

Measuring Salt Activity Coefficients in Lithium-Battery Electrolytes

Electrolyte salt activity coefficients are essential for accurate electrochemical cell models; however, values for lithium salt activity coefficients are scarce in the literature. Stewart and Newman employ concentration-cell experiments to determine the salt activity coefficient for solutions of LiPF_6 in propylene carbonate and in a 1:1 by weight solution of ethylene carbonate (EC) and ethyl methyl carbonate. In their analysis, they fit the open-circuit-potential data to a modified Debye-Huckel equation and extrapolate their result to infinite dilution to estimate a transference number of 0.38. Assuming that the transference number is independent of concentration, the thermodynamic factor, an indicator of solution ideality, increases from 1 (ideal) to 4 for salt concentrations up to 1.75 M. For LiPF_6 in EC, the activity coefficients are evaluated from melting-point-depression experiments on a differential scanning calorimeter. This method allows for the determination of activity coefficients without prior knowledge of the transference number; however, it requires accurate estimates for the relative partial molar enthalpy and precise melting point determinations for dilute solutions. For LiPF_6 concentrations ranging from 0.0625 M to 1 M in EC, the thermodynamic factor increases from 1.1 to 3.45. While the thermodynamic factors indicate non-ideal behavior, the authors conclude that modeling electrolytes ideally may not significantly affect full-cell model accuracy.

From: *J. Electrochem. Soc.*, **155** (6), A458 (2008).

Modeling Particulate Effects on the Cathodic Current Capacity in Crevice Corrosion

Much of the literature exploring the effect of electrolyte layer properties on crevice corrosion assumes a homogeneous solution layer. A more realistic scenario for many applications is an electrolyte layer, which in turn contains a certain volume fraction of entrapped dust or other particulate matter. The presence of such particulates within the electrolyte layer is expected to impact the cathode capacity by increasing the ohmic resistance of the electrolyte and decreasing the exposed electrode area, thereby limiting the amount of anodic dissolution which may take place. In this paper, models were derived for the effective electrolyte conductivity in the thin solution layer over the cathode, accounting for both of the aforementioned issues. The particles were assumed to be chemically inert and non conductive. While for most of the modeling calculations the system was considered to be a uniform distribution of particles of predetermined size and shape, supplemental analyses demonstrated that the shape and arrangement of the particles had a negligible effect on the total cathodic current. Bruggeman's equation was applied to address the volume blockage effect of particulates on the electrical properties

of the electrolyte film. The impact of particles on the exposed electrode area was addressed by proportionally reducing the value of the exchange current density. The model demonstrates that while the presence of particles in the electrolyte tends to decrease the total cathode capacity, the use of a homogeneous system is a reasonable approximation even in the presence of particulates over a wide range of physical, chemical, and electrochemical properties that are generally encountered in atmospheric corrosion.

From: *J. Electrochem. Soc.*, **155** (5), C269 (2008).

Caution of Using Constant Phase Element

Nyquist plots of electrochemical impedance spectroscopy (EIS) data frequently exhibit non-ideal behavior, such as depressed semicircles and capacitive straight lines not perpendicular to the real axis. This non-ideal behavior is commonly attributed to non-homogeneity of the electrochemical system. A constant phase element (CPE) is often employed to improve the fit of a proposed equivalent circuit model to the data. Researchers from Italy and France investigated the accuracy of using a CPE to model an oxide film with non-homogeneous properties. The authors made graded thickness oxide coatings on Nb and Ta sheets by withdrawing the electrodes during anodization. Using three different cases that could exist experimentally, they derived equations for the global impedance of the graded film based on the local electrolyte resistance connected in series with the parallel combination of local film capacity and local film resistance. The ohmic resistance-corrected phase angle was used to compare the responses of their models to one containing a CPE. Their models and their measurements were in agreement and exhibited a minimum in the corrected phase angle at high frequencies, whereas the CPE model did not. The authors caution that a model using the CPE may appear to satisfactorily fit data when in fact the nonhomogeneity does not cause CPE behavior.

From: *Electrochem. Solid-State Lett.*, **11** (6), C27 (2008).

Silicon/Graphite Composite Electrodes for High-Capacity Anodes: Influence of Binder Chemistry on Cycling Stability

The use of silicon as an anode in lithium batteries has long held the attention of the research community because of the high capacity of this material when compared to graphite anodes (3579 mAh/g for Si vs. 372 mAh/g for graphite). However, the material experiences a large volume change (280%) during lithiation/delithiation, which in turn leads to rapid capacity fade. The two oft-used routes to accommodate the volume change include embedding the Si particles in a carbon matrix along with the use of a binder to maintain interparticle contact. It has been argued that the binder has to be flexible in order to allow

the particles to expand without losing mechanical integrity. However, recent reports suggest that surprisingly, a brittle binder, carboxymethylcellulose (CMC), performs better compared to flexible binders. However, no clear understanding exists for this counterintuitive observation. Hochgatterer, Winter, and their colleagues have shed light into this phenomenon using electrochemical cycling with various binders along with infrared spectroscopy. The best results were obtained with sodium-CMC as the binder. The authors propose a condensation mechanism that results in the formation of a bond between the binder and the silicon. The authors conclude that it is not the binder's flexibility that is the key; rather, the chemical bond between the active material and the binder results in the silicon particles being held in shape during cycling.

From: *Electrochem. Solid-State Lett.*, **11** (5), A76 (2008).

Nanostructured Block Copolymer Dry Electrolyte

Recent years have seen increased interest in polymer electrolyte-based batteries because of their lighter weight and more shape-conforming features compared with those using inorganic glass or ceramic electrolytes. Researchers at the University of Maryland recently reported on the synthesis and characterization of a new type of solid-state polymer electrolyte with enhanced lithium transport based on a self-assembled diblock copolymer. The diblock copolymer consists of a poly(ethylene oxide) (PEO) block and a random copolymer of methyl methacrylate (MMA) and lithium salt of methacrylic acid (MAALi). Lithium bis(oxalato)borate, LiBC_4O_8 (LiBOB) was used as salt in the dry electrolyte. Impedance and temperature studies were carried out to characterize the conductivity performance of the electrolyte. The diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] with added LiBOB (in the molar ratio ethylene oxide: LiBOB = 3:1) was used to form flexible translucent films, which exhibited an average ionic conductivity value of $1.26 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature, an improvement of one order of magnitude compared to similar molecular weight PEO homopolymers. Transmission electron microscopy showed structured domains of lithium, templated by the microphase separation of the block copolymer. The improved conductivity was attributed to reduction of crystallinity and introduction of secondary lithium domains in the conductive polymer matrix. ■

From: *J. Electrochem. Soc.*, **155** (6), A428 (2008).

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