

Improved performance of graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells with electrolyte additivesMengqing Xu¹, Liu Zhou¹, Arnd Garsuch², and Brett L. Lucht¹¹Department of Chemistry
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There is significant interest in the development of higher energy lithium ion batteries (LIB) for electric vehicles. One method of improving the energy density of lithium ion batteries is to increase the operating voltage of the cells by increasing the working potentials of positive electrode employing for example lithium nickel manganese spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as the active material.¹ However, cycling of lithium-ion cells to high voltages (~5.0 V vs lithium reference electrode, LRE) proceeds with relatively low (99% and less) coulombic efficiency.² Among the primary contributors to the poor cycling efficiency are the electrochemical oxidation reactions of the electrolytes at the high positive potentials of positive electrode.³

The failure mechanism of graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells cycled at 25 °C and 55 °C (1.2 M LiPF_6 in 3:7 EC/EMC) have been analyzed by electrochemical methods and ex-situ surface analysis of the electrodes. Graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells cycle well at 25 °C, but have rapid capacity fade upon cycling at 55 °C. Independent electrochemical analysis of anodes and cathodes extracted from cells cycled at 55 °C suggest that both electrodes have significant capacity loss, although the cathode capacity can be recovered with longer charging times. Ex-situ surface analysis of the cathode with SEM reveals that the bulk cathode particles and the cathode laminate are retained while XPS confirms the presence of a cathode electrolyte interface composed of the decomposition products of the electrolyte. Ex-situ analysis of the anode reveals a thick anode solid electrolyte interphase (SEI), anode delamination, and the presence of Mn. The results suggest that both the anode and the cathode contribute to performance loss in graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells.⁴

We are using this mechanistic information about capacity fade in graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells to develop novel additives to improve the performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cycled to high voltage (4.9 V vs Li). The additives include Lewis basic species which inhibit the thermal decomposition of LiPF_6 and cathode film forming additives. Preliminary investigations suggest that incorporation of the novel additives into graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells significantly improves the capacity retention upon cycling at high voltage (4.9 V vs Li) and moderately elevated temperature (55 °C, Figure 1). Ex-situ surface analysis of the electrodes after cycling suggest that the additives modify the surface of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode via the formation of a stable cathode electrolyte interface (CEI). The presence of the CEI inhibits the oxidation of the electrolyte and dissolution of Mn and Ni from the surface of the cathode particles. The additives, also stabilize the SEI on the anode by preventing Mn deposition on the anode surface and damage of the anode SEI.

The details of our experimental results and our mechanistic interpretation will be presented.

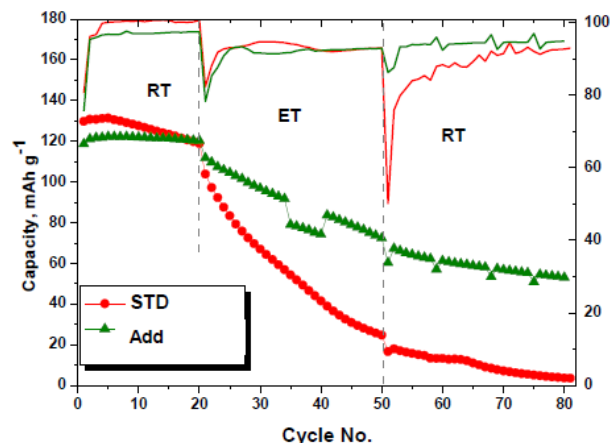


Figure 1. Cycling performance of graphite/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells at 25°C and 55 °C with and without a cathode stabilizing additive..

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