

Challenges in High Voltage Lithium-Ion Chemistry Development

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High power electric drive vehicle (EDV) batteries need to have OCV of ~300 V or higher, requiring that many cells be strung in series. The higher the cell voltage, the fewer the number of series cells that are required, lessening both the manufacturing costs and the costs for external monitoring and control electronics and hardware, these being costs that to a significant extent accrue on a per cell basis. Because the potential of state-of-the-art Li-ion anode materials is already very close to that of metallic Li, Li-ion cell voltages can only be increased by implementing high voltage cathode materials. An alternative way in which high voltage Li-ion cathodes can benefit EDVs is by enabling rapid charging-capable Li-ion batteries. The proximity of currently-used carbon anodes' electrochemical potential to that of metallic Li makes deleterious and dangerous Li metal plating likely when such anodes become significantly polarized under rapid or low-temperature charging conditions. Although the use of anode materials having significantly higher potential than carbon sacrifices energy density because of the lower resulting cell voltage, implementing such high potential anodes opposite higher voltage cathodes results in less relative impact to cell voltage and thus to energy density.

A number of Li-ion cathode materials with operating potentials of 4.5 V vs. Li and higher have been reported and are under development to varying degrees. Among high voltage cathode materials, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel (LNMO) deserves special attention because to date it has proved to be among the best-performing and most synthetically accessible of the high voltage materials. When used opposite a high potential anode such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), it can enhance the energy density of Li-ion cells relative to that obtained using other state-of-the-art cathodes. Figure 1 compares the projected energy content of LNMO/LTO cells (relative to LCO/LTO cell energy) to that projected for cells pairing LTO anode with other high capacity and high voltage cathodes that are currently commercialized or under advanced development; these are $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA), $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) cycled to 4.5 V vs. Li, and $\text{xLiMO}_2 \bullet (1-x)\text{Li}_2\text{MnO}_3$ "layered-layered" NCM (LL-NCM).

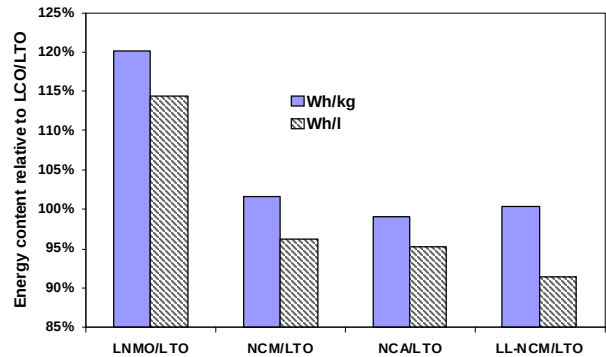


Figure 1. Projected relative specific energy and energy density of LNMO cathode, LTO anode compared to projected relative energies of different cathodes combined with LTO in equivalent cell designs. 100% = LTO.

TIAX has developed a high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode material that exhibits state-of-the-art performance (capacity, rate capability and cycle life) and is made by a low-cost solid-state synthetic approach to making high-density material. These are the essential attributes for enabling low-cost, high energy density cells. However, for this and other high voltage cathode materials, substantial technical issues must be resolved before they can be implemented in practical cells. The shortcomings of current high voltage cathode materials are often intrinsic to the materials themselves, or are due to their unfavorable interactions with electrolyte occurring at the cathode materials' high operating potentials, and which can yield further deleterious interactions with anode materials. Figure 2 illustrates the cycling capacity decline of Li-ion cells employing LNMO cathode opposite LTO or MCMB graphite anodes at room temperature and 60 °C.

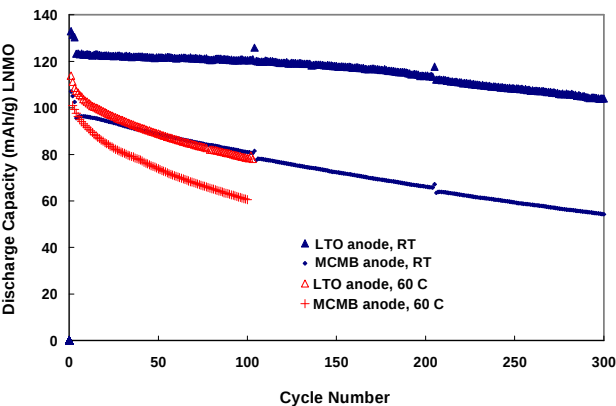


Figure 2. Ambient temperature and 60 °C discharge capacity for Li-ion coin cells with TIAX LNMO cathode (~4 mg/cm² electrode loading), LTO or MCMB graphitic anode, and 1M LiPF₆ in 3:7 EC:EMC electrolyte cycled between 3.0 V and 4.9 V at 1C charge, 1C discharge rates (1C=130 mA/g).

Researchers have sought to improve high voltage cathode performance and life by altering their bulk compositions, structures and morphologies, by modifying them with coatings of various chemistries, morphologies and uniformities, and by modifying the electrolytes. None of these approaches in isolation has fully resolved the stability issues confronting high voltage cathodes.

TIAX is pursuing strategies that integrate modifications to both the electrolyte and the LNMO cathode surface in order to extend the life of Li-ion cells made with the material. This presentation will show results of that work, and will discuss the challenges involved with developing high voltage Li-ion chemistry and elucidating the degradation mechanisms impeding its implementation.