Temperature Dependent Thermodynamic Factors and Transference Numbers of Lithium Ion Battery Electrolytes

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ABSTRACT

Modeling of lithium ion battery performance requires precise physical and chemical parameters. To a high extent, limitations in lithium ion batteries are a result of the ionic transport within the liquid electrolyte. Ionic transport is generally described and modeled by application of the mathematical model for binary electrolyte solutions, introduced by Newman and Thomas Alyea¹. In this context ionic transport is based on four different, concentration and temperature dependent transport parameters, namely the conductivity $\kappa(c)$, the binary diffusion coefficient $D_\pm(c)$, the transference number $t_+(c)$ and the thermodynamic factor or the mean molar activity coefficient $f_\pm(c)$ respectively. From these transport parameters only the conductivity can be measured easily using turn-key equipment while determination of the remaining variables is more elaborate.

In literature various techniques, such as the Hittorf method², the potentiostatic polarization technique introduced by Bruce et al.³, the electromotive force method⁴, NMR techniques and galvanostatic polarizations⁵ are used amongst others to obtain values for the concentration dependence of the transference number. Popular in recent literature, for example by Georen et al.⁶, Nyman et al.⁷ and Lundgren et al.⁸, is a numerical optimization approach by which diffusion coefficient, transference number and thermodynamic factor are determined simultaneously. The focus of this contribution is on the determination of the temperature and concentration dependent thermodynamic factor and transference number.

Electrolytes under investigation are mixtures of standard lithium ion battery salts and solvents such as $\text{LiClO}_4$, $\text{LiPF}_6$ in EC/DMC/EMC/DEC. A three electrode setup with an internal standard is used to determine the thermodynamic factor at salt concentrations of 0.1 M, 0.5 M, 1.0 M, 1.5 M and 2.0 M. Heat bath and insulation as well as temperature control allows to adjust the temperature during the experiment to 20 °C, 30 °C, 40 °C and 50 °C. Concentration cells are used thereafter to obtain values for the transference number at the same concentrations and temperatures.

Preliminary results for the temperature dependence of the thermodynamic factor of $\text{LiClO}_4$ in EC:DEC (1:1, by weight) are shown in Figure 1.

The thermodynamic factor shows a small decrease with increasing temperature, i.e. more energy has to be spend to free the lithium ion from its solvation shell at higher temperatures compared to lower temperature values. Larger differences observed between individual salts and electrolytes are addressed and an empirical explanation will be given. Analysis of transference numbers will be done accordingly.

Both, transport properties, focused on in this work, agree well with literature data for same electrolytes. Trends for additionally investigated electrolytes fit nicely to the set of existing concentration dependencies of similar electrolytes. Concentration and temperature dependent values for transference number and thermodynamic factor will allow for an improved correlation between lithium ion battery experiments and simulations. Thereby not only precision but also the significance of simulations are enhanced, which helps in understanding as well as predicting present and future lithium ion battery technologies.

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References