Investigation of Electrolyte Interaction with High Voltage Li-ion Battery Cathodes

Samuel A. Delp, Jan L. Allen and T. Richard Jow
United States Army Research Laboratory
2800 Powder Mill Road, Adelphi, MD 20783, USA

A major focus in the field of Lithium-ion battery (LIB) research involves increasing energy density (Wh/kg) of the systems. Using materials with higher capacity (mAh/g) and/or cathode materials that operate at higher voltages raises the overall energy density. There are several examples of materials with high capacity that function at higher voltages such as the spinel structure $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) (145 mAh/g, 4.7V) and the olivine structure $LiCoPO_4$ (LCP) (167mAh/g, 4.8V) LIBs that function at high voltages (above 4.5V) decompose the state-of-the-art electrolyte composed of $LiPF_6$ in a mixture of carbonate solvents. Electrolytes that resist oxidative decomposition at high voltages must be developed in order for these new cathode materials to be utilized.

Aside from the oxidative stability of the electrolyte, another common problem of LIBs is the degradation of the electrode material. For example, Mn ions from LNMO dissolve into the electrolyte where they can then deposit on the graphite anode and cause unnecessary build up of the solid-electrolyte interface (SEI), leading to increased resistance and capacity fade. The LCP olivine structure is an insulator resulting in the need for a constant voltage step in the charging process. The increased time at high voltage leads to rapid electrolyte decomposition and capacity fade. A new doped-LCP (d-LCP) material has been developed and battery testing is under way. The d-LCP experiences less capacity fade at 25 °C than electrodes made with pure LCP.

A series of electrolytes based on $LiPF_6$ in a mixture of carbonates will be examined in LNMO/Li, LNMO/Graphite, d-LCP/Li and d-LCP/Graphite cells. Any differences between the behavior of the electrochemical couple will allow us to determine whether the oxidative decomposition alone leads to the loss of capacity or if other cathode-specific interactions are occurring.