

Improved Low Temperature Performance of Lithium Ion Cells with Low Ethylene Carbonate (EC) Content Electrolytes

M. C. Smart, B. V. Ratnakumar, and S. Surampudi
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive, Pasadena, CA 91109

H. Croft, D. Tice and R. Staniewicz
SAFT America, Inc.
Battery Research and Development Facility
107 Beaver Court
Cockeysville, MD 20130

INTRODUCTION

Lithium-ion rechargeable batteries are being developed for various aerospace applications under a NASA-DoD interagency program. For the projected missions, lithium ion batteries need to be further improved, i.e., low temperature performance for Mars Landers, Rovers, and Penetrators and cycle life for the Orbiters and LEO and GEO satellites. Specifically, future Rover and Lander missions desire batteries which can operate at temperatures as low as -40°C . Penetrators require operation at temperatures lower than -60°C . In addition to extreme operating temperature requirements, high specific energy (60-80 Wh/Kg) and long cycle life (< 500 cycles) are necessary for these applications. Research and Developmental programs are underway at JPL to improve the low temperature performance and life characteristics of Li-ion cells, with the intent of using this technology for up-coming missions. This report describes our findings on the improved performance of lithium ion cells which possess ternary and quaternary electrolytes optimized for low temperature performance consisting of mixed carbonates and having low ethylene carbonate (EC) content (> 25% EC vol%). Specifically, we have demonstrated improved low temperature with lithium ion cells containing 1.0 M LiPF_6 EC+DEC+DMC+EMC (1:1:1:2 v/v), 1.0 M LiPF_6 EC+DEC+DMC+EMC (1:1:1:3 v/v), 1.0 M LiPF_6 EC+ DMC+EMC (15:15:70 v/v), and 1.0 M LiPF_6 EC+DEC+DMC+EMC (1:1:1:4 v/v). The improved performance of these electrolytes has been demonstrated in experimental three-electrode MCMB-carbon/ $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cells, as well as, in aerospace quality prototype lithium-ion cells fabricated at SAFT America, Inc.

Earlier research in the area of electrolytes at JPL has resulted in the development of a system consisting of 1.0 M LiPF_6 ethylene carbonate (EC) + diethyl carbonate (DEC) + dimethyl carbonate (DMC) (1:1:1)^{1,2} which has been demonstrated to have improved performance at low temperature in prototype AA-size^{3,4}, D-size⁵, and 25 Ahr lithium-ion cells⁶, as well as, excellent ambient temperature cycle life, and acceptable storage characteristics. In addition to advances made at JPL, other groups have developed electrolyte formulations with comparable performance, including work performed by the Army Research Lab. which has resulted in

1.0 M LiPF_6 EC+DMC+EMC (1:1:1)⁷ and efforts by Covalent Associates which yielded 1.0 M LiPF_6 EC+EMC (1:3).⁸ Although these electrolyte solutions enable efficient operation at -20°C , these formulations do not function well below -30°C . Little work has been devoted to developing electrolytes that enable the operation of lithium ion to temperatures of -40°C and below.

High EC-content electrolytes formulation are desirable in terms of stability and their electrode film forming characteristics, however, the low melting point and high viscosity of EC lead to poorly conductive solutions at low temperature. Thus, it is advantageous to employ multi-component solvent mixtures to optimize cell performance over a much wider temperature range. Linear aliphatic carbonate solvents have been demonstrated to have the most utility as co-solvents in lithium-ion systems due to their low chemical and electrochemical reactivity, in contrast to other electrolyte co-solvents investigated including formates, esters, ethers, lactones, and glymes. When assessing the relative ability of these solvents to form ionically conductive and protective surface films on the electrodes (especially on the anodes) the following trend has been observed EC > DMC > EMC > DEC. However, a reverse trend is observed for the melting points of the solvents and the viscosity. Thus, to maximize the desired electrolyte properties it is beneficial to employ ternary and quaternary solvent mixtures, rather than the traditionally used binary mixtures. In this manner, electrolytes can be formulated which possess the desirable electrode filming characteristics (imparted by EC and DMC) while still having the components which will result in electrolytes with low melting points and high conductivity at low temperatures (imparted by EMC and DEC). In the course of our studies, it was recognized that to achieve good performance at temperatures below -30°C , electrolyte formations consisting of mixtures of these solvents should possess less than 25% EC by volume, with the best performance being obtained with 15–20 % EC-content. In this paper, we would like to disclose recent results relating to the development of low EC-content ternary and quaternary lithium-ion electrolytes which result in good performance down to temperatures as low as -50°C .

RESULTS AND DISCUSSION

In order to effectively evaluate the potential of such solutions, electrolyte formulations were investigated in MCMB - LiNiCoO_2 experimental cells. When the cells containing the low ethylene carbonate (EC)-based electrolytes were compared with baseline formulations in terms of the reversible capacity after five formation cycles, comparable results were obtained with the cells evaluated, as shown in Fig. 1. This suggests that the low temperature electrolytes with low EC-content possess the requisite stability and film formation characteristics to effectively passivate the electrodes and operate with the same efficacy as cells containing the baseline high EC-content electrolyte formulations.

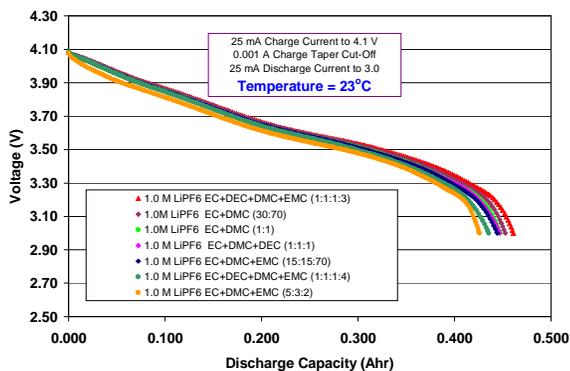


Fig. 1. Fifth lithium de-intercalation of MCMB - LiNiCoO₂ cells with different carbonate-based electrolytes.

When the cells were discharged at -20°C (cells charged at low temperature and discharged at a C/15 rate to 2.75 V), the following trend in delivered capacity was observed: 1.0M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3) > 1.0M LiPF₆ EC+DMC+EMC (15:15:70) > 1.0M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4) > 1.0M LiPF₆ EC+DMC (1:1:1) > 1.0M LiPF₆ EC+DMC (40:40:20) > 1.0 M LiPF₆ EC+ DMC (30:70) > 1.0 M LiPF₆ EC+ DMC (50:50). In addition to observing improvements in performance at -20°C , significant improvements in the performance at -40°C were observed with low EC-content electrolytes. As shown in Fig. 2, all of the four candidate low EC-content electrolytes performed better than the baseline solutions, delivering 50-65% of the room temperature capacity at -40°C , with the best performance being exhibited by 1.0M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3).

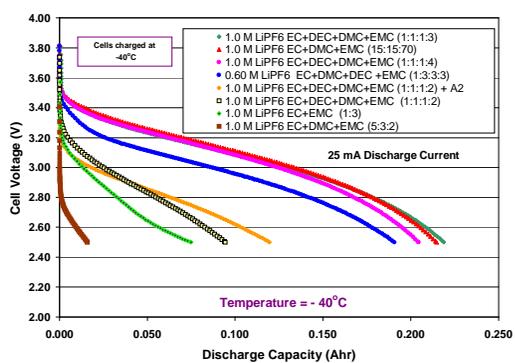


Fig. 2. Discharge capacity of MCMB-LiNiCoO₂ cells with different electrolytes at -40°C ($\sim\text{C}/15$ rate to 2.75 V).

To supplement the charge-discharge data generated, we also studied the effect of different electrolytes upon the film formation characteristics on carbon electrodes (MCMB-based materials), cathode electrodes and the subsequent impact upon electrode kinetics. The nature of the SEI (solid electrolyte interphase) layers formed on the electrodes strongly influence the rate capability (intercalation and de-intercalation kinetics) of lithium ion cells, especially at low temperatures. Thus, in order to investigate these issues a number of electrochemical characterization techniques were employed including: Tafel polarization measurements, linear polarization measurements, and electrochemical impedance spectroscopy (EIS).

All of these techniques were performed as a function of temperature (-40 to 25°C).

In addition to evaluating these electrolytes in experimental three-electrode cells, prototype 9 Ahr lithium-ion cells (DD-size Mars Rover design) were fabricated by SAFT America, Inc. to verify the observed improved low temperature performance. As shown in Fig. 3., excellent performance was obtained with cells containing the 1.0M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3) over a wide temperature range.

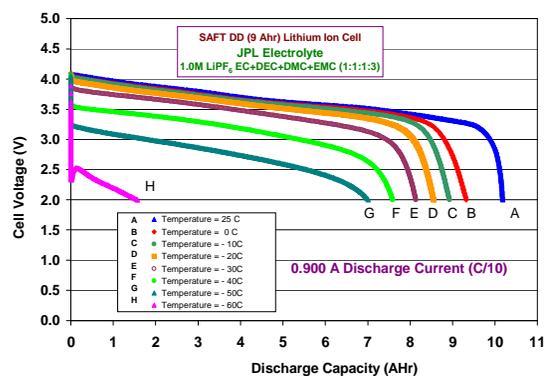


Fig. 3. Discharge capacity of a 9 Ahr prototype lithium ion cell at various temperatures. Cell charged at room temperature and discharged at C/10 rate (0.9 A) to 2.0.

When cells were charged at room temperature and discharged at a C/10 rate, over 90 WHr/Kg was delivered at -40°C and over 65 WHr/Kg at -50°C .

ACKNOWLEDGEMENT

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, for a DARPA TRP program (involving SAFT, America Inc.) and the Mars Exploration Program under contract with the National Aeronautics and Space Administration (NASA).

¹ M.C. Smart, C.-K. Huang, B.V. Ratnakumar, and S. Surampudi, Proceedings of the Intersociety Energy Conversion Engineering Conference (IECEC), Honolulu, Hawaii, July, 1997.

² M.C. Smart, B.V. Ratnakumar, C.-K. Huang, and S. Surampudi, SAE Aerospace Power Systems Conference Proceedings P-322, 1998, p. 7-14.

³ M.C. Smart, C.-K. Huang, B.V. Ratnakumar, and S. Surampudi, Proc. of the Inter. Ener. Con. Eng. Conf. (IECEC), Honolulu, Hawaii, July, 1997.

⁴ M.C. Smart, B.V. Ratnakumar, and S. Surampudi, *J. Electrochem. Soc.*, **146**, 486 (1999).

⁵ M.C. Smart, B.V. Ratnakumar, C.-K. Huang, and S. Surampudi, Proc. Vol. 98-1 for the 193rd Meeting of the Electrochemical Society, Inc., Abst. #53, San Diego, CA, May, 1998.

⁶ M.C. Smart, B.V. Ratnakumar, C.-K. Huang, and S. Surampudi, SAE Aerospace Power Systems Conference Proceedings P-322, 1998, p. 7-14.

⁷ E.J. Plichta, and W.K. Behl, Proc. of the 38th Power Sources Conf., Cherry Hill, NJ., p. 444 (June 1998).

⁸ Ein-Eli, Y., S.R. Thomas, V. Koch, D. Aurbach, B. Markovsky, and A. Schechter, *J. Electrochem. Soc.*, **142**, (L2) 73 (1996).