

Formation of Solid Electrolyte Interface on Cycled Lithium-Ion Battery Cathodes

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Introduction

Lithium-ion batteries are promising candidates for hybrid electric vehicles (HEV). Batteries that exceed the requirements for HEV, as set by the Partnership for a New Generation of Vehicles (PNGV), have been designed and built. These batteries are based on thin $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ cathodes, thin carbonaceous anodes, and a 1 M LiPF_6 ethylene carbonate (EC): diethyl carbonate (DEC) (1:1) electrolyte. A major technical barrier is that the batteries lose their high power capability during use or prolonged storage, particularly at elevated temperatures. Electrochemical impedance spectroscopy indicates that the power fade is due to an increase in cathode impedance in cycled and abused cells. X-ray diffraction and hard X-ray absorption spectroscopy clearly shows that the bulk of the cathode material is largely intact. It is conceivable that the power fade is related to electrolyte decomposition products that are formed on the surface of the cathode. The decomposition products form the solid electrolyte interface (SEI) and might affect ionic motion by pore plugging, or could contribute to resistive electrical paths to parts of the cathode structure. Although the presence of a SEI on the cathode has long been suspected, confirmation of such a layer has proved elusive. In order to study the nature of the SEI layer it is important to use structural techniques with some surface sensitivity. We have explored the use of soft X-ray absorption spectroscopy to study the nature of the SEI layers in lithium-ion battery cathodes.

Experimental Methods and Results

Soft x-ray absorption measurements were performed at beamline U7A in the National Synchrotron Light Source, (NSLS) on cathodes extracted from cycled and abuse-tested cells. Ni and Co L_3 and L_2 edges as well as oxygen and fluorine K edges were recorded, all having energies between 500 and 900 eV. These measurements, obtained in the electron yield mode, sampled to a depth of ~ 50 Å. P K-edge XAS measurements have also been carried out in beamline X-19A (NSLS).

XAS at the F K-edge demonstrates the presence of LiF in addition to poly(vinylidene fluoride) (PVdF) on the surface of cycled and abused electrodes. PVdF is a binder added to the cathode and is an essential component of the cathode assembly. The results indicate that the PVdF in the cycled electrodes is largely intact and that the LiF comes from decomposition of LiPF_6 from the electrolyte.

The precipitated LiF is most likely the major contributor to the insulating layer found on cycled and abused electrodes¹. Oxygen K-edge spectra revealed distinct differences between the surface and bulk of $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ powder samples that were used in cathode laminates of high-power lithium-ion cells. These differences were confirmed by high-resolution electron microscopy images and diffraction patterns that showed $\text{Li}_x\text{Ni}_{1-x}\text{O}$ -type surface regions (NaCl structure) on the bulk layered ($\alpha\text{-NaFeO}_2$ structure) material². P XAS measurements also show the presence of pentavalent P in the cathodes (as PO_4^{3-} and PF_6^-). Our investigation suggests that XAS is a valuable surface chemistry tool in the study of SEI formation at the cathode. Details of the experiments and further results will be presented.

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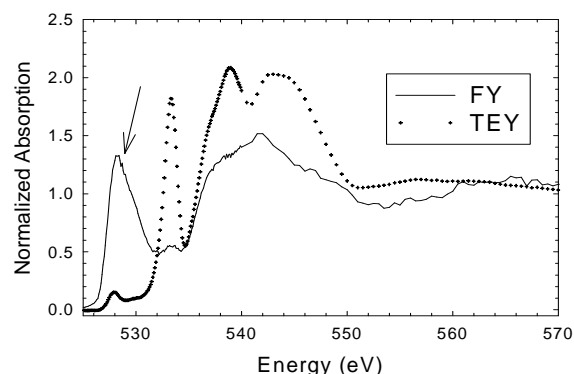


Figure 1: The O K-edge XAS spectra in fluorescence yield (FY) and total electron yield (TEY) from $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ powder. The large difference between the surface and the bulk of the material is clearly evident.

References

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