

The Use of Methyl Butyrate-Based Electrolytes with Additives to Enable the Operation of Li-Ion Cells with High Voltage Cathodes over a Wide Temperature Range

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There is continued interest in utilizing high capacity, high voltage cathode materials for use in high specific energy Li-ion cells. The Department of Energy (DoE) desires such materials to enable plug-in hybrid electric vehicles (PHEVs) and other automotive applications. NASA also has interest in higher specific energy rechargeable batteries, especially for "human rated" applications. A number of promising lithium-excess layered-layered metal oxide materials, with the composition of $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ (M=Mn, Co, Ni), have been developed by Argonne National Laboratory and have received considerable attention.¹⁻⁴ These materials have been demonstrated to provide over 250 mAh /g in many cases, as well as reasonable cycle life performance. However, a number of technical challenges with these materials still need to be overcome prior to their widespread adoption, including improving the rate capability and enabling the material to operate over a wide temperature range (especially at lower temperatures).

In the current study, we have investigated a number of wide operating temperature range electrolyte formulations that have been used in conjunction with the layered-layered metal oxide cathode materials (Toda HE5050 $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.10}\text{Mn}_{0.55}\text{O}_2$), which are coupled with carbon anodes (i.e., Conoco Phillips A12 graphite anodes). Specifically, we have investigated LiPF_6 -based electrolytes containing methyl butyrate as an electrolyte co-solvent, which has been previously been demonstrated as a viable approach to improving the operational temperature range of more traditional lower voltage electrode couples.^{5,6} In the previous studies, we have evaluated a number of electrolyte additives which serve to improve the nature of the solid electrolyte interphase (SEI) and/or cathode electrolyte interface (CEI), including vinylene carbonate (VC), lithium oxalate, mono-fluoroethylene carbonate (FEC) and lithium bis(oxalato)borate (LiBOB). In the present study, we have extended this approach by investigating other potential electrolyte additives, including lithium difluoro(oxalato)borate (LiDFOB)^{7,8}, lithium 4,5-dicyano-2-(trifluoromethyl) imidazole (LiTDI)^{9,10,11}, lithium tetrafluoroborate (LiBF_4), and di-*t*-butylpyrocarbonate (DBPC). The LiDFOB and LiTDI were synthesized at the North Carolina State University, and are currently under investigation to elucidate their solvation characteristics in electrolyte solutions.

These studies were performed utilizing

graphite/ $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.10}\text{Mn}_{0.55}\text{O}_2$ full cells in both smaller coin cells, as well in larger capacity three-electrode cells equipped with lithium reference electrodes. The three electrode cells were instrumental in allowing us to study the lithium kinetics of the respective electrodes by electrochemical techniques including Electrochemical Impedance Spectroscopy (EIS), Tafel polarization, and linear micro-polarization measurements. These measurements were performed at a number of temperatures to determine the relative kinetics, especially at low temperatures. Discharge rate characterization was performed on both types of cells containing the methyl butyrate-based electrolyte possessing the various additives described. In addition, the cycle life performance at ambient and at high temperature (50°C) was evaluated using the coin cells.

In summary, improved low temperature power capability was observed with most of the electrolytes compared with an all carbonate-based baseline (1.2M LiPF_6 in EC+EMC 30:70), being most dramatic for the formulations containing LiBOB and LiDFOB. Based on previous findings and supported by the current study, it appears that the cathode kinetics dominate the low temperature power capability in this system, and the use of methyl butyrate-based electrolytes possessing additives that effectively form desirable surface films result in improved kinetics, and subsequently improved power characteristics.

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