

Assessing Low-temperature Performance in Lithium-ion Cells using Discharge Data and an Electrolyte Model Based on Chemical Physics and Ion Solvation

Kevin L. Gering, PhD

Jon Christophersen

Idaho National Engineering and Environmental Laboratory

P. O. Box 1625, Idaho Falls, ID 83415-2209

Lithium-ion cells are seen as the next generation of power storage for electric and hybrid electric vehicles. However, lithium-ion systems with liquid electrolytes have difficulty in providing high power levels at low temperatures, which is a foremost obstacle to widespread application of this technology in hybrid electric vehicles (and other applications) to northern regions. A deeper quantitative understanding of low-temperature limitations will enable informed decisions concerning mitigation of poor battery performance at cold conditions.

Given a cell chemistry, it would be valuable to determine whether low-temperature limitations arise from fundamental charge-transfer kinetics at the electrodes, from transport limitations within the electrolyte, or from the severity of test conditions. Under the DOE Advanced Technology Development (ATD) program, a predictive model for multi-solvent electrolytes has been developed based on a chemical physics framework and key ion solvation parameters, yielding accurate predictions for numerous key transport and thermodynamic properties [1]. Application of this model to cold temperature scenarios enables evaluation of the relative contribution of electrolyte performance to overall cell performance. A complementary issue is phase separation of electrolyte components at cold conditions, a thermodynamic consequence.

Figures 1 and 2 summarize performance data for ATD Li-ion cells (18650 configuration) that underwent cold cranking tests [2] at temperatures ranging from -30 to 25 °C. Li-ion cells used for this work contain a lithiated NiCoAl-oxide cathode, a MAG10 carbon anode and an electrolyte comprised of a 3:7 mass ratio of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) with 1.2M LiPF₆. The cold crank test consists of 3, 2-second pulses at a scaled constant power, with 10-second rests in between. A lumped parameter model was used to split cell resistance into its ohmic (R_o) and polarization (R_p) resistances. Recall that the polarization term primarily represents the resistance due to lithium ion charge transfer through electrolyte regions, whereas the ohmic contribution accounts for behavior at the solid electrodes and current collectors. The figures clearly show that R_p is much less than R_o until the temperature dips below -22.3 °C, whereupon the polarization term dominates at lower temperatures. The cells failed cold crank power goals at temperatures below -15 °C.

The observed shapes and crossover of resistance curves suggest that there may be phase transitions of one or more electrolyte components. Other investigators have seen similar phase behavior regarding Li-ion electrolytes containing EC [3,4]. Region 1 could represent the start of partial phase transition of EC to a solid phase. The result of withdrawing EC from the electrolyte phase would be to shift viscosity lower, thus lowering electrolyte resistance beneath expected values. However, as the temperature is lowered further, the electrolyte conductivity drops and a greater amount of higher-resistance solid EC would be formed, causing R_p to increase steadily. It appears Region 2 represents a condition wherein solid EC has

reached a limiting amount within the cell. This region may also see the start of salt precipitation, which would occur after enough EC has dropped out as a solid to cause electrolyte permittivity to reach low values that won't allow full salt dissolution. Lowered salt solubility causes lower electrolyte conductivity and higher R_p. Solid phase formation might result in pore plugging within electrode materials, increasing R_o.

The steep increase in R_p below -20 °C may also imply the occurrence of concentration polarization (CP) as lithium ions are depleted from electrolyte in the immediate proximity of cathode particles. A step-wise Arrhenius analysis based on predicted properties (electrolyte conductivity, Li-solvent binding energies, and key solvation quantities) confirmed that electrolyte properties alone cannot account for the slope of the R_p data at the lower temperatures, and that phase formation and/or CP are likely candidates for the bulk of the observed behavior under the cold crank test conditions.

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3. L. M. Cristo and T. B. Atwater, "Low Temperature Behavior Phenomenon of 1M LiPF₆ 1EC:1DMC Electrolyte," Proceedings of the 8th Electrochemical Power Sources R&D Symposium, Portsmouth, VA, July 21-24, 2003.
4. B. Klassen et al., *J. Phys. Chem. B*, Vol. 102, pp4795-4801 (1998).

This work was sponsored by an agency of the United States Government under US DOE Contract DE-AC07-99ID13727.

