [32, 33, 91]. This is demonstrated effectively in the poor elevated-temperature performance of LiMn$_2$O$_4$ cathode materials in LiPF$_6$-based electrolytes. Here, HF contributes to the dissolution of Mn$^{2+}$ into the electrolyte, creating severe corrosion problems on the cathode [92, 93]. LiMn$_2$O$_4$, is on the other hand, quite stable in LiBF$_4$-based systems, which can be explained by the slow hydrolysis of LiBF$_4$ [33, 37]. HF does not form in significant quantities. It is then more difficult to understand why LiF forms in such large amounts in LiBF$_4$ systems. An alternative route for LiF formation is suggested involving the decomposition of LiBF$_4$ according to:

$$\text{LiBF}_4 \leftrightarrow \text{LiF} \downarrow + \text{BF}_3 \uparrow \quad (26)$$

This will be coupled to the reaction of BF$_3$ with species in the system other than water. BF$_3$ is a strong Lewis acid and is highly reactive with any electron-pair donor [94], for example carbonate solvents. It has been reported that BF$_3$ can initialise polymerisation of cyclic carbonates such that the BF$_3$ molecule interacts with the carbonyl oxygen leading to subsequent ring-opening and polymerisation propagation [95]. Possible poly(ethylene oxide)/polycarbonate were observed on the surface, and have also been observed by other researchers [96]. This may be a consequence of the formation BF$_3$. ROCO$_2$Li-type carbonates may also be attacked, which is discussed further in Section 6.3. These types of reaction may also occur for PF$_5$, the BF$_3$ analogue of LiPF$_6$, although they have not been reported in the literature. We believe that the bulky geometry (trigonal bipyramidal) causes a steric hindrance to direct Lewis-base attack on the phosphorous, which would then slow down reactions of this type. The planar BF$_3$ molecule, on the other hand, should be more accessible for such reactions. This provides an explanation to the higher degree of LiF deposits in LiBF$_4$ electrolytes.

6.3 SALT DEPENDENCE ON THE SEI THERMAL STABILITY

The results obtained on the formation and stability of the SEI layer formed in LiBF$_4$-based electrolytes and compared with the LiPF$_6$ analogue show that the anion plays an important rôle in determining the surface properties of the graphite electrode [11]. The relationship between surface chemistry and thermal stability was further investigated in
Paper IV in a comparison including the four salts LiBF₄, LiPF₆, LiCF₃SO₃ and LiN(SO₂CF₃)₂.

The salt dependence on the fresh surface layers was investigated by XPS. Graphite electrodes were pre-cycled three times at C/5 rate in electrolytes containing LiBF₄, LiPF₆, LiCF₃SO₃ or LiN(SO₂CF₃)₂ and analysed.

An example of the analysis is shown in Fig. 14, which displays the C1s spectra for all samples. Similar surface species from solvent reduction are formed for all electrolyte systems, *i.e.* lithium alkyl carbonates (ROCO₂Li) and possibly also Li₂CO₃. However, for the LiCF₃SO₃- and LiN(SO₂CF₃)₂-based systems, this contribution is larger in relation to the graphite contribution than for the other two salts. On the other hand, surface films formed in LiBF₄ and LiPF₆ electrolytes are richer in polymeric species.

**Figure 14** C1s XPS spectra for graphite electrodes cycled in an electrolyte containing EC/DMC (2:1) and 1 M of: a) LiCF₃SO₃, b) LiN(SO₂CF₃)₂, c) LiBF₄ and d) LiPF₆.
Salt reduction or decomposition products were observed on all samples. LiF was observed for all salts. Other reduced compounds were also observed that could fit the reaction products in reactions (9)-(16), Reaction scheme 2, e.g. Li$_x$PF$_y$, Li$_x$BF$_y$, Li$_2$SO$_3$, LiSO$_2$CF$_3$ and Li$_2$S$_2$O$_4$. However, these were more difficult to assign due to small shifts and lack of reference data. In general, the SEI layers are very similar for the LiCF$_3$SO$_3$ and LiN(SO$_2$CF$_3$)$_2$ systems, with a high level of solvent reduction products. These are also more compact, taking up smaller volume in the space between the graphite grains than the corresponding surface layers in the LiPF$_6$ and LiBF$_4$ systems. There were also many similarities between SEI's formed in LiPF$_6$- and LiBF$_4$-based electrolytes, such as high levels of LiF and polymer on the surface.

### Table 4

<table>
<thead>
<tr>
<th>1M lithium salt in EC:DMC (2:1)</th>
<th>Onset interval [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBF$_4$</td>
<td>60-80</td>
</tr>
<tr>
<td>LiPF$_6$</td>
<td>80-100</td>
</tr>
<tr>
<td>LiCF$_3$SO$_3$</td>
<td>110-120</td>
</tr>
<tr>
<td>LiN(SO$_2$CF$_3$)$_2$</td>
<td>125-135</td>
</tr>
</tbody>
</table>

The thermal stability of cycled electrodes in contact with electrolyte was investigated by DSC. DSC traces of graphite electrodes cycled to five different degrees of intercalation in four different electrolyte systems are displayed in Figs. 15a-d. In the temperature range 30-300°C, all traces show one or more exothermic peaks. These exothermic reactions are exclusive for cycled samples, i.e. they do not occur for fresh graphite electrodes in contact with electrolyte. The onset temperatures for the first exothermic reaction for the various samples are summarised in Table 4. The thermal stability clearly varies with electrolyte salt, with LiBF$_4$ giving the least stable and LiN(SO$_2$CF$_3$)$_2$ the most stable system.

All deintercalated samples show a small exothermic peak in the temperature region between 60°C (LiBF$_4$) and 140°C (LiN(SO$_2$CF$_3$)$_2$) (Fig. 15). These reactions are attributed to SEI decomposition, since no lithium is available for reactions, and they only occur for cycled electrodes. The large differences in onset temperature show that possibly different mechanisms control the decomposition. In reactions of lithiated samples, additional peaks appear above the SEI decomposition temperature. These peaks increase in magnitude with increasing lithium content. They are therefore associated with Li$_x$C$_6$-electrolyte reactions.
The decomposition of the SEI has been investigated by XPS on deintercalated samples heat-treated at 200°C, i.e. above the peak temperatures of the exotherms involved in the surface reactions. Both unrinsed samples and samples rinsed in DMC were analysed.

The LiCF$_3$SO$_3$ and LiN(SO$_2$CF$_3$)$_2$ systems were very similar in surface composition after heat-treatment. The C1s spectra for the unrinsed and rinsed deintercalated LiCF$_3$SO$_3$ samples are shown in Fig. 16. The spectrum for the untreated sample (no heating) is included for comparison. The topmost surface layer is seen to consist almost exclusively of a poly(ethylene oxide)-type compound (Fig. 16b). Li$_2$CO$_3$ was found close to the graphite surface, and was exposed upon rinsing (Fig. 16c).

Only minor amounts of salt reduction or decomposition products are found; among these, LiF could be identified and also reduced sulfuric species.

Figure 15  DSC traces of electrochemically lithiated graphite electrodes with electrolyte containing EC/DMC (2:1) and 1M of: a) LiCF$_3$SO$_3$, b) LiN(SO$_2$CF$_3$)$_2$, c) LiBF$_4$, and d) LiPF$_6$. 
The presence of Li$_2$CO$_3$ on the surface after storage supports the thermal transformation of metastable ROCO$_2$Li species to stable Li$_2$CO$_3$ [97] of the type:

$$\text{(CH}_2\text{OCO}_2\text{Li)}_2 \rightarrow \text{Li}_2\text{CO}_3 \downarrow + \text{CO}_2 \uparrow + \text{C}_2\text{H}_4 \uparrow + \frac{1}{2}\text{O}_2 \uparrow$$ \hspace{1cm} (27) \\
$$2\text{CH}_3\text{OCO}_2\text{Li} \rightarrow \text{Li}_2\text{CO}_3 \downarrow + \text{CO}_2 \uparrow + \text{CH}_3\text{O}^{-} + \text{CH}_3^{-}$$ \hspace{1cm} (28) \\

or, for the intercalated samples:

$$\text{(CH}_2\text{OCO}_2\text{Li})_2 + 2\text{Li}^{+} + 2\text{e}^{-} \rightarrow 2\text{Li}_2\text{CO}_3 \downarrow + \text{C}_2\text{H}_4 \uparrow$$ \hspace{1cm} (29)

The PEO species formed on the surface were thought to originate mainly from solvent decomposition and polymerisation, and not from ROCO$_2$Li decomposition. It is clear, however, that the SEI layer plays an important part in activating the polymerisation process. It is not seen to form in such large amounts in the LiBF$_4$ and LiPF$_6$ systems, and not on fresh, uncycled electrodes stored in electrolyte at 200°C. It is speculated that the formation of radicals, such as CH$_3$O$^{-}$ and CH$_3^{-}$, formed during reduction and decomposition of lithium alkyl carbonates, may be responsible for activating the polymerisation process.

The complete decomposition of the SEI formed in the LiBF$_4$-based electrolyte showed significant differences from the LiCF$_3$SO$_3$ and LiN(SO$_2$CF$_3$)$_2$ cases. The LiBF$_4$ salt undergoes complete decomposition during heating. The electrode surface is dominated by salt decomposition products (mainly LiF). Small amounts of ether-type species are
observed, but carbonates are not present at all. The graphite surface is exposed during storage. See the example shown in Fig. 17, where the C1s spectra for the unrinsed and rinsed deintercalated sample are compared to that for the untreated sample.

![C1s XPS spectra for graphite electrodes cycled in an electrolyte containing EC/DMC (2:1) and 1 M LiBF₄: (a) untreated sample, (b) sample treated at 200 °C for 24 h, and (c) as in (b) but rinsed in DMC.](image)

**Figure 17** C1s XPS spectra for graphite electrodes cycled in an electrolyte containing EC/DMC (2:1) and 1 M LiBF₄: (a) untreated sample, (b) sample treated at 200 °C for 24 h, and (c) as in (b) but rinsed in DMC.

In accordance with Section 6.2, the decomposition of LiBF₄ to LiF and BF₃, and further reactions of BF₃ with carbonate species, explain the very high level of LiF and the complete disappearance of carbonate species on the surface. We propose the following reactions:

\[
\text{BF}_3 + \text{Li}_2\text{CO}_3 \rightarrow 2\text{LiF} \downarrow + \text{BOF} \uparrow + \text{CO}_2 \uparrow 
\]

(30)

\[
\text{BF}_3 + (\text{CH}_2\text{OCO}_2\text{Li})_2 \rightarrow 2\text{LiF} \downarrow + \text{BOF} \uparrow + \text{CO}_2 \uparrow + \text{C}_2\text{H}_4 \uparrow + \frac{1}{2}\text{O}_2 \uparrow 
\]

(31)

\[
\text{BF}_3 + 2\text{CH}_3\text{OCO}_2\text{Li} \rightarrow 2\text{LiF} \downarrow + \text{BOF} \uparrow + \text{CO}_2 \uparrow + \text{CH}_3\text{O}• 
\]

(32)

These reactions provide an alternative exothermic decomposition route in the LiBF₄ compared to LiCF₃SO₃ and LiN(SO₂CF₃)₂ systems. Reactions including trace HF according to the reactions (21) and (22) (Reaction scheme 3) cannot be dismissed, however.

The decomposition of the surface layer in the LiPF₆ system shows similarities to the LiBF₄ system, in that no carbonates are observed, and the graphite surface is partly
exposed. The surface layer species consist to a large extent of salt-based products. Strong evidence is seen for the formation of hydrolysis products ($\text{Li}_x\text{PF}_y\text{O}_z$).

The shape and onset temperatures of the exothermic transitions in the DSC traces are clearly salt dependent (Fig. 15). The results provide evidence that this is the result of different thermal decomposition reactions of the SEI layer for various salts, which is confirmed by XPS. This decomposition leads to reactions between intercalated lithium and electrolyte to form additional SEI products that will also decompose and contribute to the different DSC appearance for the different salts.

The SEI layers in LiCF$_3$SO$_3$- and LiN(SO$_2$CF$_3$)$_2$-systems are clearly more thermally stable than in the corresponding LiBF$_4$- and LiPF$_6$- systems. Moreover, the decomposition of the SEI in the LiCF$_3$SO$_3$- and LiN(SO$_2$CF$_3$)$_2$-systems result in a compact surface layer that largely covers the graphite surface, and consists of solvent-based compounds, Li$_2$CO$_3$ and PEO, that are considered to be “good” SEI formers (i.e. Li$^+$ ion conductors). This contributes to a higher thermal stability of the lithiated phases. On the other hand, the transformation of carbonates to LiF in the case of LiBF$_4$ and LiPF$_6$ causes dramatic volume decrease; the graphite surface is subsequently exposed. The poorly passivated graphite surface is thus readily accessible to electrolyte reduction, which contributes to a lower thermal stability in these two cases. The XPS and DSC results are thus consistent (Fig. 15; Table 4).
7 SURFACE REACTIONS ON LiNi$_{0.8}$Co$_{0.2}$O$_2$ CATHODES

This Chapter focuses on the results obtained from the surface analysis of LiNi$_{0.8}$Co$_{0.2}$O$_2$-based cathodes removed from high-power Li-ion batteries [V]. Carbon-based anodes are also studied from the same cells; the results are very similar to those obtained from half-cells studied at Uppsala University (see Chapter 6), and are therefore not discussed further here. The materials and cells have been investigated extensively for high-power HEV applications at the Argonne National Laboratory (ANL) within the ATD program. Some results from the electrochemical characterisation are included in this summary (with the permission of ANL) to place the surface studies on the LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode material in Paper V in relation to their previous work.

7.1 ELECTROCHEMISTRY

18650-cells from ANL are subjected to accelerated calendar-life testing, in which cells are stored at 40, 50, 60 and 70°C at some potential (SOC)\(^7\). Capacity and pulse-power capability are measured continuously during storage by standard battery-test procedures given in the PNGV Battery Test Manual [98]. The pulse-power capability is measured by the hybrid pulse power characterisation (HPPC) test. This determines the available energy that can be used at specific state-of-charge and power levels, by applying a series of 18 s discharge or charge current pulses at 8-2C rate and analysing the voltage response [99]. Table 5 shows the power and capacity fade characteristics of a series of calendar-life cells [V]. The power fade is two to five times greater than the corresponding capacity fade, and increases continuously with temperature. This power loss is the main reason why the ANL cells do not meet the 15-year calendar-life target set by PNGV.

<table>
<thead>
<tr>
<th>Storage Temp</th>
<th>State-of-Charge</th>
<th>Storage Period</th>
<th>Capacity Fade</th>
<th>Power Fade</th>
</tr>
</thead>
<tbody>
<tr>
<td>40°C</td>
<td>60%</td>
<td>12 weeks</td>
<td>8.9%</td>
<td>15.0%</td>
</tr>
<tr>
<td>50°C</td>
<td>60%</td>
<td>8 weeks</td>
<td>5.5%</td>
<td>24.8%</td>
</tr>
<tr>
<td>50°C</td>
<td>60%</td>
<td>16 weeks</td>
<td>9.7%</td>
<td>28.1%</td>
</tr>
<tr>
<td>50°C</td>
<td>80%</td>
<td>4 weeks</td>
<td>5.0%</td>
<td>24.0%</td>
</tr>
<tr>
<td>60°C</td>
<td>60%</td>
<td>8 weeks</td>
<td>16.4%</td>
<td>39.3%</td>
</tr>
<tr>
<td>60°C</td>
<td>40%</td>
<td>4 weeks</td>
<td>6.7%</td>
<td>23.8%</td>
</tr>
<tr>
<td>70°C</td>
<td>60%</td>
<td>2 weeks</td>
<td>13.3%</td>
<td>33.0%</td>
</tr>
</tbody>
</table>

\(^7\) In accelerated tests, elevated temperatures are used to enhance kinetics so that the effects of long-term storage (calendar life) or cycling (cycle life) can be observed within reasonable time frames. It is important, however, to bear in mind that elevated temperatures can cause the onset of additional reactions which may never occur at ambient temperature.
The calendar-life tested electrodes are incorporated into symmetrical cells, i.e. the same material is used as both positive and negative electrode [61]. The area specific impedance (ASI) is measured separately as a function of depth of discharge (DOD) on negative and positive electrodes. The results obtained from a fresh cell and a calendar-life cell tested at 60% SOC and 70°C are compared in Fig. 18. The data clearly show that the impedance increases significantly on abuse. The complete-cell ASI value increases from 40 to 100 Ωcm² after storage. The majority of the impedance increase clearly occurs at the positive electrode; the negative electrode plays a minor rôle in this context. Additional EIS measurements show that the impedance increase on the positive electrode occurs mainly in the medium-frequency range, which corresponds to slow lithium-ion transport at the interface between liquid electrolyte and positive electrode surface, and to charge-transfer resistance [60, 61]. These results indicate that a surface film is built up on the positive electrode, similar to that observed previously on lithium metal and carbon electrodes. Identification of the LiNi₀.₈Co₀.₂O₂ electrode surface composition is therefore an important step towards determining the power fade mechanisms in these cells.

![Figure 18](image_url)  
*Figure 18 Area specific impedance as a function of depth of discharge (DOD): (a) aged cell, (b) aged positive electrode, (c) fresh cell, (d) fresh positive electrode, (e) aged negative electrode, and (f) fresh negative electrode.*

7.2 SURFACE CHARACTERISATION

7.2.1 SEM examination of LiNi₀.₈Co₀.₂O₂ laminates

The fresh laminate mainly comprise spherical secondary LiNi₀.₈Co₀.₂O₂ particles, ~5-10 µm in diameter (Figs. 19a). These are, in turn, composed of faceted primary particles (Fig. 19b). Graphite and acetylene black are also observed in the composite. The graphite has a plate-like appearance, and the acetylene black is irregular shaped with rounded edges.
Figure 19  Typical SEM micrographs from a fresh cathode laminate showing (a) oxide, graphite and acetylene black, and (b) PVdF binder. The acetylene black is indicated by double arrows in both figures.

In the calendar-life tested samples (Figs. 20a and 20b), particulate-type features are observed on the surface of the oxide particles. These features are more pronounced in samples tested for longer or at higher temperatures. Similar features are not observed on the graphite surfaces, which suggests that these particulates result from a reaction at the oxide surface.

Figure 20  SEM micrographs from a 40°C, 60% SOC, 32 week calendar-life test sample showing particulates (marked by arrows) on primary LiNi$_{0.8}$Co$_{0.2}$O$_2$ particle surfaces.

7.2.2 XPS analysis
XPS measurements are performed on LiNi$_{0.8}$Co$_{0.2}$O$_2$ powder, fresh laminates (no contact with electrolyte and tested (galvanostatic cycling and calendar-life abuse) samples.
Measurements on the fresh powder and laminate reveal that Li$_2$CO$_3$ is present on the surface of the LiNi$_{0.8}$Co$_{0.2}$O$_2$ particles (Fig. 21). This is in agreement with previous investigations on LiNiO$_2$ [100, 101]. The Li$_2$CO$_3$ is believed to form by the reaction between atmospheric CO$_2$ and LiNi$_{0.8}$Co$_{0.2}$O$_2$, possibly according to:

$$\text{Li(Ni,Co)O}_2 + \frac{x}{2} \text{CO}_2 + \frac{x}{4} \text{O}_2 \rightarrow \text{Li}_{1-x}(\text{Ni,Co})\text{O}_2 + \frac{x}{2} \text{Li}_2\text{CO}_3 \quad (33)$$

In addition to PVdF, which consists of alternating -CH$_2$- and -CF$_2$- units, and carbon additives, the fresh laminates also show, a small impurity of LiF. This is not observed on fresh anode laminates. The formation of LiF is believed to be a consequence of a dehydrofluorination reaction in the PVdF binder generating HF. The HF then reacts with LiNi$_{0.8}$Co$_{0.2}$O$_2$ (or Li$_2$CO$_3$) to form LiF [102].

![Figure 21](image_url)  

**Figure 21**  C1s, O1s, F1s, Li1s, Ni2p and Co2p XPS spectra for a fresh (uncycled) LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode laminate.

Additional compounds appear on the surface after testing. The XPS spectra for a 40°C, 60% SOC calendar-life tested sample is shown in Fig. 22. These new compounds are proposed be to organic polycarbonates and polymeric hydrocarbons; salt-based products are also observed. LiF is the main product, but decomposition products of the type Li$_x$PF$_y$ and Li$_x$PF$_2$O$_2$ are also identified. The spectral peaks observed in the samples stored at 40, 50, 60 and 70°C are similar, indicating that the same surface compounds are formed at various test temperatures. No changes are observed in the LiNi$_{0.8}$Co$_{0.2}$O$_2$ peak positions in the Ni2p and O1s spectra with time, temperature and SOC. The storage duration and state-of-charge did not change the surface chemistry. The relative intensities of the various components are, however, affected by temperature, where the
organic species appear to increase, while the inorganic salt-based (fluorine-containing) species appear to decrease. The latter effect is probably due to screening by an overlying organic surface layer. Two examples of the increase in the organic surface species are given in Fig. 23, where the intensities of the surface species peaks in the C1s and O1s spectra are seen to increase with temperature.

![Figure 23](image1.png)

**Figure 23** C1s, O1s, F1s, P2p, Li1s and Ni2p XPS spectra for a typical calendar-life LiNi0.8Co0.2O2 cathode sample, tested at 40°C, 60% SOC.

Significant changes are seen in the F1s spectra for unrinse samples and samples rinsed in DEC; a typical example with spectra, is given in Fig. 24. The LiF peak intensities in the 40°C and 50°C samples show a dramatic decrease on rinsing; the LiF:PVdF peak-intensity ratios in the rinsed sample are similar to those in the fresh laminate. The removal of LiF is probably a mechanical rather than a dissolution effect, since LiF is not soluble in DEC. On the other hand, the LiF peak intensities in the 60°C and the 70°C samples showed little change on rinsing. These observations suggest that the majority of LiF is loosely attached to the 40°C and 50°C sample surfaces, whereas it is strongly attached (chemically bonded?) to the 60°C and 70°C sample surfaces. No other peaks show any major intensity differences on rinsing, except those related to LiPF6, which are significantly reduced.
Figure 23  C1s and O1s XPS spectra for fresh and calendar-life tested LiNi_{0.8}Co_{0.2}O_2 cathode samples. Tested samples were stored at 50, 60 and 70°C at 60% SOC. Marked peaks: PVdF (▼), graphite (●), LiNi_{0.8}Co_{0.2}O_2 (○), Li_2CO_3 (◇), and additional surface layer species (↑).

Figure 24  F1s XPS spectra for calendar-life LiNi_{0.8}Co_{0.2}O_2 cathode samples, tested at 40 and 70°C, 60% SOC: comparison of unrinsed samples and samples rinsed in DEC after testing.
SURFACE PHENOMENA IN Li-ION BATTERIES

The surface species formed on LiNi_{0.8}Co_{0.2}O_{2} cathodes may result from one or more of several possibilities. Reactions between the nucleophilic LiNi_{0.8}Co_{0.2}O_{2} (negatively-charged oxygen) and electrophilic carbon in the carbonate solvents, leading to spontaneous lithium deintercalation, have been suggested [64, 71]. These would lead to the formation of lithium alkyl carbonates according to:

\[
\text{Li(Ni,Co)O}_2 + \text{ROCO}_2\text{R'} \rightarrow (\text{Ni,Co})\text{O}_2\text{-R} + \text{R'}\text{OCO}_2\text{Li} \quad (34)
\]

However, there are no indications of ROCO_2Li formation on these samples. Rather, purely organic polycarbonates are believed to be the major carbonate component. Moreover, self-discharge (lithium transport into the cathode) is observed during storage, which is a further contradiction to (34). However, electrophilic-nucleophilic interactions between oxide and solvents may still play an important rôle in the decomposition of solvents on the surface; they can for example, be responsible for the preferential deposition of surface species on the LiNi_{0.8}Co_{0.2}O_{2} particles compared to the graphite particles in the same laminate.

The observed self-discharge can give evidence of electrolyte (El) oxidation according to the general equation:

\[
\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2 + y \text{Li}^+ + y \text{El} \rightarrow \text{Li}_{x+y}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2 + y \text{El}^+ \quad (35)
\]

This type of reaction has been suggested generally for cathode materials which undergo self-discharge on storage [11]. The implication of El^+ is not clear, but removing an electron from EC, for example, could provoke a polymerisation process and hence explain the presence of polycarbonate on the surface. We have also observed polycarbonates on LiMn_{2}O_{4} electrodes, but in relatively larger amounts than for LiNi_{0.8}Co_{0.2}O_{2} [62]. These results are consistent with the conclusions drawn in that study that electrolyte oxidation could also be fed by the LiMn_{2}O_{4} disproportionation process during which solvated Mn^{2+} and lithium-rich Li_{1+x}Mn_{2-y}O_{4} are formed, or by oxygen loss from the spinel under highly delithiated conditions [103]. Such structural instabilities which could result in electrolyte oxidation are not known for LiNi_{0.8}Co_{0.2}O_{2} electrodes, and reduction of unstable Ni^{4+} in reaction (35) should be the only source for oxidation.

The instability of LiPF_6 could be another driving force for surface film formation. The hydrolysis of the LiPF_6 molecule results in LiF and Li_xPF_yO_z compounds, which are observed on all electrodes. As discussed in Section 6.2, it is not unlikely that, if PF_5 is formed in large amounts from LiPF_6 decomposition, it can act to some extent as an initiator for EC polymerisation. Zhang et al. reported that decomposition of LiPF_6, according to:

\[
\text{LiPF}_6 \leftrightarrow \text{LiF} + \text{PF}_5 \quad (36)
\]
increases markedly above room temperature, and that reactions between PF₅ and solvents produce some polymeric species [35], which would support this theory.

The presence of LiF on the cathode (and anode) surfaces may result from LiPF₆ instability (reactions (19) and (36)). Another source of LiF is the HF generation occurring in reaction (19). This is most important for LiNi₀·₈Co₀·₂O₂ and related materials with native surface impurities of Li₂CO₃ because of the favourable reactions between HF and the carbonate forming LiF [64, 101]:

\[
\text{Li}_2\text{CO}_3 + 2\text{HF} \rightarrow 2\text{LiF} + \text{H}_2\text{O} + \text{CO}_2
\]  \hspace{1cm} (37)

The HF may also react with the oxide according to the reaction:

\[
\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2 + 2x\text{HF} \rightarrow 2x\text{LiF} + \text{Li}_{1-2x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_{2-x} + \text{H}_2\text{O}
\]  \hspace{1cm} (38)

In both cases, the LiF would be adjacent to the LiNi₀·₈Co₀·₂O₂ active surface, which can have a more serious effect on cell performance than if LiF is formed randomly from decomposition reactions within the electrolyte.

The observed increase in cathode impedance with temperature could thus be due to a combination of factors which includes a thickening of the polymeric surface species, and LiF forming adjacent to the LiNi₀·₈Co₀·₂O₂ surface.
8 SUMMARY OF THE RESULTS

This work has provided some new insights into the chemical composition and morphology of surface films formed on some anode and cathode materials at ambient and elevated temperatures.

XPS has shown to be a useful technique if used carefully, providing both chemical and morphological information on the SEI layers formed on electrode surfaces. An improved morphological picture has been obtained, for example, of the SEI layer formed on a graphite electrode cycled in an EC/DMC, 1M LiBF$_4$ solution. A separation of the morphology information from the various surface components could be achieved by careful peak assignment and sputtering calibration. The methodology can be employed for other electrode and electrolyte systems.

The analysis has shown that, for the SEI layer formed in the EC/DMC, 1M LiBF$_4$ electrolyte, solvent reduction products are formed on the surface as a thin film of less than 20 Å. The majority of the polymeric/organic part of the SEI can be found on the electrolyte side of the interface, but is distributed within a thicker (up to 900 Å), highly porous layer. Large LiF crystals up to 0.2 µm in size are embedded in the SEI matrix. Synchrotron XPS has provided evidence that the SEI layer covers the graphite surface fully, but is <20 Å at its thinnest point.

XPS has also provided analytical evidence for the thermal decomposition of the SEI layer on graphite electrodes. The stability of the SEI layer formed is highly influenced by temperature. At slightly elevated temperatures (60°C), decomposition of carbonate species occurs on the surface, leading to exposure of graphite and subsequent loss of capacity on continued cycling. An additional increase in electrode resistance for graphite electrodes cycled in LiBF$_4$- or LiPF$_6$-based electrolytes could be coupled to a huge increase in LiF on the surface. Different mechanisms seem to govern its formation in the two cases. The phenomenon is totally detrimental to electrode performance at 60°C with LiBF$_4$ as electrolyte salt.

A rapid increase in temperature above 60°C leads to exothermic reactions in electrochemically cycled graphite. SEI decomposition is an exothermic reaction that is highly dependent on the choice of electrolyte salt. The SEI stability decreases with salt in the order LiN(SO$_2$CF$_3$)$_2$ > LiCF$_3$SO$_3$ > LiPF$_6$ > LiBF$_4$. The decomposition of the SEI controls the exothermic reaction between the intercalated lithium and the electrolyte.

Inactive surface films are also formed on LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathodes cycled and stored in a 1M LiPF$_6$, EC/DEC electrolyte. This film of mostly electrolyte decomposition products, consists mainly of organic/polymeric species and LiF, increases in thickness with temperature. The simultaneous increase in organic layer thickness and in amount of LiF
attached to the surface may be responsible, for at least in part, for the power-fade exhibited by Li-ion cells involving this cathode.

Surface phenomena are clearly the major factors to be considered in selecting materials for practical Li-ion batteries.
9 SUGGESTIONS FOR FUTURE WORK

In an ideal World, no other reactions would occur in a Li-ion battery than those contributing to the usable energy. However, this is not the case “in the real World”. With no electrolytes available with an electrochemical stability which matches the working potential of the Li-ion battery, surface films will inevitably form on both anode and cathode surfaces.

There is some general consensus as to what constitutes a desirable SEI layer. Carbonates, Li₂CO₃ and ROCO₂Li are good SEI components by virtue of their favourable Li⁺ ion conducting properties. By the same token, LiF is considered to be an undesirable SEI component, because of its low Li⁺ ion conductivity. Non-conducting polymers such as hydrocarbons of different types will also impede Li⁺ ion transport from the electrolyte to the electrode. The morphology and thickness of the SEI are also major factors to consider. A thicker, more porous SEI replacing the electrolyte in the space between the electrode particles results in a longer diffusion path through the SEI layer. There have been several suggestions as to how compact SEI layers can be created with a desirable chemistry, e.g., the use of electrolyte additives [49, 104-106], carbon surface pre-treatment [107-109], and a judicious choice of solvents. However, few of these approaches take account of the thermal stability in the “design” of the SEI layer. This thesis has underlined how crucial a factor this is. The surface layer that forms initially will inevitably change in both composition and morphology, which foremost will lead to loss of capacity in additional electrolyte reduction reactions. The dependence on the electrolyte salt has here been especially highlighted.

For LiPF₆- and LiBF₄-containing systems, the thermal instability of the SEI layer leading to formation of LiF, removal of carbonates, and increase in polymeric hydrocarbons are all detrimental effects, which depend on the salt instability or, more specifically, on anion type. Future work should therefore focus on anion stabilisation:

*It may be possible to “deactivate” the anion from further decomposition and reaction. In recent publications, there have been reports on the use of anion receptors in the electrolytes of Li-ion batteries [110]. The focus in these studies has been to minimise ion-pairing and, by capturing the anion, to increase the transference number for the Li⁺ ion. Both these measures lead to an increase in Li⁺ ion conductivity. The anion receptors have here been neutral molecules with one or several Lewis acid centres. It is an intriguing thought that, by tuning the Lewis acidity of the anion receptor, it may serve not only as an Li⁺ ion conductivity “enhancer” but could also improve the (thermal) stability of the SEI layer. This would be an interesting starting point for future studies.*
For the LiCF$_3$SO$_3$ and LiN(SO$_2$CF$_3$)$_2$ systems, the salt plays a minor rôle in the decomposition; the thermal stability is controlled by solvent-based reactions. Future improvements can thus be made by changing the solvent or modifying it through the use of additives:

An ideal scenario would that solvent reduction during the first cycle would result directly in thermally stable SEI products, such as Li$_2$CO$_3$, which would not deteriorate over a wide temperature range. It has long been known that a CO$_2$ additive to the electrolyte enhances electrode efficiency through the formation of a stable Li$_2$CO$_3$ layer [49, 73]. However, a pure Li$_2$CO$_3$ film would be rather rigid and could form cracks on cycling and abuse as a result of abrupt volumetric changes in the electrode matrix. Conductive polymers might here provide mechanical flexibility on charge and discharge, and under temperature fluctuations. Self-assembled monolayers (SAM’s) of hydrophobic/hydrophilic short copolymers have been shown to inhibit interfacial resistance of lithium-metal/polymer-electrolyte interfaces [104]. It could be interesting to probe further the possibility of combining the beneficial properties of Li$_2$CO$_3$ (by adding CO$_2$) and conductive polymers within the SEI layer (by adding SAM’s) from a thermal-stability point of view.

Despite innumerable publications on the subject of surface films, fundamental knowledge is still lacking as regards their formation and functionality. This is particularly true for inactive surface layers on positive electrodes. Identifying surface-related power-fade mechanisms would move EV/HEV development a major step forward. In the special case of Li(Ni,Co)O$_2$-based electrodes, basic surface characterisation should continue:

The complete surface structure of the oxide should be further characterised in terms of oxidation state variations, element enrichment and instability of the oxide structure near the surface. New experiments must be devised which combine surface-sensitivity and depth-probing in a non-destructive manner. Techniques such as TEM, STEM, synchrotron XPS and soft X-ray spectroscopy may be useful in this context. Thin-film samples can also be employed as model systems for surface studies to eliminate interference effects from binder or additives, and thereby facilitate a more absolute interpretation of the data.
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Ami Andersson
The honeycomb structure of $sp^2$-hybridized carbon atoms in graphite. Picture taken by the author at the Shell gas station in the vicinity of the Ångström Laboratory.
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