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Electrochemical Impedance and NMR Studies of Lithium Ion Batteries

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Layered nickel-oxide-based active materials are among the most widely used cathodes in commercial lithium ion cells because of high specific energy and specific power[1]. Recently, the research on $LiNi_{0.8}Co_{0.15}Al_{0.05}$ has shown that cell performance relies more on the cycling properties of the cathode than anode[2]. Therefore it is important to study the mechanical and chemical processes that may be linked to loss of capacity and power capability at the cathode.

In this work, Swagelok cells have been assembled using $LiNi_{0.8}Co_{0.15}Al_{0.05}$ (Gen 2) cathode samples from a cell that had been aged at 45C for 72 weeks, and had lost 50% of its power capability. These cells contained fresh $LiPF_6$-EC-DEC electrolyte. Three different treatments (ultrasonically washing, pressing, and ultrasonically washing and pressing) were carried out on three cathodes before assembling them into cells. Then the cells were galvanostatically cycled between 2.5 and 4.2 V at the C/20 rate.

To improve cathode performance, we need to understand the processes occurring at the electrode/electrolyte interface. Electrochemical Impedance Spectroscopy (EIS) has proven to be a powerful technique to determine the factors limiting the performance of an electrode such as electrode kinetics and the intercalation of Li[3]. To study the charge transfer properties, EIS measurements were performed on the cells at open circuit before and after cycling, in the frequency range from 10^5 Hz to 1 mHz.

Nuclear Magnetic Resonance (NMR) Spectroscopy has also been used to investigate the electrolyte decomposition products as solvent decomposition might be an important reason for the capacity fading. ^{19}F and ^{31}P NMR measurements were carried out on a Gen 2 cell electrolyte (1.2 M $LiPF_6$ in EC:EMC 3:7) using a Bruker AVQ-400 spectrometer operating at a frequency of 400 MHz. To study the phosphate species present in the electrode pores and in the film on the electrode surface, ^{31}P NMR experiments were performed with the Gen 2 cathode material using a spectrometer operating at a frequency of 65 MHz.

The galvanostatic measurements showed that the greatest improvement in capacity was obtained with the washed and pressed cathode, and the capacity of this cell was higher than the capacity of an untreated cathode. It therefore seems that the washing removes material in the electrode pores and the pressing re-establishes contact between the particles of active material.

The EIS experimental data of three cells assembled with untreated, pressed, and washed and pressed electrodes are shown in the Figure 1. For all samples, two semi-circles and a diffusion straight line appeared. The semi-circle at high frequency indicates the solid-state interface layer resistance and the second semi-circle at medium frequency represents charge transfer resistance at the $LiNi_{0.8}Co_{0.15}Al_{0.05}$ electrode surface. The straight sloping line is due to the diffusion process of lithium ions on the interface between the active material particles and electrolyte. It was clearly seen that the treatments of the electrodes drastically decreased the impedance of the cells at low frequency. Moreover, the charge transfer resistance is much smaller in the case of the washed electrode, as shown in the inset of the Figure 1.

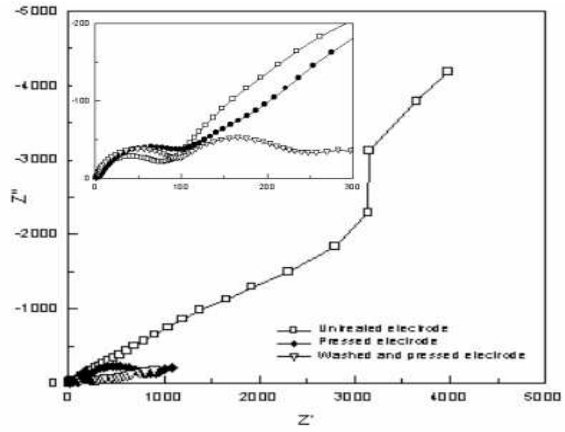

Figure 1: Nyquist plots of Swagelok cells assembled with $LiNi_{0.8}Co_{0.15}Al_{0.05}$ positive electrodes.

Figure 2 presents the ^{31}P spectrum obtained from the electrolyte of a Gen 2 cell. Fluorophosphates species (OPF_2OR, $OPF(OR)_2$…) were present in the electrolyte, thereby indicating the relative instability of $LiPF_6$ in EC:EMC under typical cell testing conditions. The presence of these compounds at the surface of the cathode, also observed by ^{31}P solid-state NMR, seems to be at the origin of the high charge transfer resistance at the surface of the untreated and also the pressed electrodes.

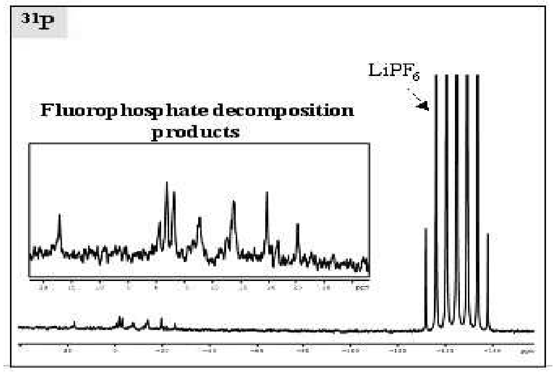

Figure 2: ^{31}P NMR spectrum of the electrolyte taken from a Gen 2 cell. The fluorophosphates species NMR shifts are shown in the inset, and the much larger $LiPF_6$ shifts are also shown.

Acknowledgment

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