

Understanding the mechanism and effects of transition metal dissolution and SEI growth in Li-ion batteries

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Li-ion batteries are good power sources for hybrid electric vehicles (HEV) and plug-in hybrid electric vehicles (PHEV). $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) cathode materials are seen as suitable candidates to replace commonly used LiCoO_2 cathodes because of improved safety, lower costs, less toxicity, and higher capacity [1-3]. However, NCM cathodes are susceptible to metal dissolution, which leads to a rise in impedance and reduced cycleability of the cells [2, 4]. It is proposed that the transition metal ions removed from NCM cathodes get reduced in the solid electrolyte interphase (SEI) layer and contribute to SEI growth. A two part study is presented to better understand the effects of dissolution on cells with NCM cathodes and SEI growth at the anode through electrochemical characterization and structural changes.

The first part of the study focused on the electrochemical performances of full cells. Li-ion cells were fabricated using commercial graphite anodes and NCM cathodes in a 2032 coin cell configuration. The electrolyte used was 1 M LiPF_6 in EC/DEC (1:1) (by weight) and termed "regular electrolyte." To simulate high dissolution levels for accelerated testing of cells, transition metal salts were added into the electrolyte in the following quantities: 10 mM of Nickel (II) Bis (trifluoromethanesulfonyl) imide (Ni-TFSI), 10 mM of Manganese (II)-TFSI and 10 mM of Cobalt (II)-TFSI, 10mM. These cells are termed "30 mM NMC-TFSI."

The first cycle charge and discharge capacities of cell with and without transition metal salts are compared in Figure 1. The cell with transition metal salts show significantly lower capacity compared to the sample without additive in the electrolyte. The decreased capacity seen in the 30 mM NMC-TFSI sample is attributed to the deposition of metal ions at the anode. These results were confirmed with electrochemical impedance spectroscopy.

The second part of the study focused on electrochemical testing of half cells followed by post-mortem spectroscopy analyses. Because of the difficulties in analyzing SEI growth on commercial graphite due to its rough surface, thin carbon films were chosen to study the effect of dissolution on the anode. Carbon thin films were grown by chemical vapor deposition of carbon on a nickel substrate. Spectroscopic techniques included focused ion beam- scanning electron microscopy (FIB/SEM), x-ray photoelectron spectroscopy (XPS), and secondary ion mass spectroscopy (SIMS). Comparison of cells containing transition metal salts additive and no additive in the electrolyte showed decreased capacities for cells containing additives.

SEM images of the SEI/carbon layers on thin film electrodes after cycling are shown in Figure 2. The increased contrast seen in Figure 2a for cells containing electrolyte additive may be due to higher electric conductivity of the SEI layer as a result of metal

deposition on the SEI layer. The increased conductivity of the layer may lead to increased thickness and impedance. Further spectroscopic analyses verify larger SEI in cases of cells containing transition metal salts in the electrolyte.

ACKNOWLEDGEMENTS

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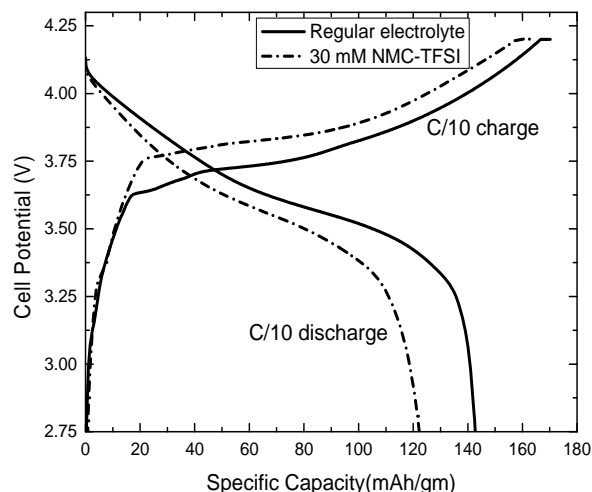


Figure 1. First cycle charge/discharge capacities of full cells comparing the effect of transition metal salts in the electrolyte.

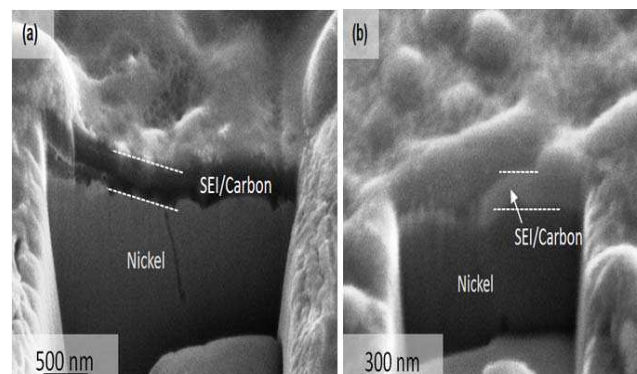


Figure 2. SEM of the SEI/Carbon layers on the anodes: (a) cell cycled at room temperature for 100 cycles in the electrolyte containing 30mM NMC-LiTFSI and (b) cell cycled at room temperature for 100 cycles in the regular electrolyte.