Abs. 364, 206th Meeting, © 2004 The Electrochemical Society, Inc.

Measurement of Activity Coefficients and Transference Numbers of Nonaqueous Electrolytes Using Anion-Reversible Electrodes

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Accurate thermodynamic and transport property measurements are necessary for Li-ion battery optimization. Transport properties are key determinants of battery performance. Poor transport properties limit charge and discharge rates and lead to concentration gradients in the electrolyte during cell operation that promote failure mechanisms including side reactions, dendrite growth, and salt precipitation. In addition, the accuracy of full-cell models, which are integral to battery optimization, depends upon accurate property values. The goal of this research is to characterize electrolyte transport completely through the development of a new, more accurate method for measuring thermodynamic and transport properties in Li-ion battery electrolytes.

Full characterization of electrolytic transport involves the measurement of several different properties. According to the Onsager reciprocal relations, $n(n-1)/2$ independent transport properties are necessary to characterize transport completely in a system of *n* different species. Each necessary transport property measurement corresponds with a binary interaction parameter, D_{ij} between any two species *i* and *j*. The table below indicates the interaction parameters that exist between a cation, anion and three solvents (indicated by the subscripts 0, 1 and 2). The three measurable transport properties: the transference number, conductivity, and diffusion coefficient, are functions of the binary interaction parameters of the system, as well as concentration and temperature. Only for a three-species system do these three transport properties fully characterize system transport.

# of species (*n*)	# of transport properties	Binary Interaction Parameters (w/ binary salt)
3	3	D_{+0}, D_{-0}, D_{+-}
4	6	D_{+0}, D_{-0}, D_{+-}, D_{+1}, D_{-1}, D_{01}
5	10	D_{+0}, D_{-0}, D_{+}-, D_{+1}, D_{-1}, D_{01}, D_{+2}, D_{-2}, D_{12}, D_{02}

Methods exist to measure each of the transport properties. Electrolyte conductivity can be measured using AC impedance, and diffusion coefficients can be measured using the method of restricted diffusion, for example. The transference number has been measured in several different ways. Recently, the method of galvanostatic polarization has been developed for use in polymer and aqueous electrolytes.[1,2,3] This method combines two experiments, galvanostatic polarization and a concentration cell, in order to back out the transference number and activity coefficient simultaneously. This simultaneous solution for the activity coefficient and transference number may introduce error in property measurement. In addition, side reactions at the lithium electrode were problematic to this technique.[2]

Independent property measurement would reduce error in the determination of transference numbers and activity coefficients. In electrolytes, equilibrium cell potentials can be used to determine activity coefficients independently. This method requires electrodes reversible to both ions in solution. Due to the lack of a suitable anion-reversible electrode, this measurement technique has not yet been applied in non-aqueous Li-ion battery electrolytes.

In the new method that we propose, the activity coefficient is measured directly using an electroactive polymer electrode, poly(3-butylthiophene), reversible to anions in solution. In addition, this method uses a reference electrode of a more positive potential than lithium (lithium titanate spinel) in order to reduce the likelihood of side reactions. The use of lithium titanate spinel provides an additional advantage in that it has a flat voltage plateau due to the formation of two-phases in the electrode.

In the present work, transport in a three-species electrolyte ($LiPF_6$ in propylene carbonate) will be characterized completely using the new, independent method of measurement for activity coefficients and transference numbers. This will allow the determination of the binary interaction parameters and assist in the study of multiple solvent electrolyte transport and electrolyte optimization.

Acknowledgement

We thank Kathy Striebel for the use of laboratory facilities. This work was supported by the Assistant Secretary of Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies of the U.S. Department of Energy under contract No. DE-AC03-76SF00098.

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