



The Buried Carbon/Solid Electrolyte Interphase in Li-ion Batteries Studied by Hard X-ray Photoelectron Spectroscopy



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ABSTRACT

In cycled Li-ion batteries, the carbon negative electrode is buried under a thin passivating layer referred to as the solid electrolyte interphase (SEI). In the present study, the increased depth sensitivity of hard X-ray photoelectron spectroscopy (HAXPES) as compared to conventional X-ray photoelectron spectroscopy (XPS) is used to study electrochemical changes at such a buried carbon/SEI. Samples from graphite/LiFePO₄ cells cycled to specific potentials during the first four charge/discharge cycles were studied. The results show dynamic changes in the SEI during cycling. Reversible, state of charge (SOC) dependent changes in the SEI thickness as well as amounts of lithium oxide, lithium fluoride, lithium and carbon active material were discussed. Moreover, the results indicate lithium enrichment close to the carbon active material surface, which could not be explained by intercalation of lithium into carbon with LiC₆ structure or by SEI formation at the surface. Potential dependent shifts in the binding energy of the carbon active material C1s feature showed the importance of internal energy calibration with an SEI feature rather than carbon active material.

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1. Introduction

Lithium-ion batteries are highly interesting as energy storage devices replacing fossil fuels in mobile applications like electric vehicles. Their high energy density, compared to many alternative rechargeable battery technologies, is an important property for such applications. The higher energy density is largely related to a higher cell voltage (~4V), which is due to the low electrochemical potential for lithium intercalation into the commonly used graphite-based negative electrodes. The low lithium intercalation potentials of graphite, however, present challenges with respect to unwanted side reactions and thus electrolyte stability. During the first lithiation, a passivating layer is formed on the surface of the graphite particle thus burying the active electrode. This passivating layer is known as the solid electrolyte interphase (SEI) [1,2]. The SEI minimizes the direct contact between the carbon electrode and the liquid electrolyte, and thereby significantly decreases further electrolyte reduction.

The surface sensitivity of X-ray photoelectron spectroscopy (XPS) has been extensively utilized to characterize the composition of lithium-ion battery electrode/electrolyte interfaces [3–5]. However, in many cases the probing depth of traditional XPS is too small to enable characterization of the entire SEI and specifically the relation between the carbon active material and the SEI. Traditionally, sputtering has been used to remove material from the electrode surface to gain access to deeper parts of the SEI and the active material. The interpretation of results from sputtered SEI layers, however, suffer severely from sputter induced transformations [6,7]. Hard X-ray photoelectron spectroscopy (HAXPES) gives new possibilities to characterize the interface in a more reproducible way without using sputtering. Specifically HAXPES enables investigation of not only the entire SEI but also of the buried carbon underneath. Hence, HAXPES presents an attractive alternative for more reliable studies of the deeper parts of the SEI as well as the carbon/SEI interface.

Previous XPS studies of the SEI on graphite based electrodes have shown state of charge (SOC) related variations in the carbon core level signals, including intensity changes proposed to stem from a thicker SEI on lithiated than on delithiated graphite electrodes [8,9]. Such changes could be interpreted as SEI instability during cycling, and may be related to chemical reactions giving rise to

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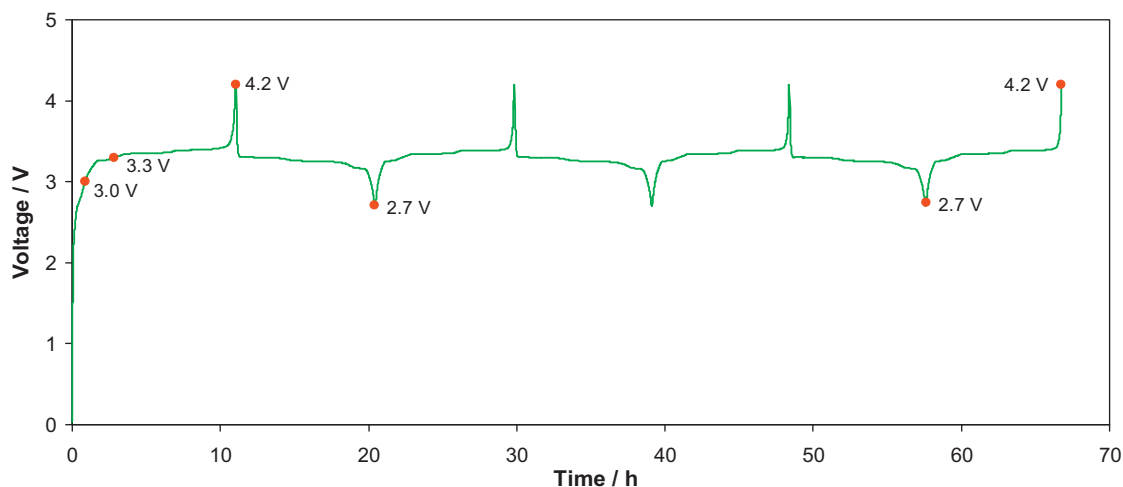


Fig. 1. Cycling curve for a graphite/LiFePO₄ cell galvanostatically cycled for 3.5 cycles between 2.7 V and 4.2 V. To study the SEI evolution using HAXPES, the cycling was stopped at the different states marked by red dots in the figure.

capacity loss during cycling and consequently to cell aging. In the present work, the increased depth sensitivity of HAXPES compared to conventional XPS has been used to study the relation between the carbon active material and SEI signals in samples with different states of charge. Changes in the intensity of the carbon active material feature (and consequent variations in estimated SEI thickness), its relation to the variations in lithium intensity as well as state of charge related variations in the relative binding energies of the carbon active material and SEI features are discussed, rendering new insights into the buried interface.

2. Experimental

Graphite/LiFePO₄ pouch cell batteries (vacuum-sealed polymer coated aluminum bags) were assembled inside an argon filled glovebox (≤ 1 ppm H₂O, O₂), as described in detail elsewhere [5]. The electrode slurry for the negative electrode contained a mixture of carbon materials (85 wt% potato-shaped graphite, 3 wt% KS6 graphite, 2 wt% Super P carbon black, and 10 wt% vinylidene fluoride trifluoroethylene copolymer, Kynar binder). The slurry was coated onto a copper current collector (13 μ m thickness). The electrode slurry for LiFePO₄ (75 wt% carbon coated LiFePO₄, 10 wt% Super P carbon black and 15 wt% Kynar binder) was coated onto an aluminum current collector (20 μ m thickness). Negative and positive electrodes were balanced to obtain an overcapacity of 20% for the negative electrode (the negative electrode was thus never fully lithiated). 1 M LiPF₆ in EC:DEC 2:1 electrolyte and Solupor separator were used. Electrodes and separators were dried in a vacuum oven overnight inside the glove box prior to cell assembly.

Cells were galvanostatically cycled between 2.7 V and 4.2 V at C/10 for up to 3.5 cycles. The cycling was stopped at different potentials as indicated in Fig. 1. A high potential corresponds to a high SOC of the cell. Cells cycled to 3.0 V during the first charge and 2.7 V during the following cycles correspond to 0% SOC (delithiated carbon), the cell cycled to 3.3 V corresponds to around 19% SOC (partially lithiated carbon) and cells cycled to 4.2 V correspond to around 100% SOC (the amount of lithiated carbon that is possible due to cell balancing). The SOC is thus estimated from the practical capacity of the cell. The sample stopped at 4.2 V in fourth cycle was discussed in our previous study [5] and is in this paper included as the final step in the series investigating SOC dependent variations.

HAXPES measurements were performed at the KMC-1 beamline at the BESSY II synchrotron (Helmholtz Zentrum Berlin, Germany) [10] using the HIKE end-station [11] and 2300 eV excitation energy. The electron take-off angle was 80° and the take-off direction was co-linear with the e-vector of the incident photon beam. The cycled batteries were opened inside an argon filled glove box (≤ 1 ppm H₂O, 1 ppm O₂) and transferred from the glovebox to the HAXPES vacuum analysis chamber using specially built equipment [12] enabling transfer without exposure to air. A number of measures were taken to minimize measurement related changes in the sample composition, as described in more detail elsewhere [5].

Generally, an internal energy calibration is used on these kinds of samples. In the present study the hydrocarbon C1s feature is used as a reference peak. This peak, referred to as C-H, is arbitrarily set to 284.4 eV. This choice of internal calibration generally gave a practical representation of the SEI peak positions. However, it is important to note that different choices of calibrations such as using the substrate Fermi level or using the cut-off for proper vacuum level measurements give another set of values. This is discussed further in the paper. Shirley type backgrounds were applied. The curve fitting and energy calibration followed procedures that are presented in more detail elsewhere [5]. The transmission function of the analyzer was approximated to be constant for the different core levels since the kinetic energy distribution of collected electrons was relatively narrow in the present investigation. Hence, a measure of the amounts can be obtained by traditional atomic percentages obtained from the relative intensities of the different elements, I_j , corrected for the Scofield cross section (σ) [13,14]. In each set of presented core level spectra, the intensities are normalized using the obtained relative atomic percentages of that element in the respective sample. A comparison can thus be made between different samples for the same core level, however not between different core levels, where instead the atomic percentages diagram should be used. For the inhomogeneous interface layers, like the SEI, the comparison between the atomic percentages shows important differences between the samples. However, absolute values can only be obtained from homogeneous samples, due to the attenuation of the HAXPES signal.

SEI thicknesses, d , were estimated based on the relative intensity of the carbon active material feature, I_{LiXC} . This was made using the approximation that the electrode below the depth d consists of

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