Application note

XPS depth profiling of lithium metal anodes for batteries using femtosecond laser ablation

Keywords
Lithium metal batteries, lithium-ion batteries, anode-free batteries, XPS depth profiling, solid electrolyte interphase (SEI), femtosecond laser ablation

Introduction

Lithium metal and anode-less battery systems potentially offer a pathway to increased energy density compared to cells with graphite anodes[1, 2]. The anode is lithium metal, which is either built into the cell from the start, or, in the case of anode-free designs, plated onto the current collector by transfer from the cathode in the first charging cycle. During repeated charge and discharge cycles, the surfaces of the anode and cathode change, with new layers forming and the structure of the surface becoming altered. Adapting the surface chemistry of the electrodes is one way to control these effects and prolong the useful lifetime of the cell.

The solid-electrolyte interphase (SEI) layer develops at the surface in the first cycle of the cell. This layer is a chemically heterogeneous structure composed of inorganic and organic species formed from components of the electrode and the electrolyte. The SEI layer is critical to understanding how the cell's performance changes over its lifetime. Measuring its initial formation and how it develops after a differing number of cycles is crucial.

X-ray photoelectron spectroscopy (XPS) depth profiling is widely used for this purpose. It has the depth resolution and chemical sensitivity necessary to investigate composition changes at nanometer depth scales.

There are several additional reasons why the technique has been adopted by battery researchers:

- XPS is good at detecting lithium, which can be difficult with other analytical methods
- XPS operates in vacuum conditions, protecting the air-sensitive materials from changing due to air exposure; it is also very easy to transfer samples into instruments from the glove box where the cell is disassembled
- XPS systems are usually equipped with sources for depth profiling, which makes it possible to measure changes in chemistry from the outer surface into the bulk of the material

Historically, monatomic argon ion beams have been used for depth profiling. But in the last fifteen years, gas cluster ion beams (GCIB) have become more widely used, and they have some advantages for analyzing lithium compounds.

Both ion beam methods can have drawbacks, however. The chemistry of the SEI layer can be quite sensitive to ion bombardment, and it is easy for both monatomic and gas cluster ion beams to cause chemical modification to the sample surface. Cluster ion beams have very different etching rates for organic and inorganic materials, which can lead to inconsistent removal of SEI components.

Femtosecond laser ablation (fs-LA) has recently been introduced as an alternative to ion beam methods. Fs-LA uses a very different mechanism for material removal: Rapid ionization of the surface causes a Coulombic explosion, where the ionized surface atoms repel each other to cause rapid material removal in the affected region. The femtosecond timescale regime is important. It prevents heating effects in the remaining sample, which could otherwise damage the chemistry.

In this application note, we show how the Thermo Scientific™ Hypulse™ Surface Analysis System was used to investigate the SEI layer formed on a lithium metal electrode using monatomic ion beam depth profiling, GCIB depth profiling, and fs-LA depth profiling.

The experiment

A lithium metal anode was cycled through one charge-discharge cycle using graphite as the cathode and LP572 as the electrolyte. A single charge-discharge cycle has been found to be sufficient for creating the SEI layer and avoids significant roughening of the surface, which could degrade the depth resolution of the XPS depth profile.

Different regions of the sample were depth profiled in the Hypulse System using monatomic argon ions with a beam energy of 4 kV, a gas cluster ion beam with an average cluster size of 300 atoms and a beam energy of 8 kV, and femtosecond laser ablation with a beam energy of 250 µJ and an elliptical ablation area with a long axis of 250 µm. A 50 µm X-ray spot was used to collect XPS data from each depth profiling method, and rapid snapshot spectrum acquisition was employed. The built-in charge neutralization system was used to ensure that insulating components in the surface did not cause sample charging during the experiment.

Results and discussion

Depth profiling of the electrode sample demonstrated the value of combining XPS analysis with fs-LA for chemically complex Li-ion battery materials. The fs-LA experiment provided rapid access to sub-surface chemistry while retaining chemically resolved information from key battery-relevant species, including Li, F, O and P. The fs-LA XPS depth profile, shown in Figure 1, reveals a heterogeneous near-surface region containing a range of different species. The surface region shows the presence of $LiPF_6$ crystallized at the surface from the electrolyte solution. Lithium fluoride (LiF) is also evident, where the salt from the electrolyte has reacted with the electrode.

Below the surface region, there is evidence of Li_2O, Li_3N, and $LiPO_2F_2$ in low concentrations together with some lithium carbide. The SEI layer is relatively thin, just a few tens of nanometers, and metallic lithium can be seen beneath it. This ability to directly track lithium chemistry is particularly important because lithium speciation is central to understanding degradation, passivation, and interphase formation in battery materials.

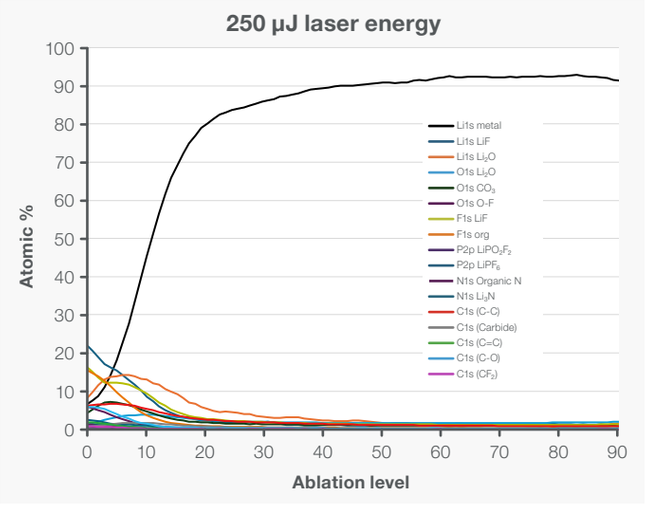

Figure 1: Fs-LA XPS depth profile of the electrode.

In comparison, argon gas cluster ion profiling provided a gentler sputtering approach for organic-rich surface layers but shows limitations for this sample. The cluster profile, shown in Figure 2, exhibits a slow etch rate through the Li-F compounds, and there is also evidence of preferential removal of organic carbon species relative to the inorganic components. No metallic lithium is observed in the Li 1s spectra through the entire profile. Four representative spectra spaced through the profile are shown in Figure 3, with spectra from the fs-LA profile for comparison. This suggests that, although cluster sputtering can preserve some molecular information, it may not efficiently expose or represent buried inorganic lithium-containing phases in mixed organic/inorganic battery interfaces.

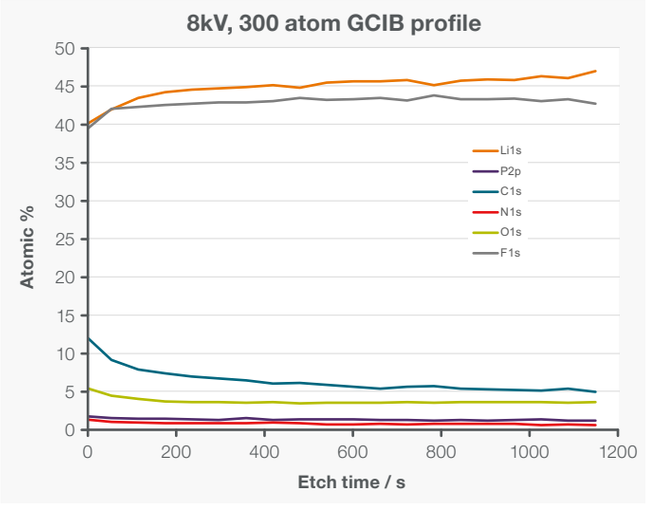

Figure 2: 8 kV 300 atom GCIB depth profile of the electrode.

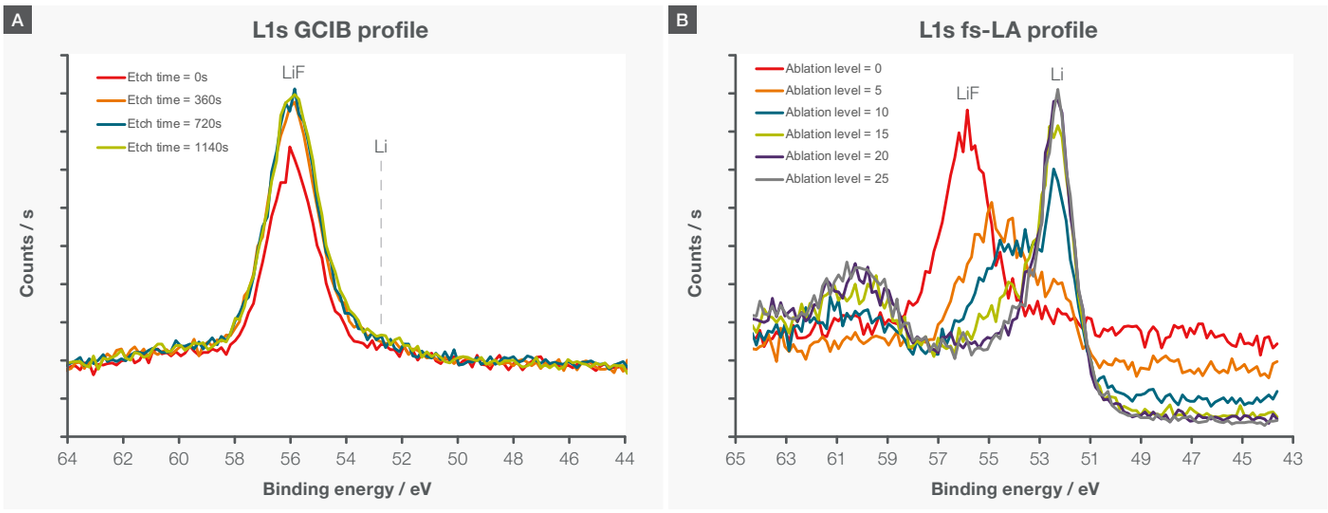

Figure 3: Li1s XPS spectra from (a) the GCIB depth profile and (b) the fs-LA profile. Only a peak due to LiF is seen in the GCIB profile, and no evidence of metallic lithium is observed. Metallic lithium is clearly seen in later levels of the fs-LA profile.

Monatomic Ar^+ profiling offers faster material removal than clusters, but the results show evidence of ion beam damage. Comparison of the P 2p spectra from the 4 keV Ar^+ and fs-LA profiles, shown in Figure 4, indicates changes to the phosphorus chemistry during ion bombardment, consistent with beam-induced modification of sensitive phosphate or P-F species, likely $LiPF_6$. This damage complicates interpretation of the true interfacial chemistry.

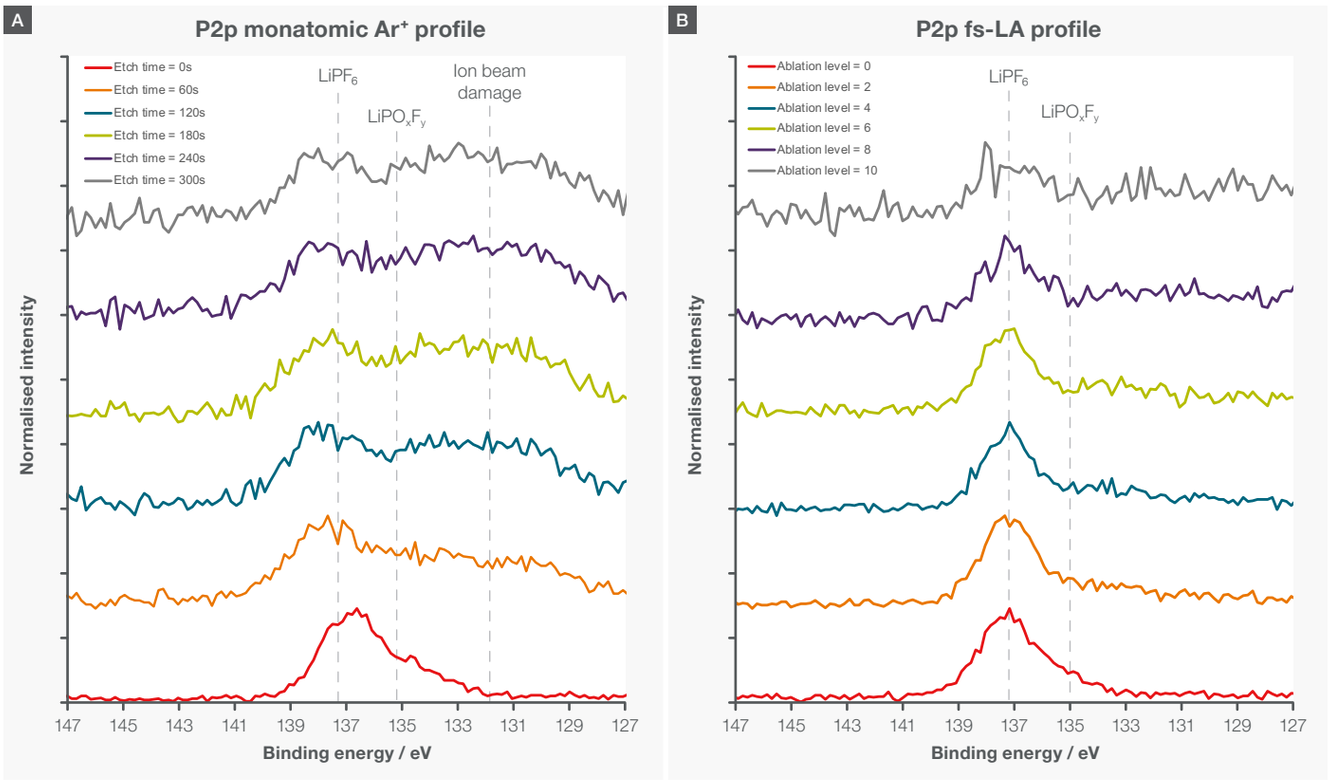

Figure 4: P2p XPS spectra from (a) the monatomic Ar⁺ depth profile and (b) the fs-LA profile. P-F chemistry is modified by exposure to the monatomic ion beam, but not by fs-LA.

Conclusion

Overall, fs-LA XPS depth profiling provides a compelling alternative approach for analyzing Li-ion battery materials, combining rapid material removal, small-area targeting, and preservation of diagnostically useful chemical-state information. Unlike conventional ion beam approaches, fs-LA can access buried layers that contain lithium without the same degree of preferential sputtering or ion-induced chemical alteration, enabling a more reliable reconstruction of complex battery interfaces.

Acknowledgements

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References

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