

Interface Engineering using Ultra-thin Self-assembled Monolayers as Surface Modifiers for High-voltage Spinel-based Lithium Ion Batteries

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High-voltage spinels, such as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) have been considered for energy storage system of electric vehicles. However, their high operating voltages (> 4.4 V) result in the oxidative decomposition of the electrolyte at the delithiated LNMO electrode surface, which subsequently promotes various side reactions, including Mn^{2+} elution, and the formation of metal fluorides. In particular, the reliability of the high-voltage spinel-based LIBs is negatively affected by the migration of eluted Mn ions from the cathode to the anode, which significantly decreases the anode capacitance. Thus, many researchers have attempted to mitigate the observed capacity fading of LNMO/graphite cells through the reduction of the direct contact area of the cathode with the electrolyte as well as via the passivation of transitional M–M and O–O bonds at the cathode surface by coating it with inorganic particles as well as by adding organic modifiers to the electrolyte. However, none of them led to a remarkable performance for LNMO/graphite cells.

In this work, the electrochemical properties of the interface between the spinel LNMO cathodes and ethylene carbonate–dimethyl carbonate (EC–DMC) electrolyte containing 1 M of LiPF_6 have been investigated to achieve good high-voltage durability and low charge transfer resistance of LNMO/graphite full cells. Coating the LNMO cathode surface by a fluoroalkylsilane (FAS) self-assembled monolayer with a thickness below 2 nm resulted in a capacity retention of 94% after 100 cycles (Figure 1) and suppression of capacity fading for both the cathode and anode of the full cell. The observed effect is likely caused by the inhibited oxidative decomposition of EC–DMC electrolyte and vinylene carbonate (VC) species at the LNMO cathode surface and formation of a stable VC solid electrolyte interface near the anode. Moreover, the obtained density-functional calculations, and UPS measurements revealed that the increase in the work function of the LNMO surface due to the formation of Si–O–Mn species primarily contributed to the inhibition of the oxidative decomposition of the electrolyte and VC molecules at the cathode/electrolyte interface.

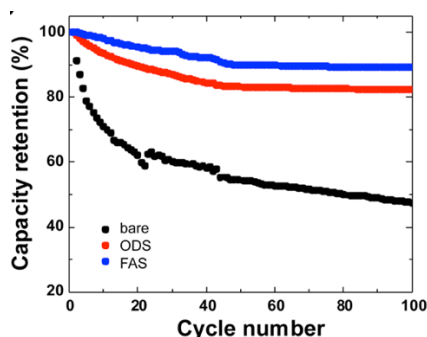


Figure 1. Coated LNMO/graphite cells observed after different number of cycles at a rate of 1 C.

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