

Using a Chemical Physics Approach for Comprehensive Modeling of Battery Electrolytes

Kevin L. Gering, PhD

Idaho National Engineering and Environmental
Laboratory
P. O. Box 1625
Idaho Falls, ID 83415-3625
ekg@inel.gov

Lithium-ion cells have received international focus as a potential means of power storage for electric and hybrid electric vehicles. Application of these cells to diverse vehicle scenarios requires that accurate electrolyte properties be known under a wide range of conditions. Typical electrolyte systems utilized within lithium-ion batteries are those having one or more aprotic organic solvents and a single lithium salt.

A predictive model for non-aqueous battery electrolytes has been developed based on the chemical physics tied to ion-ion and ion-solvent interactions. Such interactions are considered within a framework that incorporates pertinent chemical, physical, and colligative contributions of the various species. The framework used herein is the exponentially modified mean spherical approximation (EXP-MSA), a molecular model that has been used with good success in predicting properties of aqueous and non-aqueous electrolytes (Gering, 1989; Gering and Lee, 1989, Gering et al., 1989), and is currently being used to predict properties of battery electrolytes for the DOE-ATD program (Gering, 2000-2002). MSA, in original or modified forms, has been considered by several investigators to describe nonideal solutions (Simonin and Hendrawan, 2001; Zerres and Prausnitz, 1994; Lu et al., 1993; Sheng et al., 1993; Varela, et al., 2000).

The basis of the EXP-MSA model is molecular theory that describes pair-wise interaction potentials of charged species within a dielectric medium, which can be applied to electrolyte concentrations ranging from infinite dilution to saturation limits. Three pair-wise interactions are provided by EXP-MSA (long range, hard sphere, and short range electrostatic) which collectively yield an accurate picture of non-ideal solution behavior. This model overcomes limitations of the Debye-Huckel model (simple and extended forms) and requires less supporting data than the Pitzer correlation. The EXP-MSA model is the foundation for predicting activity coefficients, osmotic coefficients, solvation numbers, various thermodynamic properties, and can additionally describe phase equilibria of solid-liquid phases (solubility limits) as well as liquid-vapor equilibria (e.g., vapor pressures).

The effects of non-aqueous solvents on electrolyte properties are assessed within the EXP-MSA model by considering the solvation behavior of such solvents. This is accomplished through a novel correlation based on solvatochromic parameters of solvents (Gering, 1989), which gives the average residence time of a polar solvent around a given cation, thus yielding information regarding preferential solvation. Solvent properties incorporated by this correlation include the normalized solvent polarity parameter, the polarity index, and the dielectric constant.

Electrolyte viscosity is estimated using an “equation of state” for electrolyte viscosity recently developed (Gering, 2000-2002), which is based on the chemical physics of ion solvation and the effects of the electrostatic field on solvent orientation. Additionally, the occurrence of ion pairs and triple ions is assessed. Contributions

from predicted solvated ion sizes, electrolyte viscosity, and ion association are used in calculating key performance parameters such as electrolyte conductivity and ion transference numbers.

Predictions cover ranges of temperature and composition foreseen for vehicle systems utilizing lithium-ion cells. Generally, this includes temperatures ranging from –30 to 60 °C and salt concentrations up to 1.5 molar. Comparisons between model predictions and laboratory data for the systems PC-DME-LiClO₄ and EC-EMC-LiPF₆ show there is excellent agreement between predicted values and laboratory data for wide ranges of temperature, salt concentration, and solvent composition. This predictive capability allows electrolyte properties to be evaluated for systems not yet investigated in the laboratory or for which there is inconclusive or incomplete data.

References

- Gering, K. L., *Assessment of Battery Electrolyte Components Based on a Chemical Physics Approach*, U. S. Department of Energy Advanced Technology Development program, work in progress (2000-2002).
- Gering, K. L., **A Molecular Approach to Electrolyte Solutions: Predicting Phase Behavior and Thermodynamic Properties of Single and Binary-Solvent Systems**, Doctoral Dissertation, University of Oklahoma (1989).
- Gering, K. L., and Lee, L. L., “Prediction of Vapor-Liquid Equilibria of Binary-Solvent Electrolytes”, *Fluid Phase Equilibria*, Vol. 53, 199 (1989).
- Gering, K. L., Lee, L. L., Savidge, J. L., and Landis, L. H., “A Molecular Approach to Electrolyte Solutions: Phase Behavior and Activity Coefficients for Mixed-Salt and Multisolvent Systems”, *Fluid Phase Equilibria*, Vol. 48, 111 (1989).
- Lu, J. F., Yu, Y. X., and Y. G. Li, *Fluid Phase Equilibria*, Vol. 85, 81 (1993).
- Sheng, W., Kalogerakis, N., and P. R. Bishnoi, *J. Phys. Chem.*, Vol. 97, No. 20, 5403 (1993).
- Simonin, J. P., and H. Hendrawan, *Phys. Chem. Chemical Physics*, Vol. 3, No. 19, 4286 (2001).
- Varela, L. M., Perez-Rodriguez, M., Garcia, M., and V. Mosquera, *J. Chem. Physics*, Vol. 113, No. 1, 292 (2000).
- Zerres, H. and J. M. Prausnitz, *AIChE Journal*, Vol. 40, No. 4, 676 (1994).