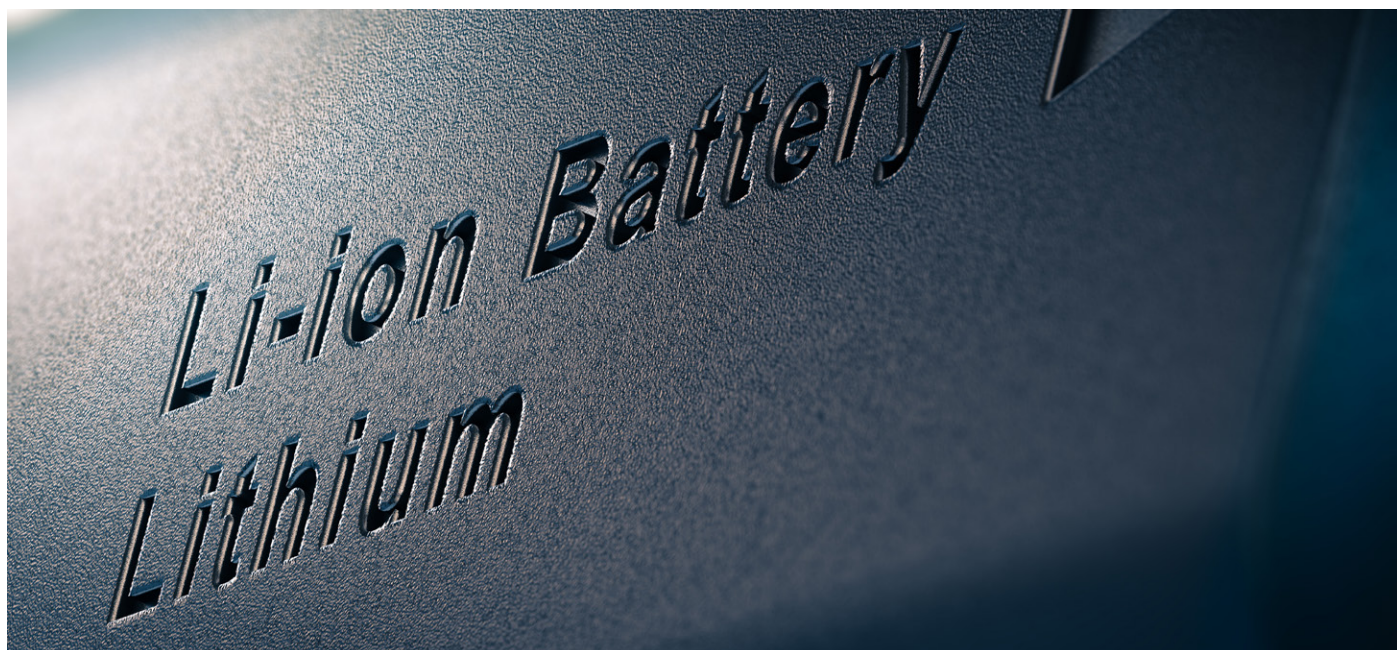
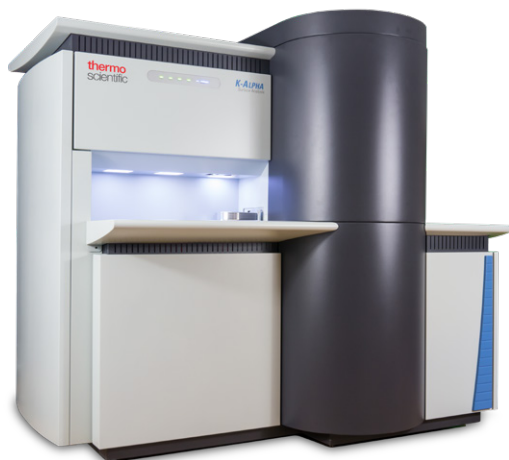


Analysis of Electrode Materials for Lithium Ion Batteries

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The Thermo Scientific™ K-Alpha™ X-ray Photoelectron Spectrometer (XPS) System was used to analyze the surface of lithium-ion battery electrodes. Due to the air-sensitive nature of these materials, the K-Alpha vacuum transfer module was used to safely transport the samples from a glove box to the instrument without exposure to ambient atmosphere. This ensured that the surface was as representative of the electrode material as removed from the cell.



Thermo Scientific™ K-Alpha™ XPS system.

Introduction

For a large number of applications, from automobiles to portable electronics, lithium-ion battery assemblies have become the energy storage solution of choice. Lithium ion (Li-ion) battery cells are lightweight compared to other battery technologies, which makes them appropriate for transport applications when combined with their relatively high energy density, and can mitigate against their higher cost. Further improving the performance of Li-ion cells, for example to increase energy density, reduce weight, decrease costs, and improve recharge times, involves developing improvements to at least one of the core components of the cell, shown in Figure 1.

When operating, the Li^+ ions transport through the electrolyte and separator film from the anode to the cathode. In the cathode, the anion stoichiometry changes, creating a compound that can store the arriving lithium ions. When the cell is recharged after use, the flow of ions is in the opposite direction, and they are stored in the anode. The anode is typically made from graphite, with lithium ions intercalated into the graphite structure.

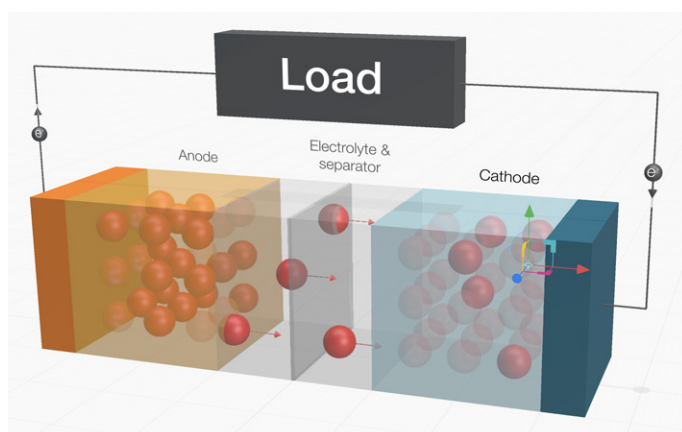


Figure 1: Li-ion cell in operation. Li-ions represented by red spheres.

The cathode is comprised of a lithium metal oxide, the exact composition of which varies depending upon the required characteristics of the cell. The most commonly used cathode materials are LiCoO_2 (LCO – lithium-cobalt), LiMn_2O_4 (LMO – lithium-manganese), LiFePO_4 (LFP – lithium-phosphate), and $\text{Li}(\text{NiMnCo})\text{O}_2$ (NMC – nickel manganese cobalt). These oxides change in stoichiometry depending on whether the cell is charged or discharged; i.e., if the flow of Li^+ is to or from the cathode.

A by-product of the charge and discharge process is the formation of the solid-electrolyte interphase (SEI) layer on the anode. The formation and development of the SEI layer competes with the reversible lithium intercalation process, and over the lifetime of the battery the presence of the SEI will contribute to the lowering of capacity, and is a contributing factor to the ultimate failure of the cell. Understanding the SEI layer is an area of significant interest, so that it can be controlled and therefore improve cell performance. XPS depth profiling offers a way of chemically characterizing the complex mix that makes up the interphase layer, allowing an identification of the chemistries that comprise the SEI.

Method or Experiment

Lithium is very sensitive to air and moisture, and so to analyze the electrode materials successfully it needs to be introduced into the K-Alpha XPS system without air exposure. To do this, the samples are loaded into the K-Alpha Vacuum Transfer Module (VTM) in a glove box. The VTM (Figure 2) is evacuated in the glove box antechamber, and then transported to the XPS system. As the VTM is held together by air pressure, it automatically opens during the pump-down cycle in the K-Alpha and is therefore integrated into the standard, automated, sample transfer process.

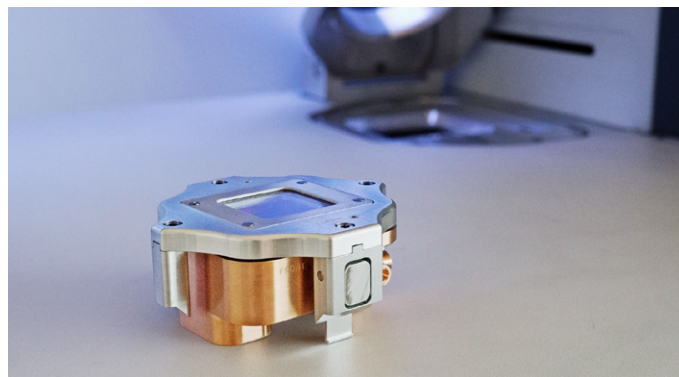


Figure 2: The vacuum transfer module allows samples that have been prepared in an inert environment to be transferred into the spectrometer chamber without exposure to air.

In these experiments, two cathode samples were investigated. One sample was a pristine, unused sample; the other sample was from a cell that had been through several charge-discharge cycles, and was in a charged state when the cell was disassembled.

Results

Survey spectra collected from the as received cathode samples are shown in Figure 3. The cathode material is $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$, prepared using a binder medium to hold the material together. The binder is a mixture of fluorine and oxygen containing polymers, and for the pristine sample is evident as a significant amount of residue on the surface. This could be important during the first use of the cathode, if the binder residue is mobile in the electrolyte, or reacts to begin the formation of a surface layer which impedes ion transport.

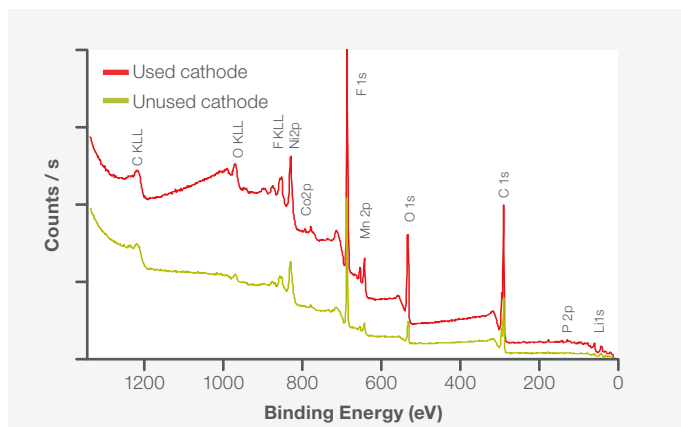


Figure 3: Survey spectra from pristine cathode (blue) and cycled cathode (red) samples.

The cycled cathode still shows the presence of the binder, and also evidence of residue from the electrolyte at the surface. Figure 4 shows the variation in the NMC components of the two samples (excluding oxygen). The relative intensities of the Ni, Mn, and Co components are very similar between the two samples, but the amount of Li detected is around 40% of that seen in the pristine cathode. This is as expected in a sample from a charged cell, where the Li ion transport has been towards the anode and away from the cathode, resulting in a depleted level of lithium in the cathode.

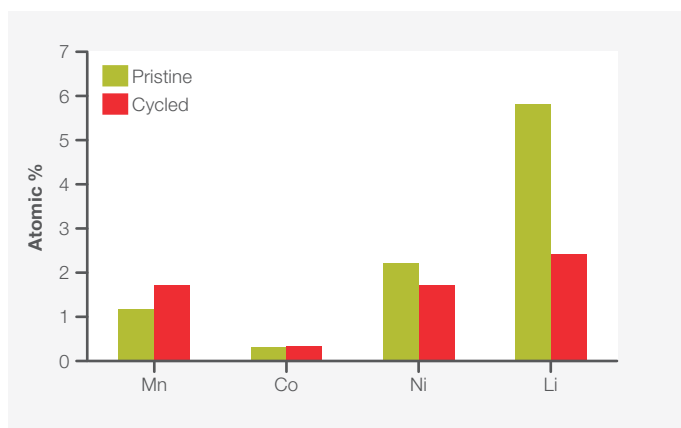


Figure 4: Composition variation for the NMC components.

Summary

By using the vacuum transfer module and the K-Alpha XPS system it is possible to analyze Li-ion battery components. Analysis of unused and cycled cathode samples determined the expected variation in lithium content.

Notes

Keywords

Air-sensitive, Anode, Cathode, Electrodes, Inert Transfer, Li-ion Battery, Lithium, NMC, Vacuum Transfer

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