

Short communication

A new look at the solid electrolyte interphase on graphite anodes in Li-ion batteries

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Available online 19 July 2005

Abstract

The solid electrolyte interphase (SEI) of graphite electrodes has been extensively studied using surface sensitive techniques such as photoelectron spectroscopy (PES) and soft X-ray spectroscopy. By combining measurements of reference compounds with graphite electrodes cycled in different electrolytes and under different conditions, knowledge of the solid electrolyte interphase (SEI) chemistry can be obtained. In this article, conclusive results concerning the chemical composition of the inorganic part of the SEI is described. The results show that Li₂O often reported to be present in the SEI could be an artifact from abusive Ar⁺ sputtering. The presence of Li₂CO₃ is a matter of debate; the compound is not observed in anodes extracted from hermetically sealed cells that are never exposed to air. The results show that cell-design and sample handling are crucial to the observed chemical composition of the SEI.

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Keywords: Solid electrolyte interphase (SEI); Li-ion battery; XPS

1. Introduction

The Solid Electrolyte Interphase (SEI) on graphite electrode for Li-ion batteries has been studied extensively because of its duality in both protecting the graphite from co-intercalation of electrolyte solvent molecules and of consuming Li-ions in the formation of the layer leading to an irreversible loss of battery capacity [1]. However, there is still considerable debate as to the nature of the chemical species formed in the SEI during battery cycling. It is clear, however, that at potentials below 0.8 V versus Li/Li⁺ electrolyte-solvent and -salt reduction products do form in the SEI.

The general structural and morphological picture of the SEI that has emerged in recent years is one of a dense inorganic matrix consisting mainly of LiF and Li₂CO₃ close to the electrode surface and a porous organic or polymeric layer extending further out from the electrode surface; typical SEI thicknesses ranges from ~20 Å to several hundreds

of Ångströms. Large crystals of LiF are also found in this matrix (see schematic picture in Fig. 1) [2].

It is also well established that the type of lithium-ion salt used in the electrolyte will influence the ratio between the inorganic and organic components of the SEI-layer. Most salts (for instance, LiBF₄, LiPF₆, LiAsF₆, etc.) give rise to a layer of LiF close to the electrode surface. The amount of LiF and the size of the LiF crystals in this layer depend on temperature, trace impurities and reactions with the organic solvents used in many liquid electrolytes [2,3]. One reason for today's interest in the relatively new LiBOB salt (lithium bis(oxalato)borate) is that it does not form LiF during cell cycling [3].

The thermal stability of the SEI on a graphite anode also correlates with the amount of LiF in the layer. Greater LiF contents are associated with lower onset temperatures for thermally activated reactions in the SEI [4–6].

Due to the small SEI thickness (~20 Å), investigation of its chemical composition is limited to just a few experimental techniques, each with its limitations and advantages. Some of the more important techniques are: Fourier transform infrared

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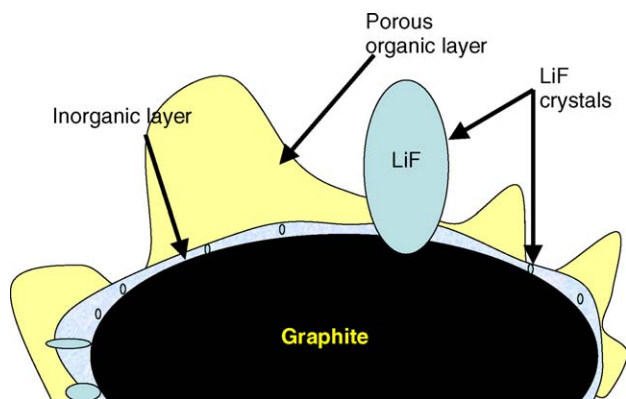


Fig. 1. A schematic picture of the SEI on a graphite particle.

spectroscopy (FTIR) [7], photoelectron spectroscopy (PES, including XPS) [2,4–7,8–10] and soft X-ray absorption and emission spectroscopy (XAS and XES) [11]. Several groups have conducted in situ electrochemical cells FTIR and confocal Raman spectroscopic studies of SEI species. However, the presence of different molecules having similar FTIR signatures and the low depth resolution ($\sim 1 \mu\text{m}$) of the confocal Raman beam, leads to a need for complementary studies using other surface sensitive techniques. In addition, some species such as inorganic salt reduction products (e.g. LiF) are not IR active and are hence not detected by the technique.

In this article, some of the different species reported to be present in the SEI will be discussed in the light of ex situ PES results based on both conventional in-house XPS and synchrotron-based PES. The SEI species investigated are the inorganic compounds, such as Li_2O , Li_2CO_3 , LiF, and salt reaction products. The results will be discussed in reference to earlier reported ex situ XPS results [9,10], and recent XAS and XES studies of SEI on graphite [11].

2. Experimental

Cell preparation and electrochemical characterisation. All cell preparation of graphite electrodes and cell cycling used for these experiments has been carried out in the same way as described in Ref. [2,4–6,8–10]. A short summary is presented here:

All electrodes were made by mixing 80 wt.% of active material with 10 wt.% carbon black and 10 wt.% binder. The electrodes were dried at 120°C over night in a vacuum furnace in an argon filled glove box (O_2 , $\text{H}_2\text{O} < 2 \text{ ppm}$). The electrolyte used was LiPF_6 in EC/DEC. The salt was dried at 80°C before mixing the electrolyte and Karl Fischer titration showed the water content to be below 10 ppm. The cells were assembled with lithium as the counter electrode, graphite as working electrode and a mechanical separator soaked in the electrolyte. The cell was sealed in a pouch cell of polymer-laminated aluminium.

Surface analyses of the electrodes by PES using Al $K\alpha$ and synchrotron radiation. The electrochemical cells were dismantled in a glove-box and small pieces of the electrodes were cut out and mounted on a sample holder and transported to the PES equipments in an Ar(g) atmosphere using a specially designed transport chamber to avoid contamination by air and moisture. Surface analysis by monochromatised Al $K\alpha$, at 1486.6 eV, was performed on a PHI 5500 system. The electrodes were dried by turbo pumping ($\sim 1 \times 10^{-6}$ Torr) in the load-lock leading to the analysis chamber for $> 12 \text{ h}$ to remove electrolyte solvents from the electrode surface prior to PES characterisation. Depth analysis in the conventional monochromatic PES was performed by Ar^+ ion beam sputtering (4 eV). The graphite peak was not discernible in all C1s spectra and the Al $K\alpha$ spectra were therefore energy calibrated against the main C1s peak set to 286.0 eV (the binding energy obtained for this peak in the spectra where the graphite C1s could be observed at 284.3 eV). To allow assessment of relative peak intensities, the C1s and O1s spectra were intensity normalised against the main C1s peak (at 286.0 eV) and the F1s, P2p and Li1s spectra were intensity normalised against the F1s peak from Li_xPF_y compounds.

The synchrotron radiation based PES measurements were performed at the beam line I411 at the Swedish National Synchrotron Radiation Laboratory MAX [12]. The excitation photon energy ($h\nu$) for a given core level was varied between 454 and 1360 eV to obtain a depth profile of the species within the surface layer. In the synchrotron radiation based PES measurements, linear background correction and energy calibration versus the main C1s peak (286.0 eV) have been applied in the data analysis. To allow an assessment of the relative amount of surface species, intensity normalisation was performed according to: C1s spectra were normalised vs. the main C1s peak (286.0 eV) and F1s spectra were normalised versus the LiPF_6 peak ($\sim 688 \text{ eV}$).

Non-conducting salt species on the analysed surfaces caused some charging effects. Therefore, peak assignments were made after calibration with reference compounds, as previously published by us [2,4–6,8–10], rather than using tabulated binding energies. Furthermore, some of the reference compounds were spin coated or simply added with a pipette on graphite anodes and then measured, to determine the binding energies on our graphite electrodes.

3. Results and discussion

There is a whole-range of different chemical substances that have been ascribed to be in the inorganic part of the graphite SEI. Here, we concentrate on the most commonly reported inorganic compounds for a closer look at their PES spectra. The aim is to obtain a clearer picture of their presence in the graphite SEI. In this article, we present results on Li_2O , Li_2CO_3 , LiF, and some other salt reduction products. The data

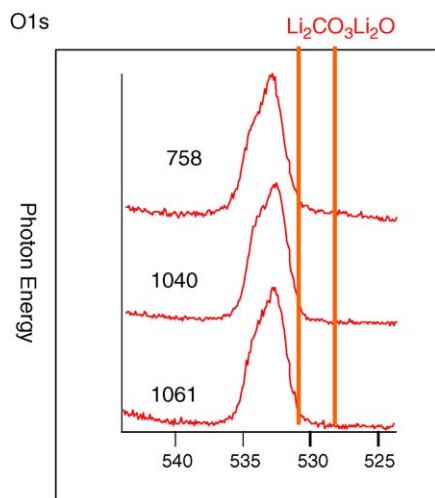


Fig. 2. The O1s depth profile of a graphite electrode cycled in 1 M LiPF₆ and EC/DEC using synchrotron based PES.

is based on graphite that has an irreversible capacity of $\sim 12\%$ during the first cycle.

3.1. Li₂O and its presence in the graphite SEI

Li₂O has been reported to be one of the compounds found close to the graphite surface. It can be formed from trace amounts of water present in the electrolyte or the composite electrodes. In our studies, by synchrotron-based XPS, we have not detected any Li₂O (see Fig. 2), which should be observable at 528.3 eV in the O1s spectrum and at 53.7 eV in the Li1s spectrum. However, depth profiles obtained using Ar⁺ sputtering always show Li₂O. We have shown earlier, using Li₂CO₃ as a model compound, that Ar⁺ sputtering generates Li₂O (Li₂CO₃ → Li₂O + CO₂) after some minutes of sputtering (Fig. 3). The previously reported Li₂O could therefore be an artifact of the sputtering process rather than a true SEI component.

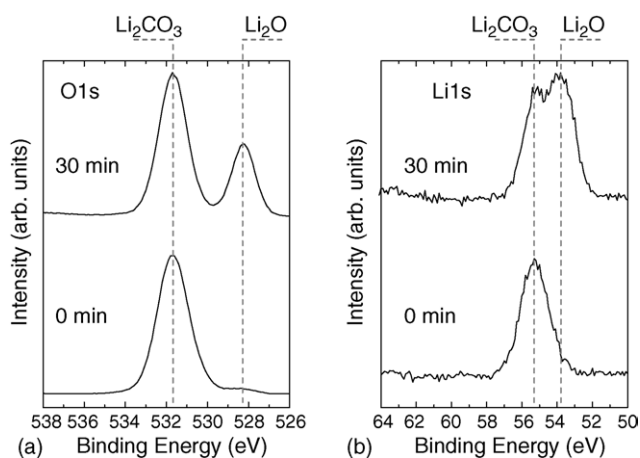


Fig. 3. O1s spectrum (a) and Li1s spectrum (b) of Li₂CO₃, non-sputtered and Ar⁺ etched 30 min.

3.2. Li₂CO₃ and its presence in the graphite SEI

Li₂CO₃ has been reported to be one of the important products of the SEI. This has resulted in successful tests to pre-treat a graphite surface with Li₂CO₃ to reduce the irreversible capacity [13]. There are also reports of more complex organic species present in the SEI converting to Li₂CO₃ at elevated temperature [14]. However, there are also a number of situations where Li₂CO₃ has been reported not to be present or not to be the main compound dominating the room temperature SEI [7,8]. The factors that can explain Li₂CO₃ absence may include the following: (a) Li₂CO₃ is not formed in the cell at any stage; (b) Li₂CO₃ forms but reacts with trace amounts of HF from the electrolyte to form LiF, water and CO₂; (c) Li₂CO₃ forms but reacts with PF₅ to form CO₂, P-O type compounds, and LiF. The presence of Li₂CO₃ appears to depend on the moisture content of the electrolyte and the type of cell used. Anodes extracted from better-sealed cells, such as the coffee-bag (pouch) cells, are less likely to show Li₂CO₃ than commonly used cells.

To test the influence of air and moisture, cycled graphite electrode surface was exposed to air for 3 h and then the PES spectrum was taken. A clear difference is seen in both the ratio between the different oxygen-species present implying a larger amount of Li₂CO₃ in the air-exposed sample (Fig. 4a), and in the broadening of the peak to lower photon energies. Not even Ar⁺ etching the electrode reveal any larger amounts of Li₂CO₃ (see Fig. 4b). This can be compared to our synchrotron based PES results where the depth profile also shows very little present Li₂CO₃ close to the electrode surface and no Li₂O (Fig. 2). The effect of air on the SEI is also clearly seen in the C1s spectrum (Fig. 5) where the most of the organic species containing functional groups such as –C–O– (at 286 eV) have reacted and left the surface forming most likely forming CO₂ so that the –C–H– species (at

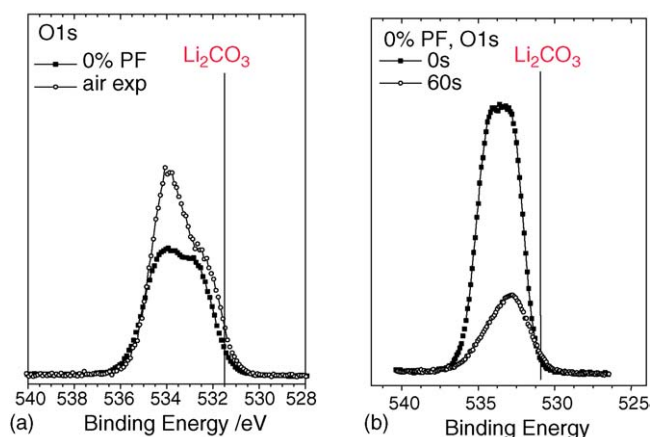


Fig. 4. O1s XPS spectra of a graphite electrode cycled one time non-exposed and exposed to air for 3 h (a) compared to an O1s spectra of sputtered and non-sputtered cycled graphite electrode (b). All electrodes have been cycled in LiPF₆ EC/EMC.

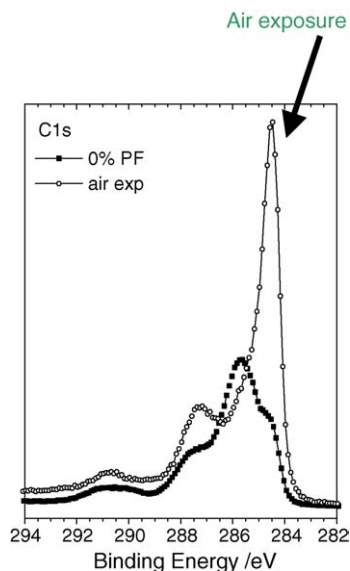


Fig. 5. Influence of air on the C1s spectrum of a graphite electrode cycled in LiPF_6 EC/EMC.

285 eV) become dominant. These data indicate that careful sample transfer into the spectrometer is very important for reliable results.

Results based on soft X-ray spectroscopy, and in particular selective excitation resonant X-ray emission spectra, are also in agreement with our PES results. Comparing the graphite SEI spectra with those from reference compounds showed that Li_2CO_3 was not present in the SEI [11].

3.3. LiF, salt-reduction products, and their presence in the graphite SEI

LiF may form as a by-product of Ar^+ etching. Our model sputtering studies of the pure salts, LiBF_4 and LiPF_6 , show that LiF are formed. LiF is easily distinguished in the F1s XPS spectra at 686 eV that is significantly lower binding energies than other fluorine containing species [2,4,5–10]. During electrochemical cycling of the cells there are, however, many reactions leading to LiF formation [14]. In particular, there is an increased amount of LiF formed as a function of temperature [2,3,8]. For cells stored at elevated temperatures and displaying different amounts of power fade there is also a correlation with increased amounts of LiF [5]. The LiF formed is distributed as large crystals in the SEI-matrix. The size of the crystals is dependent on salt used in the electrolyte, cycling temperature, and storage conditions. Rinsing cycled electrodes will mechanically remove LiF crystals, which also influences the amount of material available for analysis [15].

Salt reduction products consisting of Li_xPF_z are commonly observed in the SEI [1,3,5,6,8–11]. In some cases also $\text{Li}_x\text{PF}_y\text{O}_z$ is detected. A part of the detected increase of LiF is a result of sputter-induced decomposition of these

compounds [8]. Ar^+ sputtering seems also to induce new P-bonds, probably P–O or P–P, spectra as seen on sputtering of model compounds such as LiPF_6 and LiPF_6 in EC/DEC on a graphite surface [10]. Rinsing the electrodes results mainly in a decrease in the amount of Li_xPF_z and an increase in $\text{Li}_x\text{PF}_y\text{O}_z$ due to uncovering of the compound close to the electrode surface. During exposure to air Li_xPF_y is observed to transform to $\text{Li}_x\text{PF}_y\text{O}_z$ [8].

Because of the influence of sample preparation, handling procedures and sputtering conditions, quantitative analysis of the content of LiF and the salt reduction components Li_xPF_y and $\text{Li}_x\text{PF}_y\text{O}_z$ should be undertaken with caution.

4. Conclusions

The following conclusions are based on data from our various PES analyses:

- Li_2O detected in the SEI by depth profiling can be an artifact of Ar^+ sputtering
- Li_2CO_3 is not always observed in the SEI. The graphite-type, electrolyte quality and hermetic-seals on the lithium-ion cells may influence the presence and quantity of Li_2CO_3 . Additional work is needed to conclusively identify the effect of these parameters.
- LiF is formed during cell cycling; the amount measured in the SEI is influenced by several factors that include storage temperature, cycling duration, and the type of lithium salt in the electrolyte. LiF can also be generated by Ar^+ etching.
- Careful sample preparation and handling are important to determine the true constituents of the graphite SEI. Reactions with air and rinse solvents and air can introduce artifacts, and alter the SEI composition.

This is part of an on-going study of SEI characterisation using surface sensitive chemical analysis techniques. The work is now focused on organic compounds in the SEI.

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