Temperature-Step Impedance Spectroscopy for Exchange Current Densities at Lithium/Polymer Interfaces

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The polarization response of lithium-electrode cells is determined by the electrolyte transport properties and electrode kinetics. While transport in polymeric separators has been well characterized[1], and several accurate methods exist to measure these properties, the variation of kinetic parameters that determine interfacial resistances at lithium electrodes is rarely considered. In this work, the exchange current densities at several lithium/polymer interfaces are characterized over concentration and temperature ranges of practical engineering significance. Measurements of these kinetic parameters are obtained by temperature-step impedance spectroscopy, an efficient method that allows the straightforward determination of reaction parameters from impedance spectra of symmetric Li/polymer cells. The results of these measurements demonstrate that more consideration should be afforded to the chemical processes that occur at lithium/polymer interfaces.

In addition to illustrating the effect of temperature on interfacial resistance, which is reported in detail, the impedance experiments provide a quantitative means by which to elucidate the role of the electrolyte anion and salt concentration in determining reaction rates at lithium interfaces. Both of these latter parameters are found to have some effect on the experimentally obtained interfacial resistances. As might be expected, the effect of electrolyte concentration is more dramatic, while the selection of counterion is found to play a smaller role. Both experiments suggest means by which to minimize the charge-transfer resistance of lithium electrodes, which should increase the power density available from a lithium-electrode cell[2] and minimize the large potentials that may contribute to side reactions or lead to dendritic deposits.

The exchange current density is obtained from a series of measurements of the charge-transfer resistance, R_{ct}, at lithium electrodes, each of which is performed at a different temperature T. An Arrhenius plot of $\ln(T / R_{ct})$ is then used to extract kinetic parameters; an exemplary plot of LiTFSI in a PEO-type polymer (Zeon ZTP500), is shown in figure 1. Activation enthalpies and entropies, which are used to compute exchange current densities, are obtained from the slope and intercept respectively. Obtained activation enthalpies, which are obtained from the slope, are very accurate and repeatable within a small tolerance, because the temperature stepping allows cancellation of error; the activation entropies are somewhat more variable. The linearity of this curve verifies that undesired side reactions and contact resistances are negligible.

The exchange current density at a lithium/polymer interface is found to exhibit a maximum with respect to concentration (figure 2), suggesting that an optimal electrolyte composition may exist to minimize charge transfer resistance. The identity of the anion appears to modify the rates only slightly in most cases, consistent with the reactant being the solvated lithium ion (i.e. no electron transfer to the ion pair). The effect of changes in the polymer solvent is also reported to investigate the influence of molecular weight (viscosity), polarity and solvation on the interfacial kinetics.

Variation of interfacial resistance with factors such as temperature, concentration and nature of the electrolyte plays a large role in determining the cell polarization and is critical for accurate simulation of cell performance[2].

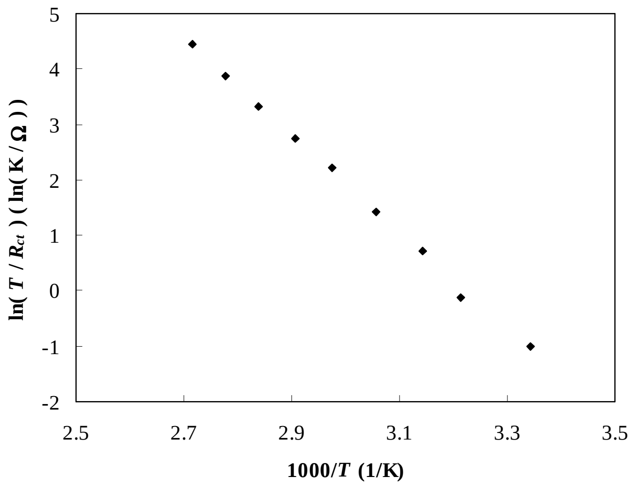

Figure 1. Arrhenius plot of $\ln(T / R_{ct})$ versus temperature. Kinetic parameters are obtained from the slope and intercept.

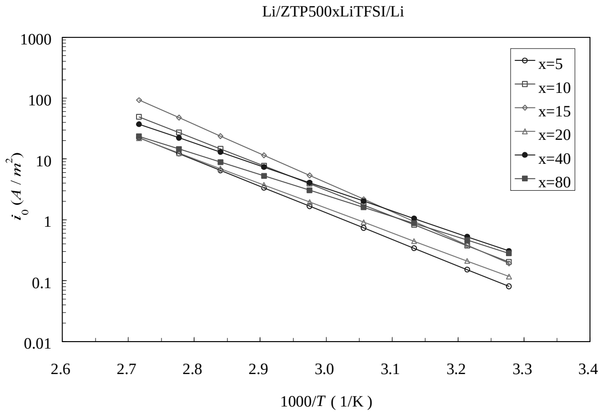

Figure 2. Arrhenius dependence of exchange current density on temperature at several concentrations of LiTFSI in Zeon ZTP500 polymer.

Acknowledgement. This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098

References.

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