

Ester-Based Electrolytes that Enable Lithium-ion Cell Operation at Very Low Temperatures (-40° to -70°C)

M. C. Smart, B. V. Ratnakumar, K. B. Chin, and S. R. Narayanan

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

In order to enable future missions to Mars and the outer planets, NASA requires rechargeable energy storage devices with high specific energy, long life, and the ability to operate at low temperatures. Due to the attractive performance characteristics, lithium-ion batteries have been identified as the battery chemistry of choice for a number of future applications, including planetary orbiters, rovers and landers.¹ Some future applications typically will require high specific energy batteries that can operate at very low temperatures (down to -80°C), while still providing adequate performance and stability at ambient temperatures. Currently, the state-of-art lithium-ion system has been demonstrated to operate over a wide range of temperatures (-40° to +40°C), however, the performance is severely limited at temperatures below -40°C. These limitations at very low temperatures are due to poor electrolyte conductivity, poor lithium kinetics through the electrode surface layers, and poor ionic diffusion in the electrode bulk.

To address these limitations, we have focused our efforts upon the development of electrolyte solutions that possess high conductivity, good chemical and electrochemical stability, good electrode passivating characteristics, and a wide liquid range (low freezing point). One approach in the development of improved low temperature electrolytes involves the use of low melting, low viscosity co-solvents to further improve the low temperature conductivity and performance of lithium-ion cells. Aliphatic esters have been identified as promising co-solvents to improve electrolyte characteristics at low temperature and research in this area has been actively pursued at JPL^{2,3} and by others^{4,5,6,7}. In our studies, a distinct trend was observed with respect to the stability of the surface films formed in contact with ester-containing electrolytes. In solutions containing low molecular weight co-solvents (i.e., methyl acetate and ethyl acetate) the surface films appear resistive and inadequately protective, whereas, electrolytes containing higher molecular weight esters resulted in surface films with more desirable attributes, being preferred as candidate co-solvents for improved low temperature performance. Thus, our current focus has been upon the development of electrolyte formulations that contain higher molecular weight esters, which are anticipated to yield improved low temperature while still providing adequate long term stability and life characteristics.

In this paper we would like to present our recent results relating to the investigation of various electrolyte formulations that contain ester co-solvents upon the performance of lithium ion cells. More specifically, we have investigated the use of a number of organic ester co-solvents, including methyl butyrate, ethyl butyrate, methyl propionate, ethyl propionate, and ethyl valerate, in ternary and quaternary lithium-ion electrolytes. Emphasis was placed upon determining the effect of electrolyte type upon the low temperature performance in experimental MCMB-LiNi_xCo_{1-x}O₂ cells and characterizing their

influence upon the lithium intercalation/de-intercalation kinetics. These cells were subjected to electrical characterization (charge and discharge at different temperatures and rates), as well as, electrochemical characterization (EIS, linear polarization and Tafel polarization).

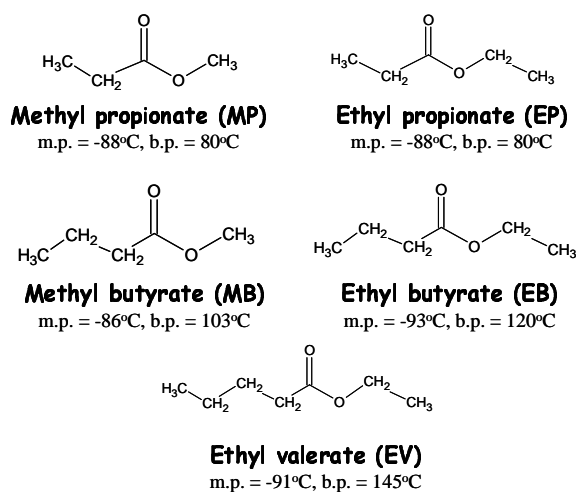


Fig. 1. Chemical structures and physical properties of ester co-solvents studied.

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