

Toward standardizing the measurement of electrochemical properties of solid-state electrolytes in lithium batteries[☆]

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Abstract

A brief discussion on transport measurements for lithium ion conducting polymer electrolytes is given. An engineering approach to obtain a complete set of transport and thermodynamic properties for a binary salt dissolved in a polymer electrolyte solvent is described. The technique is based on concentrated solution theory and requires a minimal amount of experimentation. Results from measurements on a representative polymer electrolyte system are given. The measured transport and thermodynamic properties of the polymer electrolyte are used to simulate the performance of symmetric Li/polymer/Li cells and compare to experimental data. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

This paper is intended to stimulate thought and discussion in the technical community on standardization of the experimental determination of the pertinent electrochemical properties of solid electrolytes. This standardization is needed for comparison and modeling of these electrolytes in a practical lithium battery. The appropriate electrochemical properties include transport, thermodynamic, and physical parameters that generally depend on concentration and temperature. It is far beyond the scope of this work to put forward definitive measurement techniques for the complete set of electrochemical properties on all types of

solid electrolytes. Instead, we start by narrowing the range of properties and solid-electrolytes that will be discussed. This paper will focus on examining the transport and thermodynamic properties of a binary lithium salt dissolved in a dry polymer solvent. By doing this, we hope that comparisons between various techniques, including our work, will lead to improved understanding and methodology for examining this important class of solid electrolytes.

It is relatively easy to set forward a standard technique for the measurement of the conductivity of the solid-state electrolyte [1]. Unfortunately, this quantity by itself is not necessarily indicative of how easily lithium ions are transported through the electrolyte. The challenge then becomes how best to quantify the transport of lithium ions in the solid electrolyte. For the case of a dissolved binary lithium salt in a polymer solvent, one can take an engineering approach by first assuming the salt is totally dissociated. An appropriate set of transport parameters (generally taken as conductivity, diffusion coefficient, and cation transfer number) can then be defined by the use of established solution transport theory, either concentrated or dilute [2]. A series of experiments can be developed to determine the

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transport parameters. If concentrated solution theory is used, the series of experiments must include a determination of the salt activity coefficient in the polymer. Doyle and Newman [3] have presented a comparison of techniques based on dilute and concentrated solution theory.

The dilute solution theory is much easier to implement, but there is ample evidence that for many cases the polymer electrolyte is not thermodynamically ideal, and the transport parameters are a strong function of concentration. One example of a concentrated solution theory approach is outlined in the work of Doeff et al. [4]. While not always simple, these approaches are usually designed to not require unique diagnostic equipment. A particularly appealing quality of Doeff et al.'s approach is that it produces parameters that can be directly utilized in an electrochemical model of the electrolyte in a practical lithium battery [5,6].

A concentrated solution transport model can be developed for any initial assumption of the chemical state of the binary lithium salt in the electrolyte (e.g., degree of dissociation and ion pairing), but the complexity of the model and the number of parameters rise dramatically with the number of species. This level of complexity is not usually pursued since for most electrolytes accurate knowledge of its chemical state is not available and is not needed as long as all the species are in equilibrium. The assumption of equilibrium is usually valid in liquid electrolyte systems, but may break down in polymer systems where the time constants to attain equilibrium could be much longer.

A more basic approach is to first use one or more sophisticated probes, such as spectroscopic or X-ray techniques, to examine the chemical state of some or all the constituents. Then, this information is used to develop an engineering transport model, and electrochemical experiments are conducted to measure the desired parameters. An even more involved approach is to use the probing technique to also examine the transport of the lithium ions in the polymer electrolytes [7,8]. These methods contribute valuable information on the chemical state of the lithium ion as well as its transport through the polymer. While the results from these techniques are more open to interpretation, they should prove to be the best way to fully examine the mechanisms for lithium ion transport. Another important category, not considered here because they are more theoretical than experimental, is the *ab initio* studies on the solid electrolyte [9].

At Argonne National Laboratory, both basic and applied approaches to making transport measurements on solid electrolytes are being pursued, as are molecular dynamics simulations. The Electrochemical Technology Program at Argonne is working with 3M (3M) and Hydro-Québec (HQ) in support of an effort to develop a lithium polymer battery for electric vehicles [10,11]. Under this program, numerous candidate polymer electrolytes have been examined. The methods used to determine the transport and thermodynamic properties of a polymer elec-

trolyte system over a wide salt concentration and temperature range are presented here. In addition, techniques utilized to check the measurements are also given.

2. Experimental

Care was taken to minimize the exposure of the polymer electrolyte laminates to moisture. All handling of materials and assembly of cells were accomplished in either an inert atmosphere glove box or a dry room. Cell studies were conducted in an inert atmosphere glove box. The present study was conducted with a binary lithium salt, i.e., $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, dissolved in a dry polyether copolymer. 3M supplied Argonne with a series of polymer electrolyte laminates used in the study. The laminates were less than 100- μm thick and covered a wide concentration range from relatively dilute to near the salt solubility limit [12].

Following the approach of Pollard and Comte, symmetric (Li/polymer/Li) cells were built to determine the electrolyte conductivity and salt diffusion coefficient with AC impedance spectroscopy [13]. Lithium, supplied by HQ, was vacuum laminated to both sides of the polymer electrolyte to form 4- cm^2 symmetric cells. An EG&G Princeton Applied Research Model 273A Potentiostat/Galvanostat coupled to a Solartron Model 1260 Frequency Response Analyzer was used to measure the AC impedance of the cells (1 mHz–100 kHz) over a range of temperatures (40–100°C). Duplicate cells and cells made with a double layer of polymer electrolyte laminate were also assembled and examined. These cells were used as an internal check on the standard set of cells and to help identify the complex impedance arcs of the AC impedance results.

After the AC impedance studies were conducted, sample cells were chosen to conduct DC polarization studies. The symmetric cell potential was monitored as increasing current steps were applied to a cell in alternating directions. The currents applied to the cells ranged from relatively low levels to a value greater than the steady-state mass transfer limiting current. This was accomplished using a computer-controlled cycling system developed in-house. The AC impedance of the cells was again examined for changes in the lithium–polymer interface after the DC studies were conducted.

The AC impedance studies were combined with concentration cell (Li/polymer₁/polymer₂/Li) measurements to determine the transference number and the activity coefficient as outlined by Doyle and Newman [3]. Strips of polymer approximately 1 cm in width were cut from the polymer electrolyte laminates. A reference concentration was chosen that was near the maximum in the conductivity and salt diffusion coefficient curves. Each of the concentration cells was assembled by overlapping part of a reference salt concentration strip and a strip at another

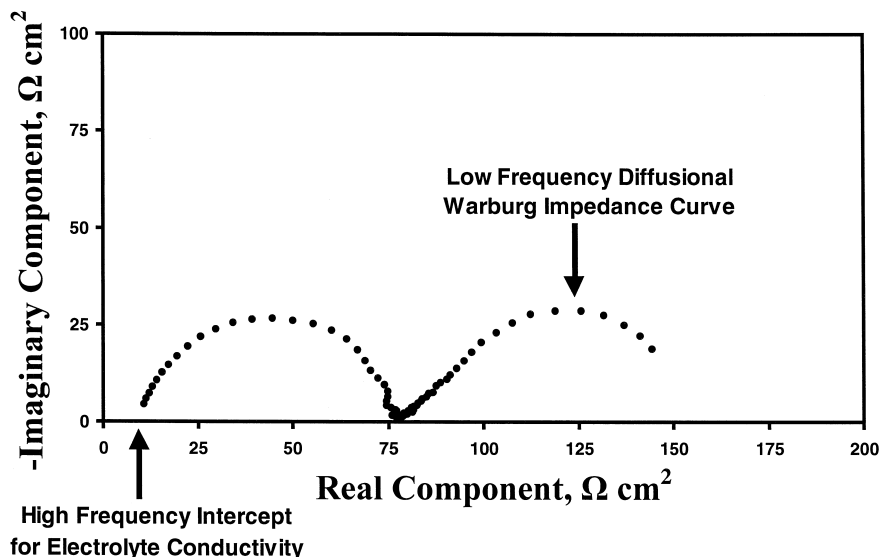


Fig. 1. A typical complex impedance plot (1 mHz–100 kHz) taken on a Li/polymer/Li cell.

concentration. A small piece of lithium was attached to the end of each strip opposite the overlapped portion. Care was taken to keep about a few millimeters of electrolyte between the lithium and the overlapped regions on each of the polymer electrolyte strips. The potential of the concentration cells was measured with a high impedance Hewlett Packard 3457A Multimeter over a range of temperatures (40–100°C). Measurements were made on duplicate cells to determine reproducibility, and the last potential measurement on each cell was a repeat of the first to test the cell's stability.

3. Results and discussion

A typical complex impedance plot for one of the symmetric (Li/polymer/Li) cells is given in Fig. 1. The

conductivity (κ) of the electrolyte was obtained from the high-frequency intercept of the complex impedance curve. Over the full spectrum taken, two dominant arcs are clearly evident. The high-frequency arc is taken to be associated with the kinetics of electrochemical reaction at the lithium–polymer interfaces, and the low-frequency Warburg impedance curve is associated with the transport of lithium ions in the electrolyte. This was confirmed by impedance measurements on cells that differed only in electrolyte thickness. In essentially every cell studied, there was a slight instability in the impedance measurements taken between the two primary arcs. This was generally associated with lithium ion transport in the solid–electrolyte interface (i.e., the SEI layer).

A characteristic resistance (R_{MT}) and time constant (τ) were obtained for each of the cells by fitting the low

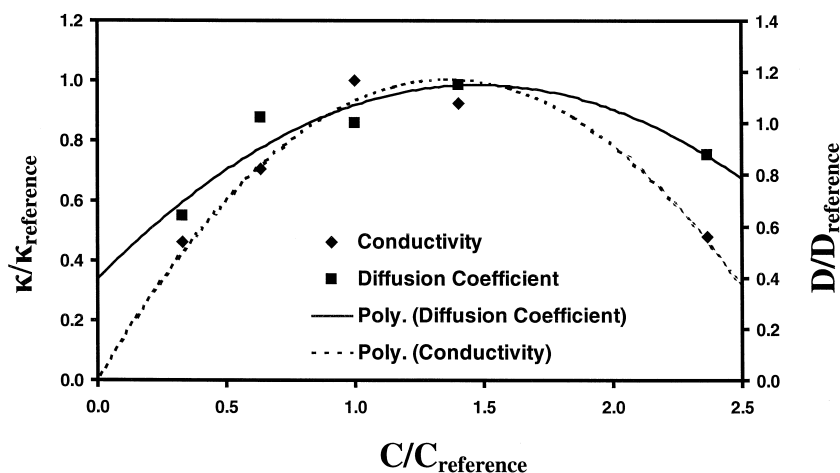


Fig. 2. Electrolyte salt concentration dependence of conductivity (κ) and salt diffusion coefficient (D) for a polymer electrolyte.

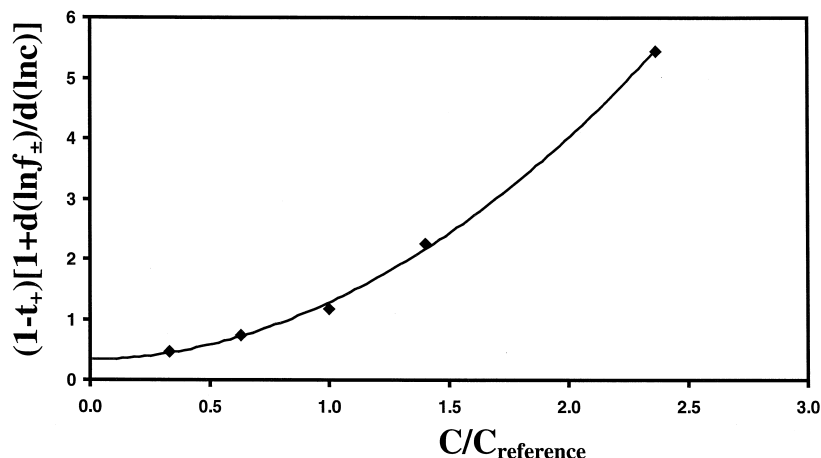


Fig. 3. Electrolyte salt concentration dependence of cation transference number (t_+^0) and the mean molar activity coefficient of the salt (f_{\pm}) obtained from AC impedance results on polymer electrolyte.

frequency (ω) Warburg impedance (Z_{MT}) curve to the complex function ($j = \sqrt{-1}$) in Eq. (1) [14].

$$Z_{MT} = R_{MT} \frac{\tanh(\sqrt{j\tau\omega})}{\sqrt{j\tau\omega}} \quad (1)$$

Following the development Pollard and Comte [13], using concentrated solution theory, τ can be related to the salt diffusion coefficient (D) and electrolyte thickness (δ) through Eq. (2).

$$\tau = \frac{\delta^2}{4D|_{c=c_i}} \quad (2)$$

An example of the change in the salt diffusion coefficient and conductivity as a function of salt concentration in the electrolyte is shown in Fig. 2. Also shown in the figure is the second-order polynomial fit of data used in the modeling effort. The fact that both curves exhibit a maximum is a strong justification for using concentrated solution theory.

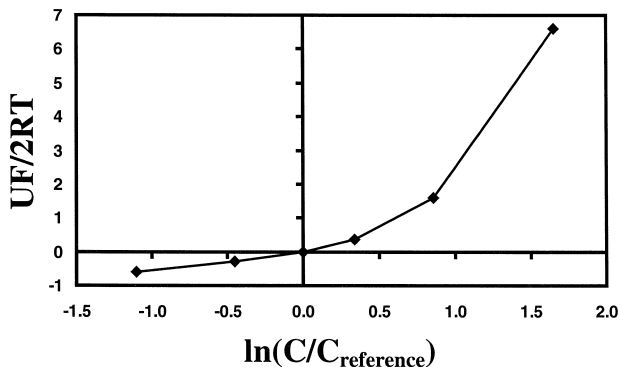


Fig. 4. Typical concentration cell measurements on Li/polymer₁/polymer₂/Li cell.

The characteristic resistance can be related to the cation transference number (t_+^0) and the mean molar activity coefficient of the salt (f_{\pm}) through Eq. (3) [13].

$$R_{MT} = \frac{2RT\delta}{F^2 c_i D|_{c=c_i}} \left(1 - c_i \bar{V}_e\right) \times \left[\left(1 - t_+^0|_{c=c_i}\right)^2 \left(1 + \frac{d \ln f_{\pm}}{d \ln c} \Big|_{c=c_i}\right) \right] \quad (3)$$

In Eq. (3), c is the concentration of salt in the polymer electrolyte, and \bar{V}_e is the partial molar volume of the salt, which is assumed to be constant. An example of the change in the bracketed quantity in Eq. (3), as a function of salt concentration in the electrolyte, is given in Fig. 3. While it is not possible with the AC impedance results to determine independently the cation transference number and the mean molar activity coefficient of the salt, there clearly is a salt concentration dependence. As outlined by

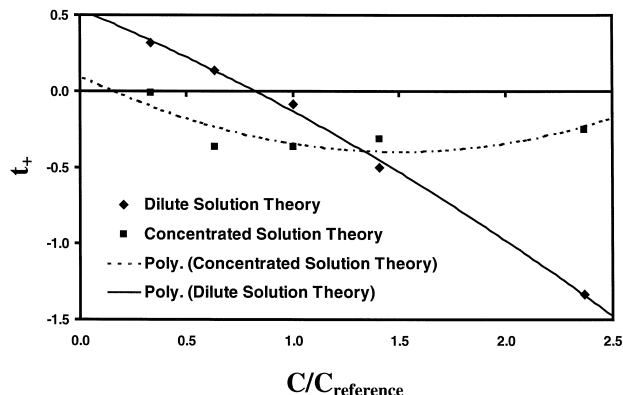


Fig. 5. Electrolyte salt concentration dependence of cation transference number (t_+^0) for a polymer electrolyte.

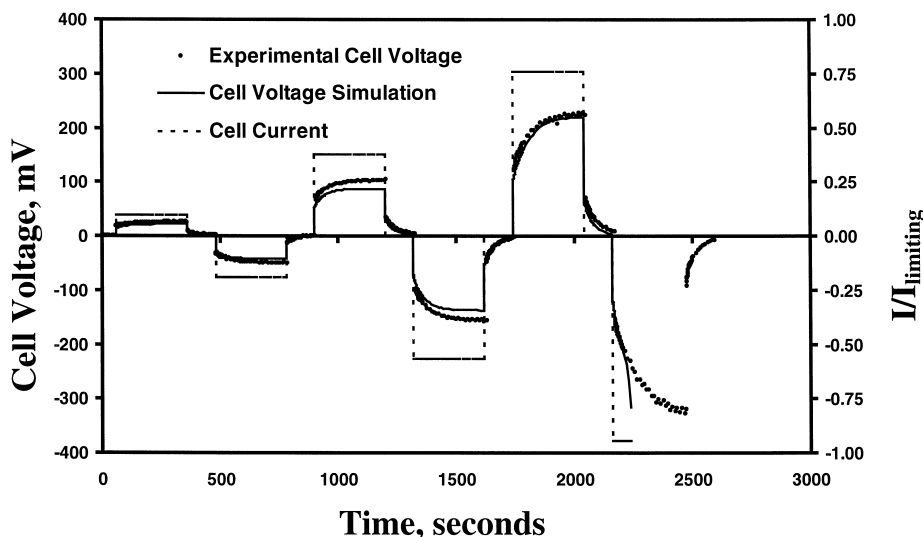


Fig. 6. Comparison of simulation and experiment on a Li/polymer/Li cell.

Doyle and Newman [3], these results when combined with potential (U) measurements from concentration cells, described above and presented in Fig. 4, can be used to separate the two coefficients. The resulting cation transference numbers are given in Fig. 5. Note that the cation transference numbers based on concentrated solution theory are mostly negative. The reasons for, and implications of, a negative cation transference number have been discussed in the literature [3,15]. For this discussion, it is enough to state that at least some of the mobile lithium ions in the electrolyte form a complex with anions, giving them a net negative charge. Furthermore, the concentrated solution theory still remains valid as long as all the ionic species in the electrolyte are in equilibrium.

Fig. 5 also gives the results for the cation transference numbers obtained directly from the AC impedance data,

assuming dilute solution theory is applicable. Dilute solution theory greatly reduces the level of complexity and more significantly the number of experiments needed to produce a complete set of transport properties. Both the concentrated and dilute solution theories must generate equivalent sets of transport parameters in order to justify the simplification of the dilute solution approximation. The discrepancy between the two sets of calculated cation transference numbers is quite significant, thus, indicating that the dilute solution theory is not adequate to describe this system. In essence, the dilute solution theory lumps all the salt activity coefficient effects into the cation transference number.

Following the work of Doyle et al. [5], an electrochemical model was developed for simulating the Li/polymer/Li cells under controlled-current conditions. Two slight

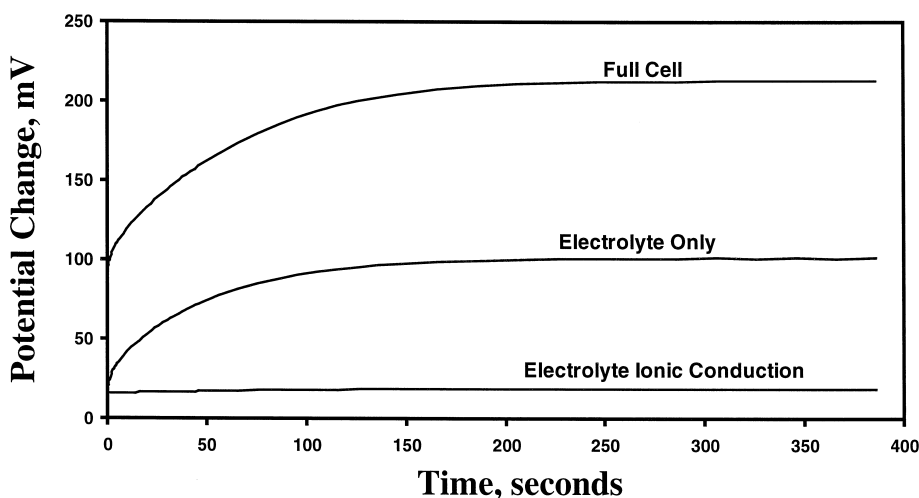


Fig. 7. Simulation of voltage change of Li/polymer/Li cell after a current step to 75% limiting current.

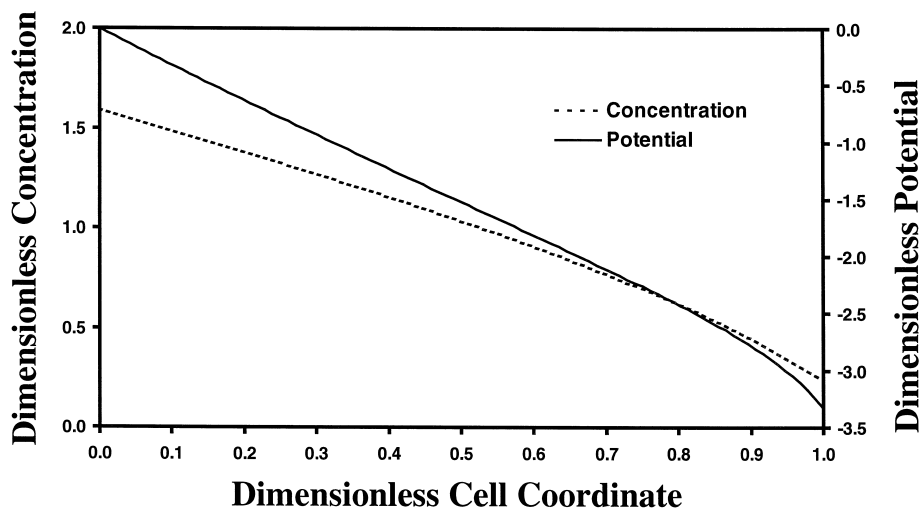


Fig. 8. Steady-state polymer electrolyte concentration and potential distribution of Li/polymer/Li cell at 75% limiting current.

variations were used in the present study. First, the model was developed with transport equations based on a volume-averaged velocity [13,16]. A diffusion overpotential term accounting for the transport of lithium in the SEI layer on each of the lithium electrodes was added to the model. In general, this was a relatively small effect but was included for completeness based on the AC impedance results. The kinetic parameters for the lithium electrodes were also established from fitting the AC impedance results [14].

A comparison of the electrochemical model simulations and DC polarization studies on one of the Li/polymer/Li cells is given in Fig. 6. The work covered a wide current range and included both current steps and cell relaxation. In general, the agreement is quite good. The most significant difference between theory and experiment occurred near the limiting current, at about 2200 s. The electrochemical model clearly indicated a lower limiting current than was actually measured, as shown by the simulated cell voltage rising dramatically. Obviously, at or near limiting current the salt concentration gradient in the polymer electrolyte is as high as it can be, and this case would be the most severe test of the measured transport parameters. This difference between theory and experiment could also be explained by an effective roughening of the lithium–polymer interface resulting from the relatively high plating rate of the lithium. However, AC impedance measurements on the cell after the DC polarization studies did not indicate any significant change of the interface.

An expanded version of the simulation shown in Fig. 6 for the cell potential change after a current step to 75% of limiting current is given in Fig. 7. Fig. 7 also gives the contribution of the electrolyte to the total cell potential. Clearly, transport effects in the polymer electrolyte make up a significant portion of the overall cell impedance. These effects can vary greatly, and it is difficult to make a general statement about them, but they need to be quanti-

fied to determine their relative impact on cell performance. The contribution due to ionic conduction is small, as shown in Fig. 7. Because the cation transference number is negative, the electric field gradient, although small, is actually causing the lithium ions to travel in the wrong direction. This effect has to be overcome by a corresponding increase in the salt concentration gradient.

The steady-state salt concentration and potential gradients in the electrolyte for the Li/polymer/Li cell at 75% of limiting current are shown in Fig. 8. Considering how much the transport and thermodynamic parameters change with concentration, the gradients are surprisingly linear. Figs. 7 and 8 combine to indicate the power of this electrochemical modeling effort. Due to the cell dimensions involved in these studies (typically less than 100 μm), extracting this information would be extremely difficult by any other technique. Further, these studies are extremely valuable for identifying cell performance limitations.

4. Conclusions

Even for the apparently simple case of a binary salt dissolved in a polymer electrolyte, the number of approaches and techniques to quantify the lithium ion transport in the solid electrolyte is large. The more basic approaches, while critical for understanding the mechanisms of lithium ion transport in a particular electrolyte, are not optimal as a standard for comparison of various solid electrolyte systems because of their experimental complexity. One of the many engineering approaches to defining and measuring the transport parameters would have the greatest chance of acceptance by the technical community.

The engineering approach taken here, based on concentrated solution theory, has been previously suggested in the literature, but not generally adopted by the technical com-

munity. The present work clearly demonstrates that all the transport and thermodynamic parameters can be obtained for a binary salt dissolved in a polymer electrolyte with only two sets of experiments: AC impedance studies on symmetric cells and potential measurements on concentration cells. This approach does not involve significant DC polarization of cells and can obtain equivalent results as other approaches that do. While there are a number of alternative approaches to obtain these transport and thermodynamic parameters, one based on concentrated solution theory must be used to fully describe the transport processes.

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