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A RAPID METHOD FOR THE DETERMINATION OF LITHIUM TRANSFERENCE NUMBERS

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ABSTRACT

We describe the Electrophoretic NMR (ENMR) method for the determination of lithium ion transference numbers (T_{Li}). The work presented is a proof-of-concept of the application of the ENMR method to lithium ion transference measurements for several different lithium salts in gelled electrolytes. The NMR method allows accurate determination of T_{Li} values, as indicated by the similarity of T_{Li} in the gelled electrolytes to those in aqueous electrolyte solutions at low salt concentration. Based on calculated tradeoffs of various experimental parameters, we also discuss some conclusions concerning the range of applicability of the method to other electrolytes with lower lithium mobility.

INTRODUCTION

Lithium ion-conducting polymer electrolytes are of increasing interest for use in lithium-polymer batteries (1). Lithium transference numbers, the net fraction of current carried by lithium in a cell, are key figures of merit for potential lithium battery electrolytes. Non-unity lithium transference numbers lead to concentration polarization in cells employing those electrolytes. Vincent and co-workers (2) have discussed extensively the problems encountered with the application of various transference number measurement methods to polymer electrolytes. A substantial amount of polymer electrolyte development has been carried out with the aim of increasing lithium ion transference numbers. A relatively rapid and reliable method of determining the effectiveness of new polymer structures or lithium salts in increasing the lithium transference number is needed. Modeling of battery performance also requires these quantities. Finally, knowledge of the ion transference numbers gives us an additional window into the physical chemistry of these electrolytes.

Fritz and Kuhn (3) compared transference numbers measured by several different methods for a model electrolyte and showed large differences in the measured transference numbers depending on the method used. From their work, they conclude that published results for many non-aqueous systems and polymer electrolytes are almost certainly unreliable. The classical Hittorf method provides rigorous measures of transference, but this method is difficult to apply to polymeric systems. Ma and co-workers (4) have developed a theoretically rigorous methodology for the determination of transference numbers using electrochemical measurements. This approach is cumbersome, involving three kinds of measurements: concentration cell measurements to determine salt activity coefficients, restricted diffusion measurements to determine the salt diffusion coefficient, D_{salt} , and a galvanostatic polarization measurement to determine the transference numbers are all necessary. Furthermore, the combination of these

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measurements to yield the desired transference numbers may lead to significant errors in the derived parameters. Their published work to date focused on sodium salts in PEO at 85 °C. Interestingly, they report that the lithium transference numbers determined by their method are negative over substantial ranges of composition. Olsen et al (5) have reported a comparison of Hittorf and dc polarization measurements in plasticized, cross-linked PEO hybrid electrolytes. They showed that the dc method yielded systematically higher transference numbers and attributed that to the contribution of salt diffusion to the observed concentration gradient relaxation. Their Hittorf results indicate increasing transference numbers with salt concentration but the scatter in the data is large and the trend is weak.

We have developed another approach to the determination of transference numbers in polymer and gelled electrolyte systems. The method is simple and allows the rapid determination of net transference numbers. We use electrophoretic NMR (ENMR), a method in which the net mobility or flow velocity of marker nuclei is followed, to study transference in lithium battery electrolytes. We described our initial work in a recent publication (6).

Here we expand that description of the ENMR method. We first discuss the method in detail to highlight differences between this and other proposed transference number measurement methods and especially to distinguish the ENMR method from other NMR methods used in the past. We then review our proof-of-principle demonstration of the method for determination of T_{Li} in lithium battery electrolytes. Finally, we describe, based on calculated tradeoffs of various experimental parameters, the range of applicability of the method to other electrolytes with lower lithium mobility. The use of this method for the study of non-aqueous gels more directly relevant for lithium batteries is described in a companion paper in this volume.

EXPERIMENTAL

We described elsewhere (6) all experimental details relevant to the experiments discussed below. In brief, the experiments were performed using a home-built probe insert to a micro-imaging probe operating at 155.5 MHz. Samples were agarose gels loaded with aqueous solutions of desired concentrations.

RESULTS AND DISCUSSION

Basis of the Method

The ENMR experiment employs a constant current pulse in conjunction with an NMR diffusion experiment to measure the transference number of lithium. This enables us to directly measure the different net ion fluxes which contribute to the observed concentration polarization in a Hittorf cell. Rather than measuring the results of long-term polarization by sampling concentrations in the electrolyte, we directly probe, on a time scale of a few seconds for each signal average, the ion mobilities underlying the development of the concentration profile. The transference number of lithium is the ratio of the observed flux to the total ionic flux (i.e. the current). The role of the NMR in this

experiment is simply as a measuring tool for the net displacement of lithium nuclei from their original positions.

We wish to make a careful distinction between the ENMR method and the previously reported method for measuring transference numbers based on the ratio of the Li NMR self-diffusion coefficient to the sum of lithium and anion diffusion coefficients. The latter method has been justifiably criticized (2) based on the contribution of various ion aggregates, including neutral species (salt) diffusion, to the diffusion coefficients used to calculate the transference numbers. For a transference measurement, we wish to measure the migratory flux of ionic species only.

ENMR does exactly that. Though an NMR diffusion pulse sequence is the basis for the ENMR method, the signatures of diffusion and migration are different and completely separable in these experiments. Isotropic diffusion within the material, typically achieved on the timescale (>10 msec) or lengthscale (order of microns) of these experiments, is manifested as a signal attenuation whereas an ionic flux along the direction of current flow results in a phase-shifted signal. The magnitude of the phase shift is quantitatively related to the net ionic mobility (constant voltage experiment) or transference number (constant current experiment) and is thus the measured quantity in our experiment. Equation 1 gives the relationship between the measured phase shift and the transference numbers for the ENMR experiment with constant current:

$$\Delta\phi = g\delta\Delta IgT_{Li}/cFA \quad [1]$$

where $\Delta\phi$ is the phase shift in radians, g is the nuclear gyromagnetic ratio, δ is the gradient pulse time, Δ is the time between gradient pulses, I is the current, g is the gradient strength in Gauss/cm, A is the area of the current carrying electrolyte, c is the concentration of the lithium salt in the gel, and F is the Faraday constant. We will further probe the implications of diffusional attenuation in our assessment of the capability of ENMR to provide information on polymer electrolytes with relatively low ion mobility.

Experimental Validation of ENMR

A plot of the measured phase shift versus current density according to Equation 1 gives the transference number from the slope of the line. It should be noted that an accurate value of the salt concentration is needed to derive the transference number. Though we in principle know this concentration from the gel composition, we have included the measurement of the salt concentration as a routine part of our experimental protocol. This avoids the need to know gel densities and prevents errors due to, for example, solvent evaporation. The concentration is measured by the ratio of the NMR signal intensity of lithium in the gel versus that of a reference standard.

The dependence of T_{Li} on the LiCl concentration in aqueous agarose gels is shown in Figure 1. Also plotted in Figure 1 is the curve predicted by Robinson and Stokes (7) for T_{Li} in aqueous solutions of LiCl. The observed decrease in T_{Li} with increasing salt concentration in the gel (points in Figure 1), which is more rapid than that observed in solution, may be attributed to low actual dielectric constants of the gel

electrolytes, as illustrated by the fairly good agreement between the data and the values expected from Robinson and Stokes' theory with a low dielectric constant. This data, especially points at low concentration, was discussed elsewhere in the context of the proof of concept of the method (6). The limiting values of the transference numbers at low salt concentration satisfactorily approach those measured in aqueous solutions.

In Table I, we summarize data obtained for samples containing different lithium salts. The anion dependence of T_{Li} is such that $Cl^- < ClO_4^- < CF_3SO_3^-$ at the same salt molarity. This trend is consistent with that in solution electrolytes: as the anion size increases the lithium transference number increases.

Range of Applicability of the ENMR Method

The key limiting factors affecting the application of the ENMR method to solid polymer electrolytes are the signal-to-noise ratio (S/N) of the experiment and the magnitude of the phase shift achievable. These two elements are intertwined in a rather complex way. We present a brief description of the various experimental parameters influencing this trade-off. A more quantitative analysis will be presented elsewhere.

The signal-to-noise ratio is affected by factors which are more or less fixed by the physical state of our NMR probe (filling factor, resonance frequency, Q of the NMR coil etc.) as well as by factors which differ in various experiments, such as number of signal averages and so on. It should be recognized that there is significant signal attenuation because of ordinary relaxation of the perturbed magnetization (characterized by the spin-lattice relaxation time) and because of diffusion. These zero-current attenuations are a key constraint on our ability to increase the magnitude of the phase shift.

The S/N ratio is in principle arbitrarily increased by signal averaging, albeit at a cost of instrument time. However, in the present experimental mode, in which we use blocking electrodes, small amounts of material are consumed during the ENMR experiment. For the data shown above, relatively little material is destroyed per scan--roughly 0.5% maximum composition change assuming one equivalent of electrons per mole of electrolyte consumed, the most conservative assumption. This is not a problem for gel electrolytes where high inherent S/N and high ion mobility make the measurements easy with few averages (typically, 4). For polymeric electrolytes, this could be more of a problem. Thus, we want to minimize the necessary number of scans. (We are also exploring ENMR cells using controlled redox reactions which will eliminate the problem.)

As seen from equation 1, we can increase the response (phase shift) of the experiment to ion transference by increasing the current density, time parameters, Δ and δ , the diffusion and gradient pulse time parameters respectively, or by increasing the gradient strength used. Increasing the latter two parameters corresponds to increasing the sensitivity of the NMR method to a given size of displacement, while increasing the current density or time parameters increases the magnitude of that displacement. The usable current density is limited by the composition change in the electrolyte and by the intrinsic ionic mobility in the electrolyte as discussed above. The simplest approaches to increasing phase shifts seem to be increased gradient strength or time for motion.

However, the gradient strength and motion time also affect the attenuation due to relaxation and diffusion. Longer motion time leads to greater signal attenuation due to both factors: Relaxational attenuation exponentially increases with time while diffusional attenuation exponentially increases with the cube of time. Furthermore, the gradient strength and pulse time also exponentially increase the attenuation due to diffusion, with the dependence on gradient strength squared. The only saving feature from the point of view of acquiring ENMR results for solid polymer electrolytes is that the diffusion coefficient of lithium is quite low and the relaxation time is long. We now have experimental evidence that we can indeed achieve adequate S/N for PEO samples at $T > 50^{\circ}\text{C}$ for typical ENMR times using our present gradient probe at maximum strength. Stronger gradient pulse strengths will enable us to carry this work down to the room-temperature range.

CONCLUSION

We presented here a description of the proof-of-principle experiments for ENMR as well as substantial qualitative description of the method, its promise, and the factors trading off in limiting the range of applicability of the method. This method will be suitable for the determination of transference numbers in a wide range of electrolyte systems and we hope to explore several new corners of the physical chemistry of electrolytes using this tool.

REFERENCES

1. F. Gray, *Solid Polymer Electrolytes Fundamentals and Technological Applications*, VCH, New York (1991).
2. P.G. Bruce and C.A. Vincent, *Faraday Discuss. Chem. Soc.*, **88**, 43 (1989).
3. H. P. Fritz and A. Kuhn, *J. Power Sources* , **41**, 253 (1993).
4. Y. Ma, M. Doyle, T. Fuller, M. Doeff, L. Dejonghe and J. Newman , *J. Electrochem. Soc.*, **142**, 1859 (1995).
5. I. Olsen, R. Koksang and E. Skou, *Electrochimica Acta.*, **40**, 1701 (1995).
6. H. Dai and T. A. Zawodzinski Jr.,*J. Electrochem. Soc.*, **143**,107 (1996).
7. Robinson and Stokes, *Electrolyte Solutions*, Butterworths, London (1959).

Table I.
Anion Dependence of Li^+ Transport Properties at 25 $^{\circ}\text{C}$

Salt	[Li^+] (M)	T_{Li^+}
LiCl	0.10	0.30 ± 0.02
LiCl	0.25	0.30 ± 0.02
LiCl	0.38	0.25 ± 0.01
LiCl	0.47	0.22 ± 0.01
LiCl	0.74	0.23 ± 0.01
LiClO_4	0.15	0.32 ± 0.02
LiClO_4	0.4	0.31 ± 0.02
LiClO_4	0.73	0.29 ± 0.01
LiCF_3SO_3	0.17	0.45 ± 0.02
LiCF_3SO_3	0.36	0.42 ± 0.02
LiCF_3SO_3	0.65	0.37 ± 0.02

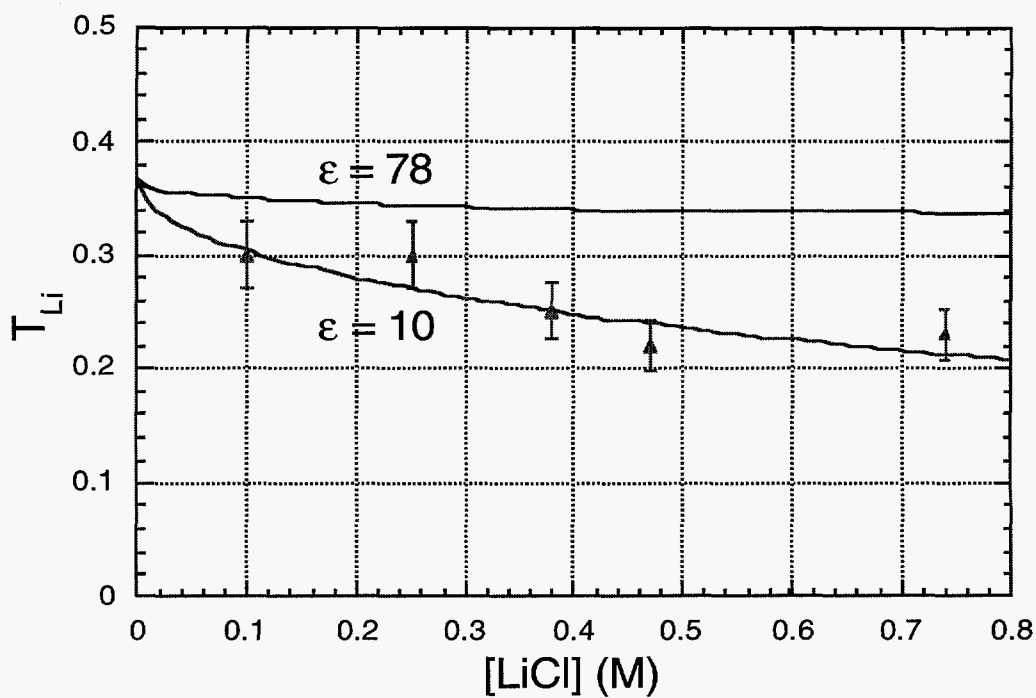


Fig.1 Concentration and dielectric constant dependence of T_{Li} in aqueous LiCl electrolytes at 25^o C. Solid lines: theoretical curves given by Robinson and Stokes (7) at different dielectric constants. Dots: Measured by ENMR in aqueous LiCl with 1% agarose.