

Power Fade in High-Rate Lithium-Ion Batteries

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Lithium-ion batteries are promising candidates for hybrid electric vehicles (HEV). Batteries that exceed the requirements for HEV, that have been set by the Partnership for a New Generation of Vehicles (PNGV), can be designed and built. A major technical barrier is that the batteries lose their high power capability during use or prolonged storage, particularly at elevated temperatures. This problem has to be solved to meet the daunting requirement of the PNGV target of a 15 year calendar life. The USDOE Advanced Technology Development (ATD) Program addresses these technical barriers. In this program 18650 cells, with high power designs, were made by commercial vendors. Several National Laboratories carry out cycle life and abuse tests on the cells. Brookhaven National Laboratory (BNL) is one of the laboratories that do diagnostic tests on fresh and failed cells in an effort to determine the source of the power fade. The work at BNL focuses on the use of synchrotron x-ray techniques to study electrode materials.

Electrochemical impedance spectroscopy (EIS) at several laboratories, including BNL, indicated that the power fade was due to an increase in cathode impedance in cycled and abused cells (1, 2).

BNL extracted cathodes from tested 18650 cells that had $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ cathodes. The active material was removed from one side of the aluminum foil current collector. Electrodes (2.8 cm^2) were punched out and were assembled with lithium foil anodes, a Celgard separator, and fresh electrolyte in a spectro-electrochemical cell (3). *In situ* high-resolution x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS) studies were done in the transmission mode at the National Synchrotron Light Source (NSLS) at BNL. One of the XRD Beam Lines (X7A) has a position sensitive detector and it was possible to collect complete spectra in 3 minutes. This permitted time-resolved studies using charging rates as high as 2C.

When cells with fresh $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ cathodes were charged at the C rate three hexagonal phases could be identified by XRD. The initial phase H1 is converted to H2 with a slight expansion along the c-axis. At the end of charge some of the material is converted to the H3 phase with a contraction along the c-axis. No residual H1 phase remained at the end of charge. The polarization was higher and the capacity was considerably less in cells with electrodes from cells tested at 70°C . The cells reached the voltage cutoff before any H3 phase was formed. In several cells large amounts of residual uncharged H1 material remained. On termination of charge the residual H1 material reacted by local cell action to form an intermediate composition with a c-axis intermediate between that found for the H1 and H2 phases. These results indicate that much of the active material cannot be charged at high rates. However, the material is not completely electrically isolated since it can be converted by local cell action after termination of charge. Complete conversion of the H1 material can also be achieved by charging at low (C/5) rates. The XRD results indicate that the bulk of the cathode structure in the cycled and abused cells is intact. No new crystalline

phases could be detected. Similarly, XAS did not detect any new amorphous phases or any separation of Co from the cathode structure. The power fade appears to be due to an insulating coating on the surface of the cathode material.

Recently our diagnostic work has focused on XAS techniques with surface sensitivity. This has included XAS in the electron yield mode at the Ni K-edge and XAS in the fluorescence and electron yield mode at the Ni and Co L-edges and at the K-edges of low Z elements such as O and F.

The XAS signals at the Ni K-edge, in the electron yield mode, were noisy and contained spikes. This was traced to charge buildup on the sample, indicating a resistive coating on the electrode.

XAS at the O K-edge gives information on the type of bonding and charge distribution between the O and transition metal. XAS in the electron yield mode probes depths of 50 \AA or less, whereas in the fluorescence mode it probes depths of about 1000 \AA . The O K-edge XAS for LiCoO_2 in the electron yield and fluorescence mode are very similar, indicating similar Co-O bonding on the surface and in the bulk of the material. The O K-edge XAS for both LiNiO_2 and $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ differ from that found for LiCoO_2 , indicating different metal oxygen bonding in Ni based materials. Furthermore, there are large differences in the fluorescence and electron yield data, which indicates that in the Ni based cathodes the surface composition differs from the bulk. Also the O K-edge data for fresh and cycled electrodes was very similar to that found for $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$. This strongly indicated that there are no surface decomposition products of the $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ on the surface of the cycled electrodes. The data obtained at the Co and Ni L-edges do not agree with the data published in the literature. The literature data has been interpreted as indicating the presence of Ni(II) on the surface of the particles. So far our spectra do not support this. XAS data at the F K-edge were different for the fresh and cycled electrodes. The results indicate that there is deposition of LiF on the cycled cathodes. This presumably comes from the decomposition of LiPF_6 from the electrolyte.

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