The Use of Methyl Propionate-Based Electrolytes with Additives to Improve the Low Temperature Performance of $LiNiCoAlO_2$-Based Li-Ion Cells

M. C. Smart[1], M. R. Tomcsi[2], L. D. Whitcanack[1], B. V. Ratnakumar[1], M. Nagata[2], and V. Visco[2]

[1]Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive, Pasadena, CA 91109

[2]Quallion, LLC
Sylmar Biomedical Park
12744 San Fernando Road
Sylmar, CA 91342

Both NASA and the Department of Energy require energy storage devices that can effectively operate over a wide temperature range to enable a number of applications. To meet these needs, Li-ion batteries have emerged as the most viable option, due to their high specific energy, long life, and the fact that they possess organic non-aqueous electrolytes that can be readily modified to allow operation over a wide temperature range. NASA desires Li-ion batteries to enable the operation of planetary rovers and lander over a wide temperature range (i.e., -40°C to +40°C). The Department of Energy is currently pursuing the development of Li-ion systems for electric vehicles (EVs), hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs), which are required to operate from -30°C to +60°C. The current state-of-art Li-ion systems typically display a reasonably wide temperature range of operation. However, poor power capability at lower temperatures is usually observed (below -20°C). In addition, this poor performance at low temperatures is often exacerbated after exposure to high temperatures, due to degradation that leads to capacity loss and impedance growth.

To enable good performance over a wide temperature range (-40° to +60°C) over the entire life of the cell, our efforts have been focused upon developing improved Li-ion electrolytes, which have high ionic conductivity and good stability. To address the deficiency in low temperature performance, our approach has been to utilize low viscosity, low freezing ester co-solvents in $LiPF_6$-based multi-component electrolytes. Using this approach, we have demonstrated improved low temperature performance in a number of systems, including $LiNiCoO_2$[1,2,3] $LiNiCoAlO_2$[4,5] $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$[6], and $LiFePO_4$[7,8].

In recent work, in collaboration with Quallion, we have demonstrated improved wide operating temperature range performance of MCMB-$LiNiCoAlO_2$-based prototype cells containing electrolytes with methyl propionate (MP) and ethyl butyrate (EB) (i.e., electrolytes consisting of $LiPF_6$ in EC+EMC+X, where X = MP or EB). In this study, we demonstrated the ability to support 5C discharge rates at -40°C (a five-fold improvement over the baseline), while still offering reasonable high temperature resilience and cycle life.

To improve the high temperature resilience of these systems, our current efforts have focused upon utilizing electrolyte additives which are targeted at producing protective surface layers on the electrodes. Due to the high power capability observed at low temperature with some formulations investigated, we have focused upon $LiPF_6$-based electrolytes with methyl propionate used as a co-solvent in large proportion. The electrolyte additives utilized include mono-fluoroethylene carbonate (FEC), lithium oxalate, vinylene carbonate (VC), and lithium bis(oxalato) borate (LiBOB). Based on the favorable results in experimental cells, we are investigating a number of electrolytes that consist of methyl propionate with varying amounts of mono-fluoroethylene carbonate (4, 10, and 20%). In one case, we have entirely replaced the cyclic carbonate ethylene carbonate with FEC.

These electrolytes have been investigated in experimental three-electrode cells (equipped with lithium metal reference electrodes), and have also being evaluated in hermetically sealed prototype 0.25Ah MCMB/ $LiNiCoAlO_2$ cells (manufactured by Quallion, LCC). The experimental cells were instrumental in establishing the relative electrode kinetics, as well as the influence of electrolyte additives upon the kinetics at extreme temperatures. A general trend observed was that the presence of FEC resulted in enhanced lithium kinetics at the anodes at low temperatures, whereas VC and LiBOB were observed to improve the kinetics at the $LiNiCoAlO_2$ cathodes. A number of performance tests were implemented on prototype 0.25Ah cells, including discharge rate characterization over a wide temperature range (down to -60°C) using various rates (up to 20C rates), charge rate characterization, and cycle life performance under various conditions (including cycling at high temperatures). As part of these studies, we demonstrated the ability to support 20C discharge rates at -20°C with cells containing a MP-based electrolyte (1.2M $LiPF_6$ + 0.10M LiBOB in EC+EMC+MP (20:20:60 vol %), representing an 11-fold increase in discharge energy compared with the baseline (i.e., 62.2 Wh/kg vs. 5.5 Wh/kg). In addition to evaluating candidate electrolyte in the 0.25 Ah, select electrolytes were also investigated in larger capacity, aerospace quality 12 Ah MCMB-$LiNiCoAlO_2$ Li-ion cell manufactured by Quallion, LLC.

ACKNOWLEDGEMENT

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA) and supported by the DOE BATT-ABR program.

1. M. C. Smart, B. V. Ratnakumar, K. B. Chin, and L. D. Whitcanack, *J. Electrochem. Soc.*, **157 (12)**, A1361-A1374 (2010).
2. M. C. Smart, B. L. Lucht, S. Dalavi, F. C. Krause, and B. V. Ratnakumar, *J. Electrochem. Soc.*, **159 (6)**, A739-A751 (2012).
3. M. C. Smart, B. V. Ratnakumar, and S. Surampudi, *J. Electrochem. Soc*., **149 (4)**, A361-A370 (2002).
4. M. C. Smart, B. V. Ratnakumar, M. R. Tomcsi, M. Nagata, V. Visco, and H. Tsukamoto, 2010 Power Sources Conference, Las Vegas, NV, June 16, 2010.
5. M. C. Smart, M. R. Tomcsi, C. Hwang, L. D. Whitcanack, B. V. Ratnakumar, M. Nagata, V. Visco, and H. Tsukamoto, 221st Meeting of the Electrochemical Society, Seattle, WA, May 6-10, 2012.
6. M. C. Smart, B. V. Ratnakumar, and K. Amine, 218th Meeting of the Electrochemical Society, Las Vegas, Nevada, Oct. 13, 2010.
7. M. C. Smart, B.V. Ratnakumar, A. S. Gozdz, and S. Mani, 214th Meeting of the Electrochemical Society, Honolulu, HI, Oct. 12-17, 2008.
8. M. C. Smart, A. S. Gozdz, L. D. Whitcanack, and B. V. Ratnakumar, 220th Meeting of the Electrochemical Society, Boston, MA, October 11, 2011.