Morphology Study of the SEI Layer in Lithium-Ion Batteries Under Plating Conditions

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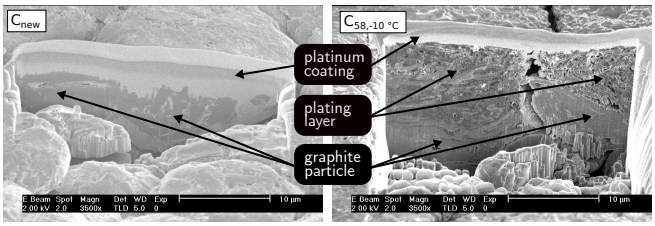
Abstract

Lithium plating as a more and more important ageing mechanism in modern lithium-ion batteries (LIB) is still not fully understood. Especially the impact of the solid electrolyte interphase (SEI) layer on plating and vice versa is still subject of many questions. Optical measurements have shown that during the plating process a porous layer grows on the anode surface which is significantly thicker than the SEI under normal operating conditions. The composition of this layer most likely consists of degenerated electrolyte and inactive metallic lithium that lost electrical contact with the anode and can no longer be utilized in the cell reaction. To obtain a better understanding of the layer and the plating process in general, Focused Ion Beam (FIB) cross sections of opened 18650 round cell anodes have been optically analyzed and their surface has been investigated regarding the chemical composition using X-ray Photoelectron Spectroscopy (XPS) measurements.

Measurements

FIB cross sections

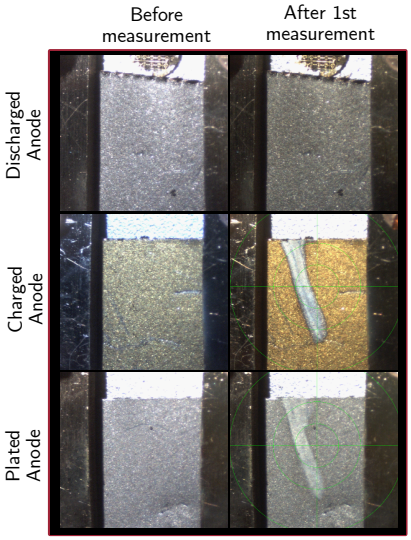
- Cross sections have shown that the plating process creates a significantly thicker layer than the normal SEI growth.
- Normal SEI = 40-80 nm, plating SEI > 5 µm (58 cycles)



FIB cross sections of a new LIB anode (left) and a plating aged anode (right)

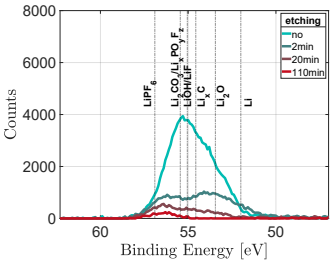
XPS surface analysis

- XPS allows an elemental surface composition analysis with a very low penetration depth (8-10 atomic layers - ca. 2 nm) and is capable of detecting lithium.
- Argon assisted etching was used to obtain data for different depth profiles to detect changes in the material composition.
- The surface of the samples showed significant changes during the measurement.
- Further experiments showed that the surface changes only appeared on samples that are fully charged or have recently been plated.
- The surface changes also influenced the XPS spectra.
- The effect was identified as electron induced lithium plating [1]. It occurs only if the sample is not electrically isolated due to a double layer forming on the surface of the sample.



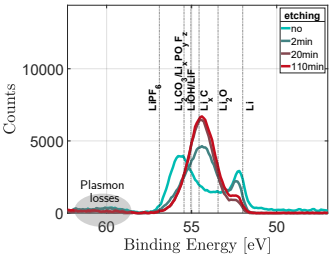
Results

Fully discharged graphite: C_6



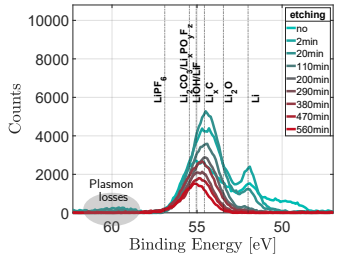
- Expectation: SEI layer with lithium content in various compounds. Etching should reduce the lithium content.
- Observation: Lithium content decreases during etching. No plasmon losses visible. Lithium metal line is not clearly identifiable.

Fully charged graphite: LiC_6



- Expectation: Surface similar to discharged sample (SEI). Etching should reveal more lithium content in the LiC_6.
- Observation: Stronger lithium compound peak on the surface. Deeper etching reveals two distinct peaks. Possible lithium metal presence due to visible plasmon losses [2].

Fully discharged graphite with plating (1 cycle): C_6



- Expectation: Different SEI composition due to the plating effect. Metallic lithium within the SEI layer.
- Observation: Possible lithium metal presence due to visible plasmon losses, especially at deeper etching levels. Lithium metal peak could also be present.

➡ For the plated sample the etching was continued stepwise to a total time of 560 minutes until the C peak resembled the normal C_6 peak. Normal SEI is 40-80 nm, which was penetrated after 110 minutes - plating layer thickness (after 1 cycle) approx. 0.2-0.4 µm.

➡ Increased metallic lithium presence in the first etching steps for plated and discharged anode. This is most likely caused by the electron induced plating effect.

Conclusion

For LIB materials the destinction between the present elements and compounds is very hard since the common materials often have binding energies that are very close to each other. It is however clearly visible in the peak at 52 eV and the corresponding plasmon losses of the fully charged and plated samples that metallic lithium is present on the surface of the sample. Keeping in mind the penetration depth of the XPS measurement of only two nanometers this amount of lithium should not be present on the surface and thus must be caused by the electron induced plating effect. A migration of lithium to the surface of the fully charged sample is to be expected since there is lithium present in the anode bulk material. For the plated samples this means that there must be more lithium available in or close to the SEI to show an equal peak in the spectrum and also a visible change on the surface during the measurement compared to the discharged sample, that shows neither the peak in the spectrum nor any change on the surface. This means that even after only one cycle of plating the SEI of the plated sample must either have a different composition or there must be dead lithium in the SEI. Additionally, the electron induced plating effect could be used as an instrument to spatially identify plating outside of the XPS environment in the future.

References

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