

Applications Note

XPS analysis of solid-electrolyte interphase layer formed on a lithium-ion battery negative electrode

MO496(A)

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Overview

This applications note demonstrates the use of both conventional (Al K α) and higher photon energy (Ag L α) excited X-ray Photoelectron Spectroscopy (XPS) to characterise the solid electrolyte interphase layer formed on a graphite anode during charge/discharge cycles. Samples were prepared in a glove box at the manufacturing site and transported to the XPS analysis laboratory using an air sensitive sample transport accessory.

Introduction

The use of lithium-ion batteries (LIBs) as high energy density storage devices for modern electronic consumer goods is ubiquitous. However, there are a number of technical challenges such as growth of insulating secondary electrolyte interphase (SEI) layers at the interface between the negative anode and electrolyte.

The formation of a solid-electrolyte interphase layer on Li-ion battery anodes is important to the overall performance of the battery. In order to be effective, the SEI must be Li-ion conducting, allowing Li-ion transport through the layer and into the negative electrode. However, it must also be electronically insulating to prevent continuous reduction of the electrolyte.

An understanding the chemical state of the SEI as a function of charge-discharge cycles can be gained using X-ray photoelectron spectroscopy. (XPS). The investigation of battery materials during operation can be undertaken by carefully dismantling manufactured battery cells that have undergone a number of charge/discharge cycles.

Experimental

The battery structure under investigation have a graphite anode with LiPF₆ and DMC electrolyte material. The separator material is Celgard 2500. The coin-cell type LIBs were disassembled in an Argon filled glovebox at the manufacturing site. The measured oxygen concentration during sample preparation was 0.28 ppm and dew point –86.8 °C ensured that there were no changes in sample chemistry during disassembly. Samples were transported from the manufacturer to the XPS analysis lab. using the air-sensitive sample transporter (Kratos part number WX-663). This ensured that the LIB samples were not exposed to ambient conditions prior to introduction to the photoelectron spectrometer.

Three battery states studied are:

1. As manufactured (no charge / discharge)
2. Single charge / discharge cycle
3. 100 charge / discharge cycles.

XPS analysis was conducted using the monochromatic Al K α and Ag L α excitation sources. Spectra were collected in large area (700 x 300 μ m) mode, ensuring best sensitivity to low cross section core level photoemission peaks.

Results and Discussion

Al K α excited survey spectra, shown in figure 1 were acquired from graphite anodes of the battery samples.

The photoemission peaks observed in the survey spectra indicated that electrolyte material as well as the graphitic

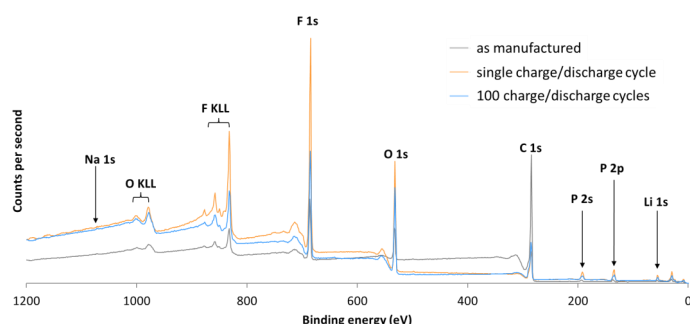


Figure 1: XPS survey spectra from graphite electrode for 3 battery samples with different number of charge/discharge cycles.

electrode were present. Quantification of the spectra showed that relative concentration of both Li and F increase and C decreases as the battery undergoes charge/discharge cycles.

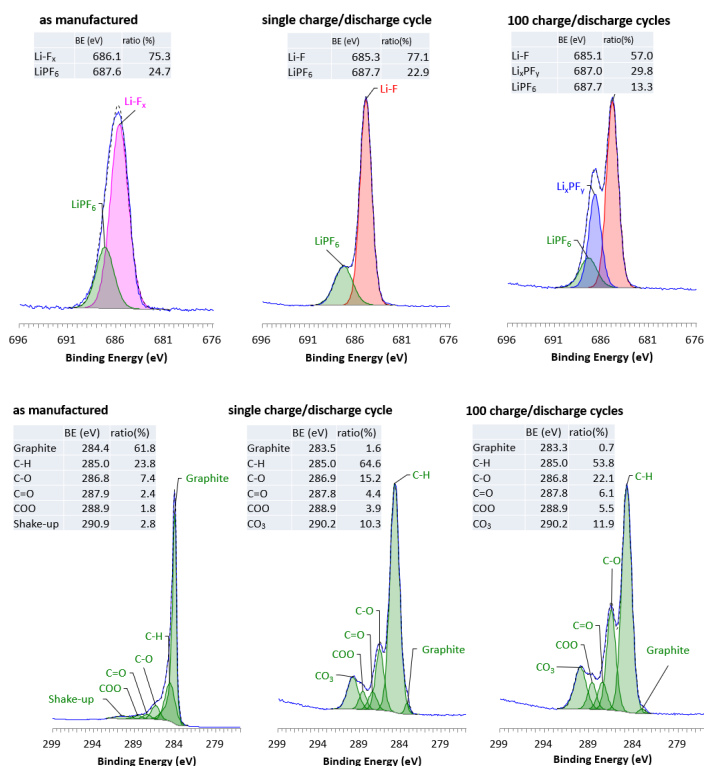


Figure 2: F 1s (top) and C 1s (bottom) narrow region scans as a function of the number of charge/discharge cycles.

This observation is complemented by high energy resolution scans of the elements to provide insight into chemical changes resulting from the charge/discharge cycles.

From the curve-fitted F 1s spectra shown in figure 2, it is noted that even the uncycled, as manufactured battery, shows some degradation of the bound LiPF₆ electrolyte material to LiF_x. After the single charge/discharge cycle a peak assigned to LiF is observed in the SEI layer formed at the anode. After further cycles the chemistry changes further with Li_xPF_y decomposition products of the electrolyte material included in the SEI layer.

The C 1s spectra acquired from the anode are also shown in figure 2. The C 1s envelope from the as-manufactured battery is dominated by the asymmetric graphitic peak at 284.4 eV binding energy as well as a hydrocarbon-like component at 285.0 eV. There are also several components associated with carbon bonded to oxygen, ether C-O (286.8 eV), carbonyl, C=O (287.8 eV) and ester, -O-C(=O)- (288.9 eV). After a single charge/discharge cycle the graphitic carbon component is significantly attenuated by the organic oxygenated species. A component assigned to a carbonate group -CO₃ (290.2 eV) is also measured, which increases further in the 100 cycle SEI layer.

Figure 3a shows the changes induced in the carbon chemistry

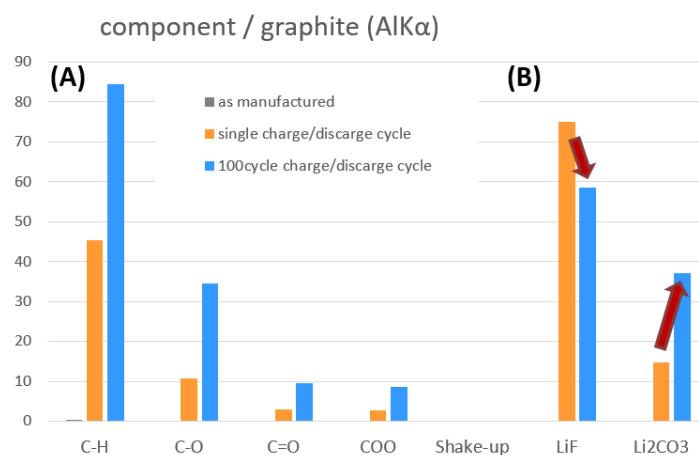


Figure 3: (a) change in the carbon species identified in figure 2 relative to the as-manufactured anode surface. (b) change in the relative concentration of the LiF and Li₂CO₃ species as a function of charge/discharge cycles relative to the graphite component.

relative to graphite component of the uncycled graphite anode. This highlights the increase in hydrocarbon and carbon-oxygen species induced by the charge/discharge cycles. The attenuation of the graphite component suggests that the SEI layer thickness is ca. 8–9 nm, the sampling depth of Al K α excited C 1s photoelectrons.

Figure 3b shows that the LiF concentration decreases, whilst the Li_2CO_3 increases as the number of cycles increases.

It is proposed that the SEI layer measured at the surface of the anode is composed of both organic carbon containing materials and inorganic LiF , Li_xPF_y and Li_2CO_3 .

XPS measurements were repeated for the same samples using the higher photon energy $\text{Ag L}\alpha$ monochromatic X-ray source. The C 1s high resolution scans are shown in Figure 4.

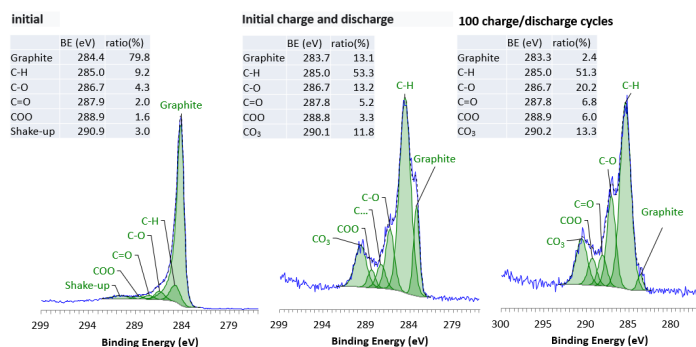


Figure 4: $\text{Ag L}\alpha$ excited C 1s narrow region scans as a function of the number of charge/discharge cycles.

Using the higher photon energy source to measure the C 1s region is adventitious in this study as the sampling depth is increased by approximately a factor of two. The greater sampling depth is demonstrated by the increased graphitic signal relative to the organic content for samples. The SEI layer at the outermost surface layer contributes less to the sampled volume. Using the higher kinetic energy peaks to measure deeper into the sample is preferable to removing the surface

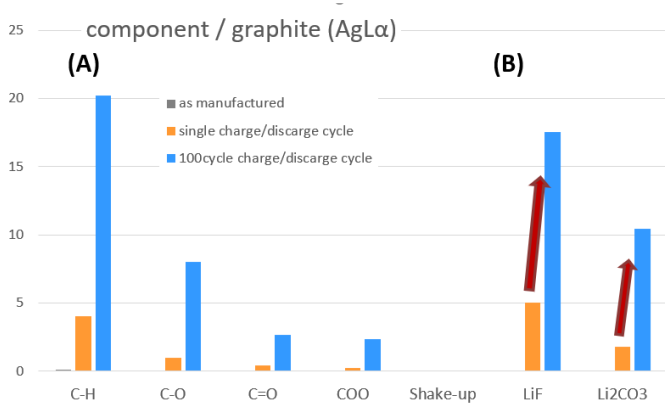


Figure 5: (a) change in the carbon species identified in figure 4 relative to the as-manufactured anode surface. (b) change in the relative concentration of the LiF and Li_2CO_3 species as a function of charge/discharge cycles relative to the graphite component.

layer by sputtering as this process could easily result in preferential sputtering or ion-induced stoichiometric changes of mobile atoms within the surface layer.

Figure 5 shows the ratio of carbon containing species for the cycled batteries relative to the graphite component measured using the $\text{Ag L}\alpha$ excitation source. A similar increase is observed for the organic and inorganic species with increasing number of charge/discharge cycles. In contrast to the $\text{Al K}\alpha$ excited spectra, the relative change for the LiF and Li_2CO_3 species are both seen to increase as the number of charge/discharge cycles increases.

The increase in the LiF concentration using the $\text{Ag L}\alpha$ excitation

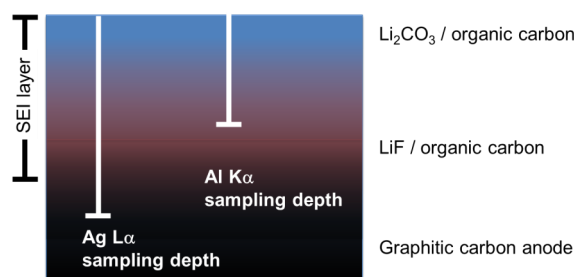


Figure 6: Schematic diagram of the SEI layer structure after 100 charge/discharge cycles.

source suggests that the LiF is formed closer to the anode surface, deeper into the sample. The Li_2CO_3 chemistry is thought to be located closer to the outermost surface. A schematic model for the SEI layer structure is shown in figure 6.

Conclusions

An air-sensitive sample transporter device was successfully employed to move samples from manufacturing site to the spectrometer without exposure to ambient conditions. XPS was used to characterise the SEI layer formed on a graphite anode after a single charge/discharge cycle and also 100 charge/discharge cycles. It was confirmed that the SEI layer is composed if mainly organic carbon materials, LiF , Li_xPF_y and Li_2CO_3 . Using the $\text{Ag L}\alpha$ higher photon energy source it was possible to determine that the LiF was formed closer to the anode, below the Li_2CO_3 .

Acknowledgement

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