

Molecular Simulations of Lithium and Anion Transport in Liquid Carbonate Electrolytes

Dean Wheeler, Greg Gessel, and Aaron Henrichsen
Department of Chemical Engineering
Brigham Young University
Provo, UT 84602 USA

Battery power is diminished by kinetic and transport losses during the passage of electric current. If the electrolyte, both in the separator and porous electrode regions, exhibits poor ion-transport behavior, losses can be significant for high-power applications. While lithium-battery materials with improved ion-transport characteristics have been developed over the last few years, there is much that we do not understand about the underlying molecular causes for poor transport behavior. We have performed molecular dynamics simulations of lithium-battery electrolytes based on liquid carbonates in order to gain this information.

Molecular dynamics (MD) is a computational technique in which assumed intermolecular potentials are used to generate trajectories of a modestly sized collection of molecules. From such trajectories desired physical properties can be calculated. MD shows promise as a predictive tool for transport properties since unlike other methods it can explicitly account for molecular geometry, electrical charges and polarity, steric hindrance, and an arbitrary number of species. This work builds on previous work in which we established that MD can be used to calculate a full set of mass-transport coefficients for a solution containing an arbitrary number of species [1, 2]. The simulations are based on concentrated solution theory, that is, the Stefan-Maxwell equation for multicomponent diffusion [3].

Our earlier work [1], as well as that of the Balbuena group [4], shows that it is difficult to get results for transport properties from molecular simulations that quantitatively agree with experimental measurements [5]. For instance, the simulations overpredict the interaction between counterions in LiPF₆-liquid carbonate systems, leading to electrical conductivities that are too low by about a factor of five. Thus, one of the greatest difficulties in performing molecular simulations is obtaining accurate and yet computationally inexpensive intermolecular potentials.

We recently developed an interaction model for use in molecular dynamics that treats in an effective way the polarizability of species, a phenomenon that is particularly important in describing interactions between highly charged moieties such as ions. The model is computationally inexpensive and is simple to apply to small ab initio gas-phase calculations as well as large-scale periodic MD simulations. This ability to bridge length scales means that we are better able to develop effective interaction potentials from high-level quantum chemistry (electronic structure) calculations.

We will report on the results of our new model in terms of predicted mass-transport properties for LiPF₆ salt in liquid carbonate solvents. As part of the presentation we show that the model correctly predicts the maximum in electrical conductivity for the electrolytes, as a function of

concentration, and that this is related to ion association.

References

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