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Transport Properties of a High Molecular Weight Poly(propylene oxide)-$LiCF_3SO_3$ System

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Abstract

Conductivities (σ), salt diffusion coefficients (D_s), and cationic transference numbers (t_+^0) are reported for a high molecular weight polypropylene oxide (Parel™)-$LiCF_3SO_3$ polymer electrolyte system at 85° C. Transference numbers were determined as a function of salt concentration using a recently described electrochemical method based on concentrated solution theory. For the Parel-$LiCF_3SO_3$ system, t_+^0 is slightly positive for electrolytes with O:Li ratios of 15 or 12:1, but decreases to negative values for more concentrated solutions. This implies that negatively charged ionic aggregates such as triplets are more mobile than free cations in this concentration range. Such behavior is commonly seen in binary salt/polymer electrolytes, which typically exhibit a high degree of non-ideality. The non-unity transference numbers and microphase separation in the Parel-$LiCF_3SO_3$ system strongly suggest that salt precipitation or phase separation will occur in operating cells containing these electrolytes, due to the development of large concentration gradients during passage of current.

Introduction

To fully describe the behavior of a binary salt/polymer electrolyte in an operating cell, it is necessary to know three transport properties. Typically, conductivity (σ), salt diffusion coefficient (D_s), and cationic transference numbers (t_+^0), are chosen.[1] While the first two properties are relatively easily obtained, measurement of transference numbers has been fraught with difficulty and confusion. This is due, in part, to inaccurate simplifying assumptions concerning the ideality of the solutions, as well as experimental difficulties. We have recently developed an accessible electrochemical method related to the Hittorf method, and based on concentrated solution theory, to measure t_+^0 for binary salt/polymer solutions.[2,3] The calculation requires information from three different electrochemical measurements; concentration cells, restricted diffusion, and current interrupt experiments. To avoid large propagation of errors, careful statistical analysis of the data is often required. One goal of this work was to identify and quantify sources of errors to ensure confidence in the transference number calculations.

This study is part of an ongoing effort to systematically characterize the transport properties of solid polymer electrolytes as a function of salt concentration and type, as well as polymer structure. Parel™, a high molecular weight (M_w=5 x 10^5 g/mole) polypropylene oxide, was initially chosen because it has good film-forming properties and is well-characterized.[4]

Experimental

PAREL™ (Zeon Chemicals Inc., Illinois, USA), a commercially available polypropylene oxide (PPO) (M_w=5 x 10^5 g/mole, M_n=2.5 x 10^5 g/mole), containing 5 mole % glycidyl ether groups, distributed randomly, was purified prior to use. To remove additives, the polymer was subjected to Soxhlet extraction with methanol for 7 days, and then dried in a drying pistol at 65°C under vacuum, over P_2O_5, for another 7 days. $LiCF_3SO_3$ (Aldrich Chemical Company) was dried under vacuum over P_2O_5 to remove adventitious water. Dried polymers and salts were then transferred directly to the glove-box under vaccuum without exposure to air. Dimethoxyethane was dried and filtered through activated alumina (ICN Alumina N, Super activated I) prior to use. Reagents were stored in a dry, inert atmosphere glove-box, and all film preparation, handling, and cell assembly was carried out in the same atmosphere.

Solutions of Parel-$LiCF_3SO_3$ in dimethoxyethane were prepared by dissolving 2g Parel and the appropriate amount of $LiCF_3SO_3$ in 50 mL dimethoxyethane. These were then cast onto Teflon and allowed to dry, to form films approximately 50-100 μm thick. O:Li ratios of the dried films ranged from 2 to 400 (5.65 -0.06 mol/dm^3). Samples with O:Li ratios greater than 80 were prepared by successive dilutions of more concentrated $LiCF_3SO_3$ solutions to avoid preparation errors.

Densities of films were determined by placing weighed samples in a specific gravity bottle of known volume, filled with heptane. The weight of the bottle before and after displacement of the liquid allows the volume of the electrolyte to be calculated. O:Li ratios could then be converted to molar salt concentrations, using the measured film densities.

Differential scanning calorimetry (Perkin-Elmer DSC-7) was employed for thermal characterization of PPO-$LiCF_3SO_3$ films over a temperature range of -100 to +100° C, in a helium atmosphere. Samples were rapidly cooled to -100° C and heated to 100° C at a scan rate of 5° C/min, and then subjected to a second cooling and heating between the same limits at a 5° C/min rate. This allows observation of any salt precipitation phenomena and an accurate determination of T_g, during the second heating cycle, because the thermal history of each sample was controlled.

A Solartron™ SI 1254 four-channel frequency response analyzer and a 1286 electrochemical interface were used to measure the impedances of electrolyte films of known thickness in constant-pressure or constant volume cells with blocking electrodes. The cell holder design was chosen according to the nature of the sample; those with low salt concentrations tended to flow under pressure. For these films, a spacer of known thickness was utilized, and the film was allowed to flow under heat and pressure until the spacer was completely filled. Samples with high salt concentrations were more rigid and did not undergo this treatment. Cells were equilibrated in a convection oven with the temperature controlled to within ±0.5° C, for at least one hour prior to measurement. Measurements were taken at 10° intervals between 30-90° C, and conductivities at 85° C (e.g., Figure 1) were determined by interpolation. The thickness of these samples was determined with a micrometer, both before and after the measurements.

Concentration cells were assembled as previously described,[1] and potentials determined using a Keithley 642 electrometer. Cells of configuration Li/polymer electrolyte/Li were assembled under an inert atmosphere and equilibrated at 85° ±0.5° C prior to galvanic polarization with a MacPile II (Biologic, Claix, France) multichannel

potentiostat/galvanostat, for diffusion coefficient determinations and current interrupt experiments used in the transference number calculations. For the latter, cell potential readings were plotted against dimensionless time, T, (equation 1) and the results extrapolated to T=1.[5] This allows the potential to be determined without complications from double layer charging, but before significant diffusion occurs.

$$T = \frac{t_i^{1/2}}{t^{1/2} + (t - t_i)^{1/2}} \tag{1}$$

To evaluate the size of the random errors and locate the major error sources for the diffusion coefficient and transference number determinations, standard deviations were calculated for all separate experiments. The systematic errors that may be associated with the methods could not be estimated because no appropriate reference method was available. The number of independent measurements for the diffusion coefficients and current interrupt experiments were both between 6 and 10 for each salt concentration; more experiments were carried out when large variations were noticed in the results. Between 6 and 15 independent experiments were performed for the concentration cell experiments.

The stickiness of the electrolyte films and their tendency to flow at elevated temperatures complicated the sample thickness measurements needed for conductivity and diffusion coefficient determinations. For this reason, the entire cell sandwich (electrolyte and two lithium or stainless steel electrodes) was measured both before and after the

experiments and compared. A sandwich of three stainless steel plates of known thicknesses was used to calibrate the micrometer used in the measurements.

For the transference number calculations, the errors associated with all experimentally derived parameters in equation 3 were estimated utilizing common equations and rules; e.g., see Miller and Miller.[6] This was, however, difficult to determine for dlnc/dU, in equation 3 (i.e., concentration cell experiments). Instead, the error associated with each coefficient of the polynomial fit of U vs. ln C was calculated and employed. The total error of the differentiated polynomial could then be written as a function of ln c to evaluate the contribution to the error in the transference number.

Results and Discussion

The presence of more than one phase in the polymer electrolyte system complicates analysis of the transport property data. For this reason, it is desirable to investigate the thermal properties prior to study. While polypropylene oxide/salt mixtures are typically amorphous at room temperature and above,[7] salt solubility limits are often lower than in analogous polyethylene oxide (PEO) systems. Precipitation upon heating PPO/salt solutions to moderately elevated temperatures has also been observed in some instances.[8,9,10] Microphase separation is a common phenomenon in both low and high molecular weight PPO polymer electrolytes, and is characterized by double glass transition temperatures for samples that appear homogeneous at room temperature.[4,11,12,13] Generally these materials consist of a salt-poor PPO (low T_g) phase interspersed with a salt-rich (high T_g) one; the relative amounts of which are determined by the overall polymer-salt

composition. This microscopic liquid-liquid separation arises as a consequence of the relative strengths of the cation-polymer interactions and ion-ion long-range coulombic interactions that oppose dispersion.

For this work, the phase behavior of pure Parel and Parel-$LiCF_3SO_3$ samples with O:Li ratios ranging between 80:1 and 3:1 was investigated using differential scanning calorimetry (DSC). Films made from Parel-$LiCF_3SO_3$ solutions appeared homogeneous and fully amorphous (clear) to the eye at room temperature, and no melting transitions were observed between -100 and 100° C. Conductivity measurements as a function of temperature showed the expected VTF behavior[14] from 30-90 °C with no anomalies, indicating that the solutions were amorphous throughout this temperature range, and that salt precipitation does not occur.[8] Parel-$LiCF_3SO_3$ solutions with O:Li ratios of 20:1 and 15:1, however, exhibited two T_gs in the DSC experiments, indicating that microphase separation occurs in this system. The thermal behavior of Parel-$LiCF_3SO_3$ polymer electrolytes will be the subject of a separate publication.[15]

Macroscopically phase-separated polymer electrolyte systems (e.g., some high molecular weight PEO/salt solutions at slightly elevated temperatures) typically consist of a liquid component and one or more crystalline polymer-salt complexes that are poorly conducting.[16] The salt content of the conductive phase may not be the same as that of the bulk. Furthermore, an element of tortuosity is introduced because of the presence of regions of crystalline compounds. It is, therefore, difficult to correlate the measured transport properties with the bulk compositions of the polymer-salt mixtures without additional information.

Microphase-separated polymer electrolytes differ in several important respects from these macroscopically heterogeneous systems. In the former, there is spectroscopic evidence of continuous rearrangement of salt-rich and salt-poor micro-domains due to Brownian motion, reminiscent of water-in-oil micro-emulsions.[17,18] This dynamic disorder may cause seemingly contradictory results when ion transport properties (e.g., diffusion coefficients) are measured by different methods. The contradiction is resolved when the relative time-scales of the motional perturbation and the experiments are considered.[18] Diffusion measurement techniques that are rapid in comparison to the micro-domain fluctuation (e.g., spectroscopic methods) probe both the Brownian and the ionic motion, making it difficult to de-convolute information obtained from these experiments. In contrast, restricted diffusion methods, and the electrochemical techniques used to measure transference numbers in this study, are slow (from many minutes to hours), and should accurately reflect the time-averaged bulk ionic motion. The dynamic microphase separation commonly found in PPO electrolytes, therefore, does not present the same difficulties as macroscopic phase separation does; these systems can be considered simple binary salt-polymer solutions for the purposes of the transport property measurements. It is important to note, however, that no direct information about either the existence of microphases or the details of ionic speciation[1] can be obtained directly using this method alone; a purely macroscopic description of the polymer electrolyte system is obtained. This is, however, entirely adequate to predict the behavior of polymer electrolytes in working electrochemical cells.[19]

At 85° C, the conductivities of most of the Parel-$LiCF_3SO_3$ electrolyte films are sufficient to allow measurement of electrochemical properties necessary for the transport

property data (Figure 1). Additionally, several other polymer electrolyte systems have been studied at this temperature,[1,3] facilitating comparison. In general, conductivities of Parel-$LiCF_3SO_3$ electrolytes are somewhat lower than that of most PEO-based solutions at the same temperature. As in these previously investigated systems, however, a conductivity maximum is found at intermediate salt concentrations (for Parel-$LiCF_3SO_3$ this occurs at O:Li ratios between 20 and 12:1). This behavior is often explained as a trade-off between increasing numbers of charge carriers, and ion aggregation and increased viscosity due to ionic cross-linking, which lowers the conductivity as the salt concentration passes a critical value. This is more clearly seen when the concentration dependence of the molar conductivity (conductivity normalized by salt concentration) is plotted (Figure 2). The very steep rise in molar conductivity to a maximum, followed by a sharp decrease is characteristic of PPO electrolytes.[20] Prud'homme et al.[4] have noted that the maxima in reduced temperature (iso-viscosity) plots of conductivity or molar conductivity in PPO electrolytes roughly coincide with the critical composition at which microphase separation is observed, suggesting that a percolation threshold is reached at this point.

Restricted diffusion experiments were carried out to determine salt diffusion coefficients (D_s) for the Parel-$LiCF_3SO_3$ electrolytes. Symmetrical cells containing films of known thickness are subjected to galvanic polarization for a short time. The relaxation of the cell potential back to 0 V ($\Delta\Phi$) is then monitored after the current is turned off. At long times, equation 2 holds true:

$$\ln \Delta\Phi = \frac{\pi^2 D_s}{L^2} t + A_1 \qquad (2)$$

where D_s is the differential salt diffusion coefficient, t is time, L is the electrolyte thickness, and A_1 is a constant. Figure 3 shows the salt diffusion coefficients determined in this manner for the Parel-$LiCF_3SO_3$ electrolyte system. Because the conductivities of several samples were relatively low, and some samples exhibited flow (e.g. L was not constant), it was unexpectedly difficult to obtain data of high quality. An additional complication was the tendency for $\Delta\Phi$ to be small, even for relatively large perturbations. To overcome this problem, several cells were built for each concentration and the experiments repeated up to ten times. The thickness of the electrolyte was measured both before and after experimentation, and the average L was used in equation 2. Figure 3 also shows the 95% confidence intervals based on a statistical analysis of these results.

A local maximum also occurs in the salt diffusion coefficient data, although at much lower concentrations than for the molar conductivity. This is in contrast to a recently studied low molecular weight PPO (polypropylene glycol-4000)/$LiCF_3SO_3$ system, which showed a correlation between these two transport properties,[18,21] although not with the ionic diffusivity measured by ^{19}F pfg-NMR.[22] This was explained by the differing time scales of the various experiments, and that of the fluctuations of the salt-rich microdomains. A similar argument may be made for the apparent discrepancy in the present results. It has been observed that microdomains in high molecular weight PPOs are larger and less labile than in the low molecular weight analogs, due to chain entanglement and end group effects.[4] We speculate that the microphase fluctuation in Parel-salt systems is much slower than in low molecular weight PPO electrolytes; perhaps on a similar time scale as AC impedance experiments. If this is true, AC conductivity results on Parel electrolytes should be interpreted with caution, as they might not accurately reflect the

bulk ionic properties in the critical concentration range where microphase separation is significant. Additional spectroscopic studies designed to address this question may shed further light on this issue, and are planned for the near future.[23]

Transference numbers are calculated from the results of three different experiments, according to equation 3.[1]

$$t_-^0 = 1 - t_+^0 = \frac{mc_\infty F(\pi D_s)^{1/2}}{4}\left(\frac{d\ln C}{dU}\right) \tag{3}$$

In equation 2, c_∞ is the bulk molar salt concentration, D_s is the salt diffusion coefficient as determined by the experiments described above, d lnC/dU is the reciprocal of the local slope of concentration cell plots, and m is a slope derived from current interrupt data.

The concentration cell data for Parel-$LiCF_3SO_3$ at 85° C is shown in Figure 4. These are obtained by measuring the potentials of thermally equilibrated symmetrical cells containing two electrolyte films of different compositions, $Li/PPO_nLiCF_3SO_3/PPO_mLiCF_3SO_3/Li$. The measurements consist of contributions from both the junction potential and Nernst potential difference at the electrodes due to the different salt concentrations. The distance between the two lithium electrodes is sufficiently large so that the concentration gradient cannot relax before the measurement is taken. In practice, a reference composition is used (e.g., m is held constant) and n is varied. The potential readings are taken as positive for n>m. Six to fifteen cells were constructed for each point and the average reading and 95% confidence intervals plotted in the figure.

Theoretically, transference numbers can be derived from the slope of a plot of cell EMF (U) vs. salt activity, A, according to equation 4.[24]

$$t_{-}^{0} = \frac{F}{2RT}\left(\frac{dU}{d\ln A}\right) \tag{4}$$

However, the thermodynamic factor (variation of salt activity with concentration) is seldom known for polymer electrolytes, and U is typically plotted versus ln C instead. The marked deviation from linearity in these plots is further evidence of their non-ideality. This is apparent in the concentration cell data for the Parel-$LiCF_3SO_3$ system shown in Figure 4.

In order to determine transference numbers, an additional experiment is, therefore, necessary. It can be shown that the concentration difference, ΔC, which develops after a symmetrical cell has been galvanostatically polarized for a short period of time, is proportional to $it^{1/2}$, where i is current density and t is time.[1] The induced cell potential, $\Delta\Phi$, measured after the current is interrupted, is equivalent to the potentials measured in the concentration cell experiments. The slope, m, of the plot of $\Delta\Phi$ vs $It^{1/2}$ is used in equation 3, and allows correlation of the electrochemically induced concentration difference with the results of concentration cell experiments. Representative plots for Parel-$LiCF_3SO_3$ electrolytes are shown in Figure 5. The slope was roughly constant at high salt concentrations, but increased gradually for intermediate O:Li ratios. For very dilute solutions, the slope increased dramatically. This is similar to behavior seen in the PEO-$NaCF_3SO_3$ electrolytes,[1] and opposite to that shown by PEO-$NaN(CF_3SO_2)_2$.[3] While

this suggests a trend for electrolytes based on anion type, information on more systems is clearly needed.

Figure 6 shows cationic transference numbers as a function of salt concentration derived from the three experiments described above, and equation 3. For dilute solutions, meaningful transference numbers could not be calculated because errors were too large. It was, however, possible to determine values for several solutions at the higher salt concentrations useful for devices. Even so, several of these numbers could not be determined with a high degree of accuracy, due to propagation of errors, and the measurement difficulties discussed earlier. It is clear, however, that t_+^0 is non-unity for the Parel-$LiCF_3SO_3$ system in this salt concentration range, and decreases with increasing salt concentration, becoming negative at very high salt concentrations. Negative transference numbers at high salt concentrations appear to be a general feature of polymer electrolytes, due to the low dielectric constants of the host materials, and the non-ideality of the solutions. Interestingly, t_+^0 is positive at significantly higher salt concentrations for the Parel-$LiCF_3SO_3$ solutions than for previously studied PEO analogs, suggesting that negatively charged ion aggregates may be less mobile in the former than in the latter.[1,3]

Negative t_+^0 values are best understood in the context of Spiro's definition of transference number:[25] the number of moles of an ion constituent that crosses a reference plane, fixed with respect to the solvent, when one Faraday of current is passed through the plane, in the absence of concentration gradients. Negative t_+^0 values indicate that negatively charged species, such as triplets containing two anions and one cation, commonly present in non-ideal solutions, are more mobile than free cations (or positively

charged ionic aggregates). These negatively charged species, however, *move in the "wrong" direction* under the influence of current (i.e., they move towards the positive electrode during cell charge, and vice versa). For a time, salt diffusion driven by the developing concentration gradient counteracts the ion migration, allowing the cell to operate.[26] For devices containing polymer electrolytes with initially high salt concentrations (e.g., those with negative t_+^0 values), polarization may occur prematurely due to salt precipitation at one electrode, particularly at high rates of discharge.[27] Better performance can be obtained simply by decreasing the initial salt concentration in the polymer solution to a range where t_+^0 is less negative.[19] If dilute solutions are chosen, however, the cell may fail due to salt depletion instead. Design factors such as electrode thickness and porosity also play a critical role in determining performance, and choice of initial salt concentration needs to be considered in this context, as well.

Figure 6 indicates that concentration gradients will develop more slowly in Parel-$LiCF_3SO_3$ electrolytes with O:Li ratios of 15:1 than in the more concentrated solutions, allowing longer operation of cells at higher current densities. The non-unity t_+^0 values indicate that such concentration gradients will, however, eventually develop. In spite of the relatively high t_+^0 values, all Parel-$LiCF_3SO_3$ solutions may be more prone to concentration gradient-driven phenomena that lead to premature cell failure than other systems that have been studied. This is due to the observed microphase separation, which can be a precursor to salt precipitation or macroscopic phase separation upon further perturbation of PPO systems.[8] Parel has sometimes been suggested for use in blends, to impart mechanical strength to a more highly conductive polymer electrolyte.[28] These

results suggest that such an approach may not be fruitful, because phase separation or salt precipitation will tend to occur during passage of charge.

The results of the statistical analysis indicates that measurement of thickness is the major source of error. Due to the stickiness of many of the samples, it was not possible to remove them from the electrodes after the experiment, and the thickness of the entire sandwich (electrodes and electrolyte layer) was measured instead. There was a standard deviation (SD) of up to ± 35 μm for samples sandwiched between lithium foils (diffusion coefficient cells), but a much lower value, ±5 μm, for the those between steel plates (conductivity cells). The larger standard deviation of the former was due to the tendency of the soft lithium foils to flow under pressure (the flow of the electrolyte film could be controlled with rigid spacers). Approximately 90% of the error in the diffusion coefficient determinations was attributable to difficulties in measuring sample thickness.

Three major error sources contribute to the uncertainties in transference number determinations; those associated with the diffusion coefficient (D_S), the slope of the concentration cell plot (dln c/dU), and the slope of the current interrupt experiments (m). Approximately 60% of the deviation in the transference number is due to the diffusion coefficient measurements and 35% to the concentration cell data. The remaining 5% is due to uncertainties in m.

Errors for these experiments can be greatly reduced by using thicker electrolyte samples. This requires, however, that the samples have sufficiently high conductivities to allow passage of current. The low conductivity of the PPO-$LiCF_3SO_3$ system imposed a practical limit on the sample thickness, and, thus, indirectly contributed to the uncertainty.

Conclusions

Thermal properties, conductivities, salt diffusion coefficients, and a partial set of transference numbers were determined for Parel/$LiCF_3SO_3$ electrolytes over a wide range of salt concentrations. Statistical examination of the methods used revealed that a large source of error was due to difficulties in measuring sample thickness and, indirectly, low sample conductivity. Two glass transitions were observed for several of the samples in the DSC experiment, although the samples appeared homogeneous and fully amorphous to the eye. This is a behavior commonly seen in PPO/salt solutions, and has been attributed to a liquid-liquid microphase separation. It is shown that microphase separation does not necessarily complicate interpretation of transport properties, because the techniques used are slow enough to measure the bulk ionic motion rather than the faster Brownian motion between the two microphases While conductivities and salt diffusion coefficients were generally lower than those measured for analogous PEO-based solutions, transference numbers were somewhat higher for concentrated solutions. While this suggests that concentration gradients will be slower to develop in operating cells with Parel-$LiCF_3SO_3$ electrolytes, the microphase separation suggests that salt precipitation and/or macroscopic phase separation may have a greater tendency to occur.

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Figure Captions

Figure 1. Conductivity as a function of salt concentration for Parel-$LiCF_3SO_3$ electrolytes at 85° C. O:Li ratios are marked above each point.

Figure 2. Molar conductivity for Parel-$LiCF_3SO_3$ electrolytes at 85° C. O:Li ratios are marked above each point.

Figure 3. Average salt diffusion coefficients, determined using equation (1), for Parel-$LiCF_3SO_3$ electrolytes at 85° C. The error bars indicate the 95% confidence intervals. O:Li ratios are marked above each point.

Figure 4. Concentration cell data for the Parel-$LiCF_3SO_3$ system at 85° C. The cells have the configuration $Li/PPO_nLiCF_3SO_3/PPO_mLiCF_3SO_3/Li$. The reference composition, m, was 2.13 mol/dm^3, corresponding to an O:Li ratio of 10:1, and readings were taken as positive for n>m. The error bars indicate the 95% confidence intervals.

Figure 5. Current interrupt data taken for representative galvanostatically polarized Li/Parel-$LiCF_3SO_3$/Li cells at 85° C. The O:Li ratio for the electrolyte is written next to each data set. The initial slope, m, is used in Equation 3 for the transference number calculation.

Figure 6. Cationic transference numbers for Parel-$LiCF_3SO_3$ solutions as a function of salt concentration at 85° C. The error bars indicate the 95% confidence intervals. The O:Li ratios are given next to each data point.

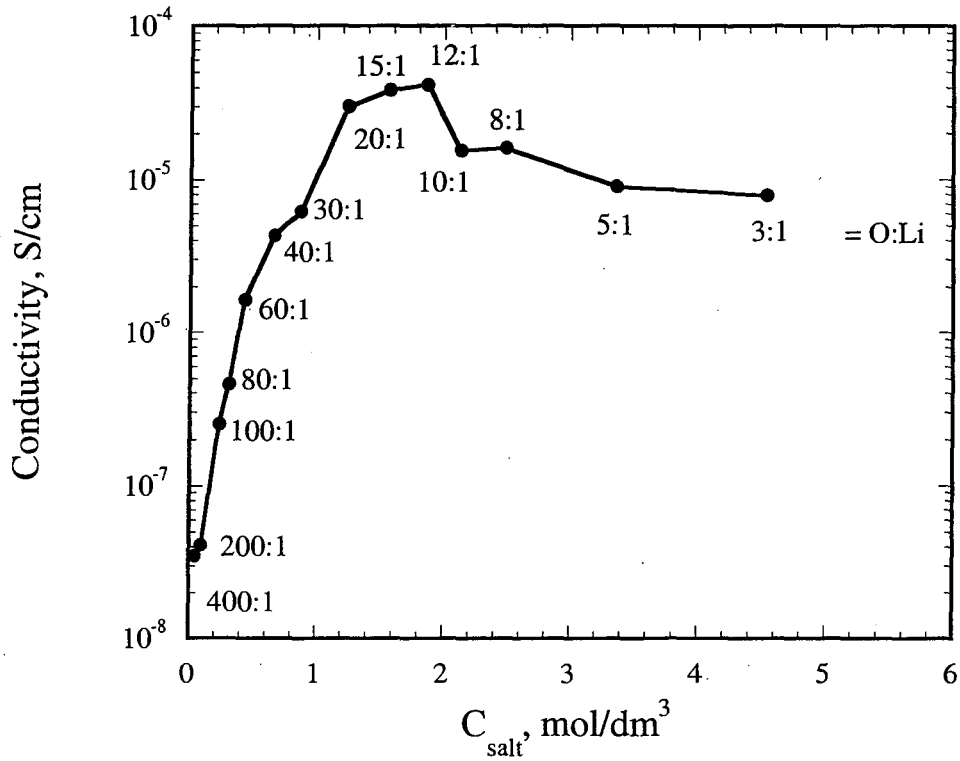

Figure 1
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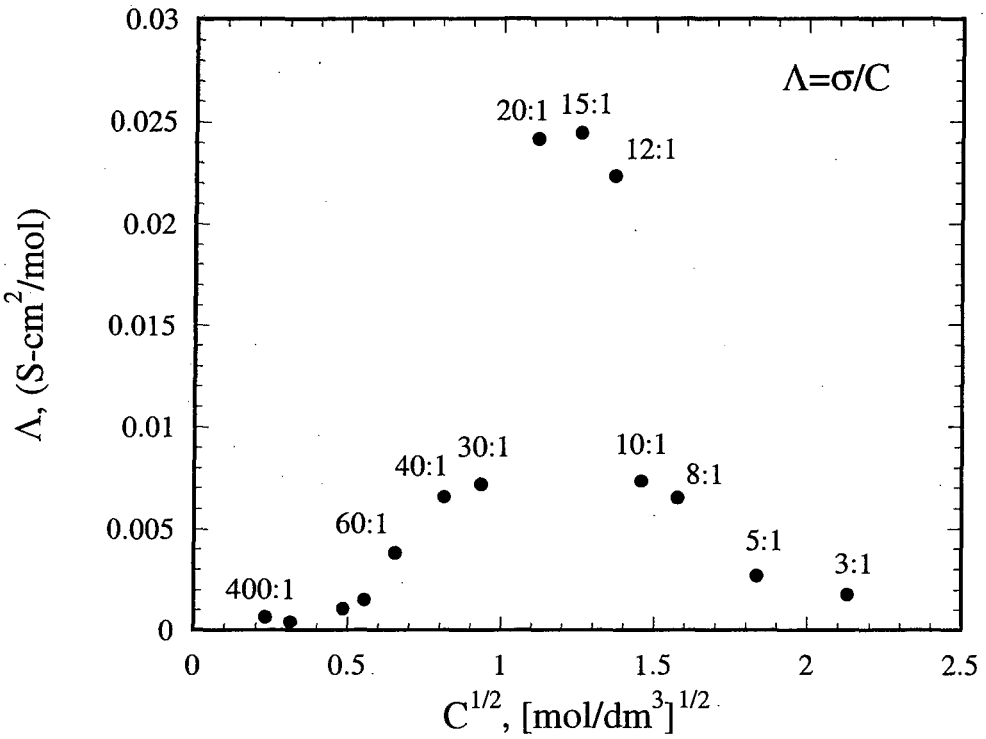

Figure 2
Doeff, Georen, et al.

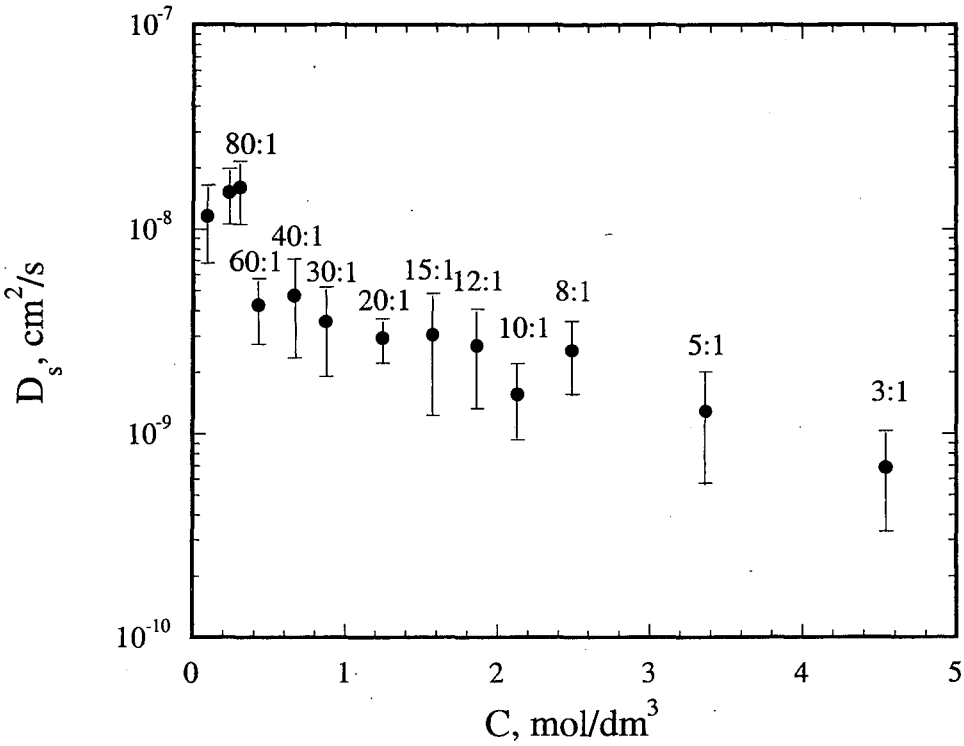

Figure 3
Doeff, Georen, et al.

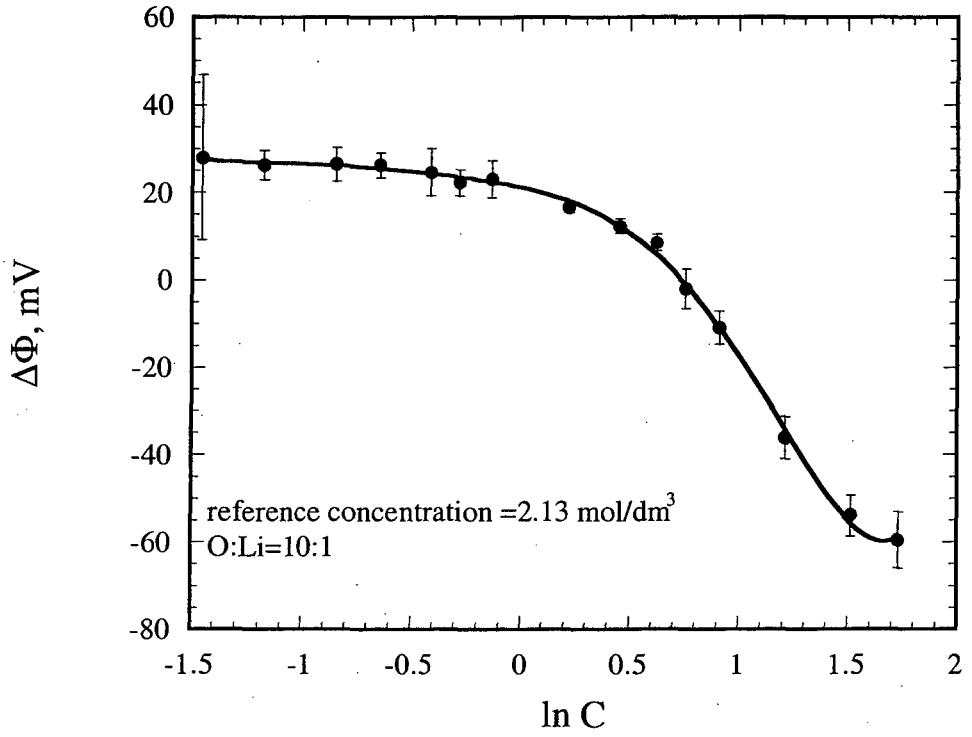

Figure 4
Doeff, Georen, et al.

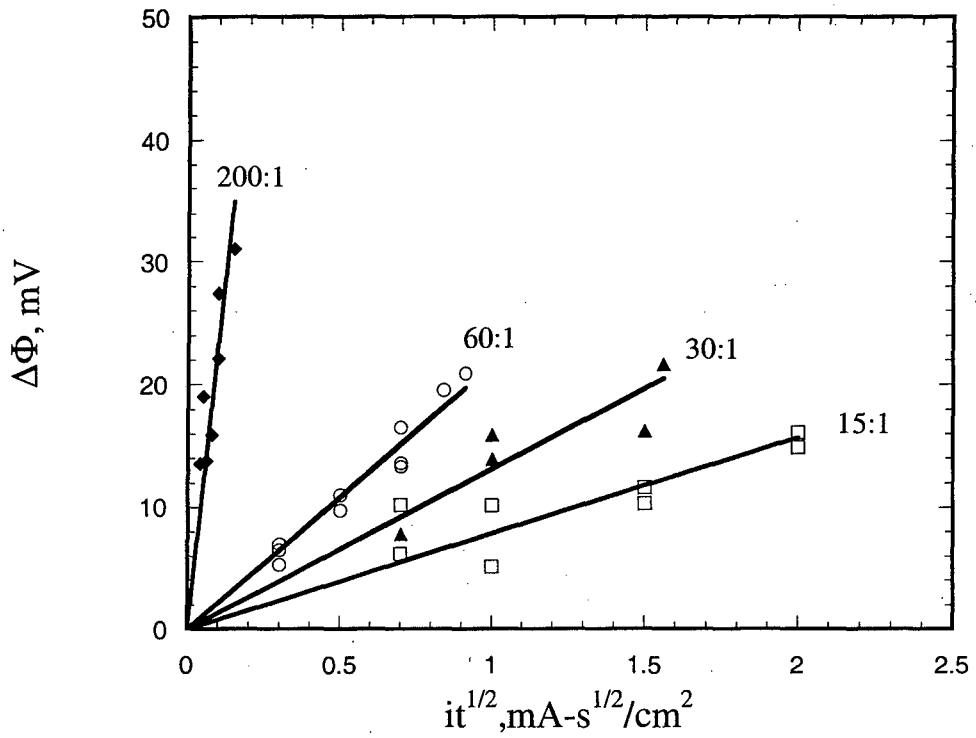

Figure 5
Doeff, Georen, et al.

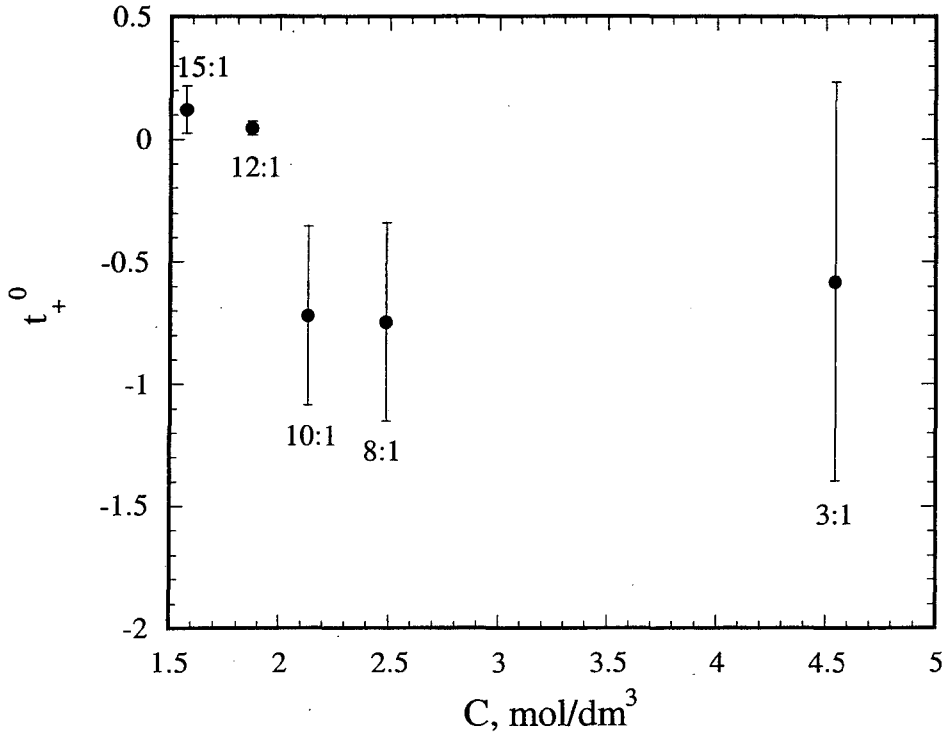

Figure 6
Doeff, Georen, et al.

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