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### Authors

Halat, David M

Mistry, Aashutosh

Hickson, Darby

et al.

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# Transference Number of Electrolytes from the Velocity of a Single Species Measured by Electrophoretic NMR

David M. Halat,<sup>1,2,3,\*</sup> Aashutosh Mistry,<sup>4,5,\*</sup> Darby Hickson,<sup>1,3</sup> Venkat Srinivasan,<sup>4,5</sup> Nitash P. Balsara,<sup>1,2,3,z</sup> and Jeffrey A. Reimer<sup>1,2,3,z</sup>

<sup>1</sup>Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, United States of America

<sup>2</sup>Joint Center for Energy Storage Research, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States of America

<sup>3</sup>Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States of America

<sup>4</sup>Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, Illinois 60439, United States of America

<sup>5</sup>Joint Center for Energy Storage Research, Argonne National Laboratory, Lemont, Illinois 60439, United States of America

Accurate measurement of the cation transference number is critical for designing batteries with a given electrolyte. A promising approach for measuring this parameter is electrophoretic NMR (eNMR). In the standard approach, the average cation, anion, and solvent velocities under an applied electric field are used to estimate the cation transference number with respect to the solvent velocity,  $t_+^0$ . In this study, we show that  $t_+^0$  can be determined from measurements of the electric-field-induced velocities of individual species. The  $t_+^0$  values obtained from eNMR experiments on a model electrolyte (LiTFSI/tetraglyme) based on single species velocities are consistent with the standard approach. An important parameter that enters into the analysis is the velocity of the electrode electrolyte interface which must be finite in an eNMR experiment. Agreement is only obtained after accounting for this velocity. The single-species approach is particularly valuable when one or more components of the electrolytic mixture are not easily accessible by NMR, for example zinc and magnesium cations.

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## List of Symbols

$c$ ,	salt concentration, mol/L
$c_0$ ,	solvent concentration, mol/L
$D$ ,	salt diffusion coefficient, $\text{cm}^2/\text{s}$
$F$ ,	Faraday's constant, $96487 \text{ C mol}^{-1}$
$i$ ,	current density, $\text{mA}/\text{cm}^2$
$L$ ,	inter-electrode distance, 33.5 mm
$M$ ,	molar mass of LiTFSI salt, $287.1 \text{ g mol}^{-1}$
$M_{\text{Li}}$ ,	molar mass of Li, $6.94 \text{ g mol}^{-1}$
$t$ ,	time, s
$t_+^0$ ,	cation transference number relative to solvent motion, <i>unitless</i> , Figs. 4 and 6
$V$ ,	voltage applied across the cell, V
$\bar{V}$ ,	partial molar volume of electrolyte salt, $\text{cm}^3/\text{mol}$
$v$ ,	velocities in the moving reference frame attached to the positive electrode electrolyte interface, $\mu\text{m}/\text{s}$
$v'$ ,	velocities in the laboratory reference frame, $\mu\text{m}/\text{s}$ , Fig. 3
$x$ ,	spatial coordinate, $\mu\text{m}$
$z$ ,	species charge, <i>unitless</i>
Greek Symbols	
$\kappa$ ,	ionic conductivity, $\text{mS}/\text{cm}$ , Fig. 2b
$\nu$ ,	stoichiometric coefficients
<i>unitless</i>	$\nu = \nu_+ + \nu_-$
$\rho$ ,	electrolyte density, $\text{g}/\text{cm}^3$ , Fig. 2a
$\rho_{\text{Li}}$ ,	density of Li, $0.534 \text{ g cm}^{-3}$
$\phi$ ,	electric potential, V
Subscripts	
+	cation
-	anion
0	solvent

The operation and performance of rechargeable batteries depends critically upon ion transport in the electrolytic phase. In most batteries, the electrolytic phase comprises a mixture of cations, anions, and solvent molecules. These mixtures are commonly referred to as binary electrolytes.<sup>1</sup> While conductivity,  $\kappa$ , describes the overall transport of cations and anions in a binary electrolyte, the cation transference number quantifies the fraction of current carried *only* by the cation in an electrolyte of uniform composition.<sup>1,2</sup> As the cation is commonly the working ion, the magnitude of the transference number directly influences the formation of salt concentration gradients during polarization.<sup>3-5</sup> Concentrated solution theory<sup>6</sup> provides a generalized understanding of ion transport in polarized electrolytes. In this theory the governing equations<sup>7,8</sup> for the molar electrolyte concentration,  $c$ , can be written as

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \left( 1 - \frac{d \ln c_0}{d \ln c} \right) \frac{\partial c}{\partial x} \right) - \frac{i}{\nu_+ z_+ F} \frac{\partial t_+^0}{\partial x} - \frac{\partial}{\partial x} (c v_0), \quad [1]$$

$$\frac{\partial v_0}{\partial x} = \bar{V} \left\{ \frac{\partial}{\partial x} \left( D \left( 1 - \frac{d \ln c_0}{d \ln c} \right) \frac{\partial c}{\partial x} \right) - \frac{i}{\nu_+ z_+ F} \frac{\partial t_+^0}{\partial x} \right\} \quad [2]$$

where  $i$  is the applied current density,  $c_0$  is the molar solvent concentration,  $\bar{V}$  is the partial molar volume of salt,  $v_0$  is the solvent velocity, and  $t_+^0$  is the cation transference number with respect to this solvent velocity.  $D$  is the salt diffusion coefficient as defined by Newman and Chapman.<sup>9</sup> It is the diffusion coefficient measured in a restricted diffusion experiment.<sup>9</sup> Predicting concentration gradients using Eqs. 1 and 2 necessitates knowledge of the concentration dependence of the transference number.<sup>10-16</sup> These predictions lie at the heart of determining the factors that limit performance under conditions of fast cycling<sup>17-21</sup> and that accelerate undesirable dendritic growth at the electrodes.<sup>22-24</sup>

Our main objective is to shed light on experimental measurement of  $t_+^0$ . Accurate electrochemical measurements of  $t_+^0$  are frequently beset by experimental difficulties. Over 90 years ago, MacInnes and Longworth<sup>25</sup> noted "determination of transference numbers have

\*Equal Contribution.

\*Electrochemical Society Member.

<sup>z</sup>E-mail: nbalsara@berkeley.edu; reimer@berkeley.edu

been difficult to carry out and have yielded results of low precision even in the hands of careful workers.” This statement retains its validity even today.<sup>26–28</sup> A commonly used method for determining the transference number was proposed by Ma et al.,<sup>29</sup> wherein  $t_+^0$  is determined using four separate electrochemical experiments.<sup>18,26,29–31</sup> Large error bars result from the need for combining results from different experiments, and the intrinsic coupling between transport and thermodynamic parameters in the expressions used to analyze the data. On the other hand, electrophoretic NMR (eNMR)<sup>32,33</sup> provides a more direct approach for determining  $t_+^0$  from a single type of experiment. In this approach, the averaged species velocities that result from the application of an electric field are measured.<sup>34–36</sup> The velocities are measured at early times, prior to the formation of concentration gradients. Knowledge of these velocities,  $v_+$ ,  $v_-$ , and  $v_0$  for the three species (cation, anion, and solvent) in the electrolyte of interest, can be used to determine  $t_+^0$ :<sup>37</sup>

$$t_+^0 = \frac{v_+ - v_0}{v_+ - v_-}. \quad [3]$$

Figure 1 schematically shows the experimental setup for eNMR measurements, with the electrolyte situated between two electrodes, where it is assumed that species velocities are measured in the stationary laboratory reference frame. Although the electrode electrolyte interface may translate based on the specific nature of the electrochemical reactions at the interface as shown in Figure 1, Eq. 3 involves velocity differences and is therefore valid for species velocities measured in any reference frame.

In this work, we ask if we can estimate the transference number,  $t_+^0$ , given *individual* species velocities measured experimentally. Using Eqs. 1 and 2, we derive expressions that relate  $t_+^0$  to individual cation, anion, or solvent velocities, and explore their applicability using recently acquired eNMR data for a series of tetraglyme-based electrolytes.<sup>38</sup>

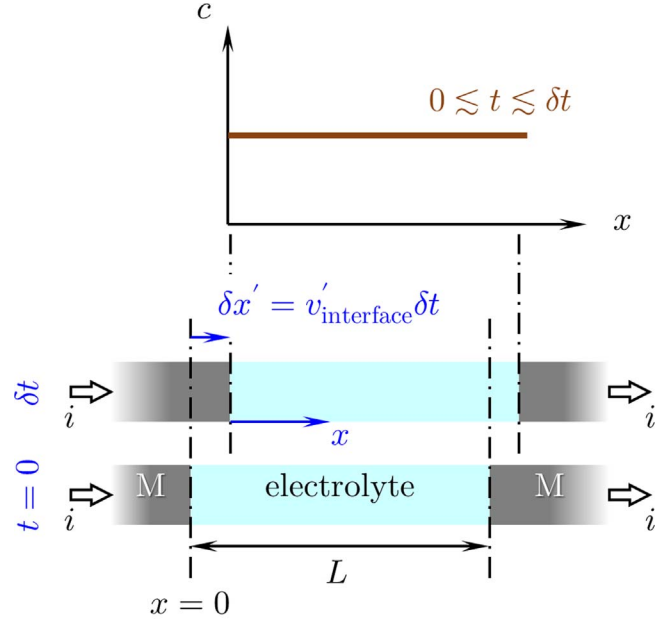
### Theory

Equations 1 and 2 describe ion transport in binary electrolytes under an applied electric field in any inertial reference frame; see Fig. 1. In general, the positive electrode electrolyte interface<sup>8</sup> moves with a finite velocity,  $v'_{\text{interface}}$ , in response to well-defined electrochemical interactions such as metal deposition or ion insertion, as well as side reactions that can consume the electrolytic phase. For example, for a non-blocking metal electrode undergoing reversible deposition and dissolution,  $v'_{\text{interface}}$  can be calculated using Faraday’s second law,

$$v'_{\text{interface}} = -\frac{M_M i}{z_+ F \rho_M} \quad [4]$$

where  $M_M$  is the atomic weight of, and  $\rho_M$  is the density of, the metal electrode,  $M$ , and  $z_+$  is the cationic charge of the metal,  $M^{z_+}$ .  $i$  is the current density passing through the electrode electrolyte interface and the electrolyte. Equation 4 assumes that the solid–electrolyte interphases (SEI) remain unchanged during the experiment. The  $x$ -axis in Fig. 1 is pointed in the direction of  $i$ . The negative sign in Eq. 4 implies that the interface would move in the direction opposite to the current flow, in the  $-x$  direction in Fig. 1. However, eNMR experiments<sup>35,36</sup> usually employ Pd or Pt electrodes that do not undergo reversible stripping and plating, and consequently the direction of movement of the electrode electrolyte interface in these systems has not been established. In Fig. 1, we show the interface moving in the  $+x$  direction. The reason for this will soon be clear.

In the analysis that follows, we use a reference frame fixed to the positive electrode electrolyte interface, one that moves with a velocity  $v'_{\text{interface}}$ . Our equations are valid regardless of the magnitude and sign of  $v'_{\text{interface}}$ . As shown in Ref. 8, Eqs. 1 and 2 can be solved



$x$  is a moving frame attached to the left electrode–electrolyte interface

**Figure 1.** A schematic diagram showing the electrodes (labelled “M”) and electrolytic phase in a typical eNMR experiment. The passage of ionic current,  $i$ , in the  $x$  direction for a short polarization time interval,  $\delta t$ , results in the translation of species in the electrolytic phase that is measured by eNMR. This also results in the translation of the electrode electrolyte interfaces.  $v'_{\text{interface}}$  is the velocity of the positive electrode (shown on the left) relative to a stationary reference frame. The concentration in the electrolytic phase is assumed to be spatially uniform during the eNMR experiment.

to obtain the cation and anion velocities in this moving reference frame,

$$v_+ = -\frac{1}{c} D \left( 1 - \frac{d \ln c_0}{d \ln c} \right) \frac{\partial c}{\partial x} + \frac{1}{c} t_+^0 \frac{i}{\nu_+ z_+ F} + v_0, \quad [5]$$

$$v_- = -\frac{1}{c} D \left( 1 - \frac{d \ln c_0}{d \ln c} \right) \frac{\partial c}{\partial x} - \frac{1}{c} (1 - t_+^0) \frac{i}{\nu_+ z_+ F} + v_0. \quad [6]$$

The corresponding solvent velocity,  $v_0$ , can be obtained by solving Eq. 2. In the subsequent discussion,  $v$  represents velocities in the moving reference frame attached to the positive electrode electrolyte interface, while  $v'$  represents velocities in the stationary laboratory reference frame.

We can show that, for the very short polarization times in eNMR experiments (e.g., 100 ms), the concentrations remain nearly spatially uniform within the electrolyte. In this limit, it was shown in Ref. 8 that each of the three species velocities can be written as

$$v_+ = \frac{1}{c} t_+^0 \frac{i}{\nu_+ z_+ F} + v_0, \quad [7]$$

$$v_- = -\frac{1}{c} (1 - t_+^0) \frac{i}{\nu_+ z_+ F} + v_0, \quad [8]$$

$$v_0 = \bar{V} (1 - t_+^0) \frac{i}{\nu_+ z_+ F}. \quad [9]$$

Equivalently, the species velocities in the stationary laboratory frame, as measured by eNMR, are

$$v'_+ = \frac{1}{c} t_+^0 \frac{i}{\nu_+ z_+ F} + \bar{V} (1 - t_+^0) \frac{i}{\nu_+ z_+ F} + v'_{\text{interface}}, \quad [10]$$

$$v'_- = -\frac{1}{c} (1 - t_+^0) \frac{i}{\nu_+ z_+ F} + \bar{V} (1 - t_+^0) \frac{i}{\nu_+ z_+ F} + v'_{\text{interface}}, \quad [11]$$

$$v'_0 = \bar{V} (1 - t_+^0) \frac{i}{\nu_+ z_+ F} + v'_{\text{interface}}. \quad [12]$$

By rearranging Eqs. 10–12, we can estimate  $t_+^0$  from each of the species velocities as

$$t_+^0 = \frac{1}{(1 - c\bar{V})} \left\{ \frac{\nu_+ z_+ F c (v'_+ - v'_{\text{interface}})}{i} - c\bar{V} \right\}, \quad [13]$$

$$t_+^0 = 1 + \frac{1}{(1 - c\bar{V})} \left\{ \frac{\nu_+ z_+ F c (v'_- - v'_{\text{interface}})}{i} \right\}, \quad [14]$$

$$t_+^0 = 1 - \frac{\nu_+ z_+ F (v'_0 - v'_{\text{interface}})}{\bar{V} i}. \quad [15]$$

Typically, eNMR experiments apply a constant voltage difference,  $V$ , across the length,  $L$ , of the cell. The current passing through an electrolyte of uniform composition in the eNMR experiment is given by Ohm's law,

$$i = \kappa \frac{V}{L}. \quad [16]$$

Substituting for  $i$  in Eqs. 13–15 using Eq. 16, we obtain:

$$t_+^0 = \frac{1}{(1 - c\bar{V})} \left\{ \frac{\nu_+ z_+ F c}{\kappa} \left( \frac{v'_+ - v'_{\text{interface}}}{V/L} \right) - c\bar{V} \right\}, \quad [17]$$

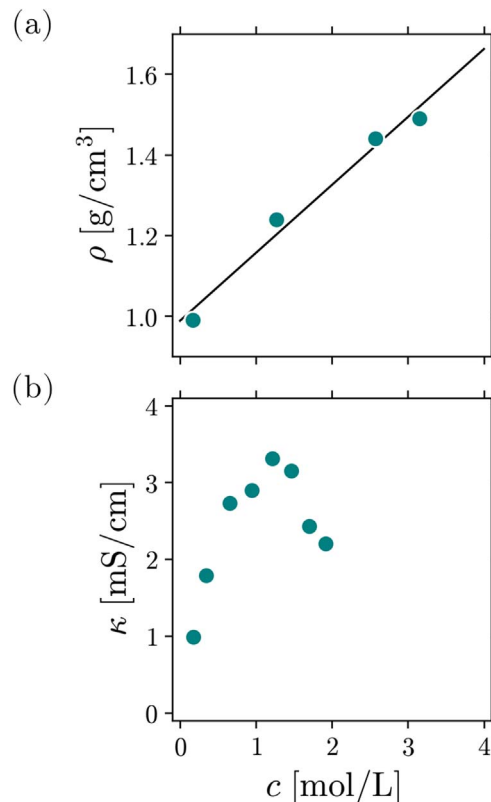
$$t_+^0 = 1 + \frac{1}{(1 - c\bar{V})} \left\{ \frac{\nu_+ z_+ F c}{\kappa} \left( \frac{v'_- - v'_{\text{interface}}}{V/L} \right) \right\}, \quad [18]$$

$$t_+^0 = 1 - \frac{\nu_+ z_+ F c}{\bar{V} \kappa} \left( \frac{v'_0 - v'_{\text{interface}}}{V/L} \right). \quad [19]$$

Equations 17–19 are new theoretical expressions that relate  $t_+^0$  to each individual species velocity, i.e.,  $v'_+$ ,  $v'_-$  and  $v'_0$ , respectively. As per Eq. 19, even measurements of solvent velocity alone can underpin  $t_+^0$ . Since  $t_+^0$  is a material property, it follows that all of the velocities on the right side must be proportional to  $V/L$ . In our prior eNMR experiments, we have experimentally verified that this linear relationship holds for all species velocities.<sup>38</sup> Rather than report the slopes,  $v'_i L/V$  ( $i = +, -, 0$ ), we report scaled species velocities obtained at  $V/L = 1 \text{ V mm}^{-1}$ .

## Results and Discussion

The subsequent discussion tests these expressions (Eqs. 17–19) using experimental eNMR species velocities in electrolytes comprising mixtures of lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) salt dissolved in tetraglyme.<sup>38–41</sup> Unlike Eq. 3 wherein  $t_+^0$  is determined from all three species velocities, Eqs. 17–19 estimate  $t_+^0$  of an electrolyte with concentration,  $c$ , from only one species velocity, if the following additional information is known: partial molar volume of salt,  $\bar{V}$ ; ionic conductivity,  $\kappa$ , at the salt concentration of interest,  $c$ ; and velocity of the positive electrode electrolyte interface,  $v'_{\text{interface}}$ , in the stationary laboratory reference frame.  $\bar{V}$  can be estimated if the electrolyte density,  $\rho$ , is known as a function of



**Figure 2.** (a) Electrolyte density and (b) ionic conductivity measurements<sup>31,42</sup> of LiTFSI/tetraglyme electrolytes at 30 °C, and the corresponding fitted trend (solid trace; Eq. 20).

concentration.<sup>1</sup> The ionic conductivity  $\kappa$  is also readily measured, e.g., from ac impedance measurements using blocking electrodes. We have previously reported thermodynamic and ionic transport data in LiTFSI/tetraglyme electrolytes as a function of  $c$ .<sup>31,42</sup> All measurements are reported at 30 °C.

The density and ionic conductivity datasets are shown in Fig. 2, along with the fitted trace

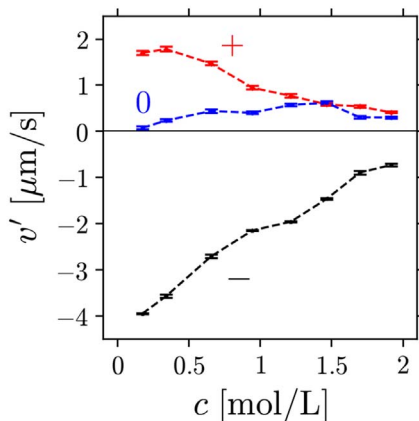
$$\rho = 0.168c + 0.989. \quad [20]$$

Equation 20 can be subsequently used to estimate  $\bar{V}$ , as per the definition of the partial molar volume,<sup>1</sup>

$$\bar{V} = \frac{M - \frac{d\rho}{dc}}{\rho - c \frac{d\rho}{dc}}, \quad [21]$$

where  $M$  is the molar mass of LiTFSI salt.

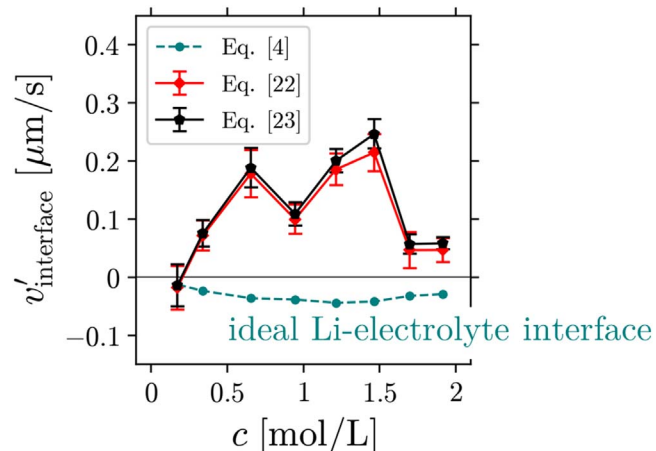
The individual species velocities measured by eNMR are reported in Fig. 3, scaled to a fixed applied electric field of  $1 \text{ V mm}^{-1}$ .<sup>38</sup> In order to determine  $t_+^0$  from single species velocities (Eqs. 17–19), we need an estimate of  $v'_{\text{interface}}$ . As Eq. 4 shows, the electrode electrolyte interfacial velocity is well-defined in some cases, e.g., reversible deposition on non-blocking electrodes. However, the nature of the reactions that occur at interfaces with noble metal electrodes like Pt or Pd in eNMR experiments are not known. Consequently, we first assume that the interface does not move in the stationary reference frame, i.e.,  $v'_{\text{interface}} = 0$ . Under this assumption, Eqs. 17–19 can be readily applied to estimate  $t_+^0$ . In Fig. 4, we compare these estimates with  $t_+^0$  determined using all three species velocities (Eq. 3). We refer to  $t_+^0$  obtained using Eq. 3 as the “standard.” In Fig. 4a we compare the  $t_+^0$  obtained using the cation



**Figure 3.** Spatially averaged species velocities of LiTFSI/tetraglyme electrolytes in the laboratory frame of reference, measured using  $^7\text{Li}$  ( $v'_+$ ),  $^{19}\text{F}$  ( $v'_-$ ), and  $^1\text{H}$  ( $v'_0$ ) eNMR experiments<sup>38</sup> at 30 °C. The velocities are scaled to an electric field of 1 V mm<sup>-1</sup>. Note that positive velocities imply motion in the same direction as the current passing through the cell. Error bars lie within the symbols.

velocity alone with the standard dataset. Here we see quantitative agreement in the dilute window up to a concentration of 1 mol L<sup>-1</sup>. At higher concentrations,  $t_+^0$  determined from the cation velocity is somewhat higher than the standard. There is, however, general qualitative agreement between  $t_+^0$  determined using Eqs. 3 and 17. In Fig. 4b we compare the  $t_+^0$  obtained using the anion velocity alone (Eq. 18) with the standard dataset. Here we see good qualitative agreement between the two methods, but quantitative agreement is lost at concentrations above 0.5 mol L<sup>-1</sup>. Figure 4c, on the other hand, shows qualitative disagreement between  $t_+^0$  determined using the solvent velocity alone (Eq. 19) over most of the concentration window. Somewhat surprisingly, we find agreement between the two methods at the two highest concentrations. The general agreement between the two approaches in Figs. 4a and 4b lends considerable support for Eqs. 17–19.

We now revisit  $v'_{\text{interface}}$ . Since  $t_+^0$  is a property of the electrolyte, independent of the method used to determine it, we can combine Eqs. 17 and 19 and thereby obtain a relationship for  $v'_{\text{interface}}$  that does not include  $t_+^0$ . Similarly, we can combine Eqs. 18 and 19 to obtain a



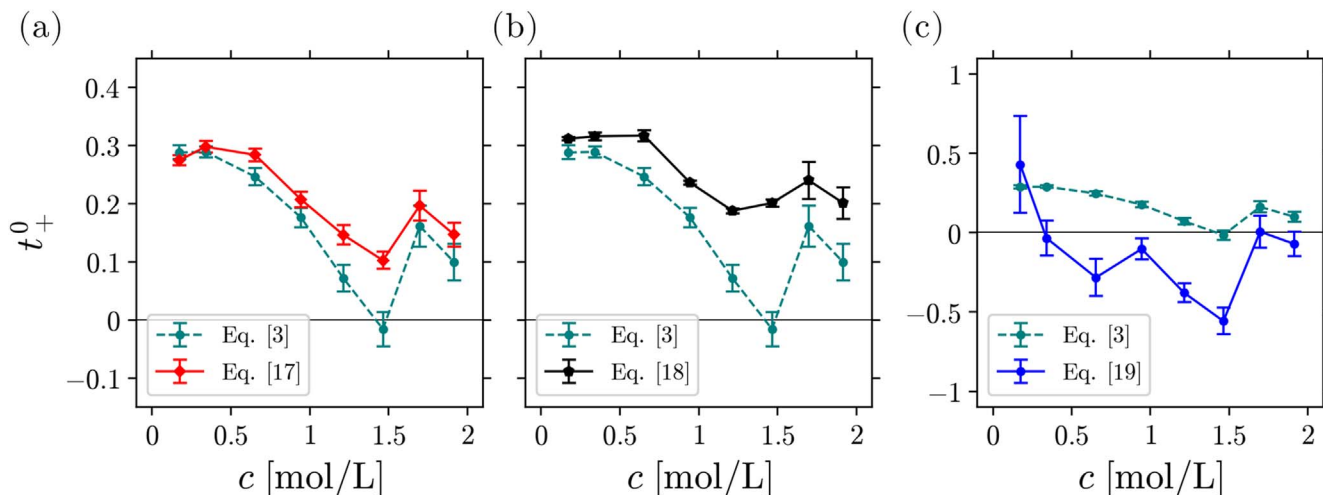
**Figure 5.** Estimated values of electrode electrolyte interface velocities in eNMR measurements of LiTFSI/tetraglyme electrolytes at 30 °C using Pt electrodes. Equation 22 uses  $v'_+$  and  $v'_0$  whereas Eq. 23 uses  $v'_-$  and  $v'_0$  to estimate  $v'_{\text{interface}}$ . The nearly overlapping trends show consistency between the two approaches. For reference, the expected values of  $v'_{\text{interface}}$  that would be obtained for reversible lithium metal electrodes are shown as filled circles (Eq. 4).

second relationship for  $v'_{\text{interface}}$ . These two relationships are given below.

$$v'_{\text{interface}} = (c\bar{V})v'_+ + (1 - c\bar{V})v'_0 - \frac{\bar{V}}{\nu_+z_+F} \kappa \frac{V}{L}, \quad [22]$$

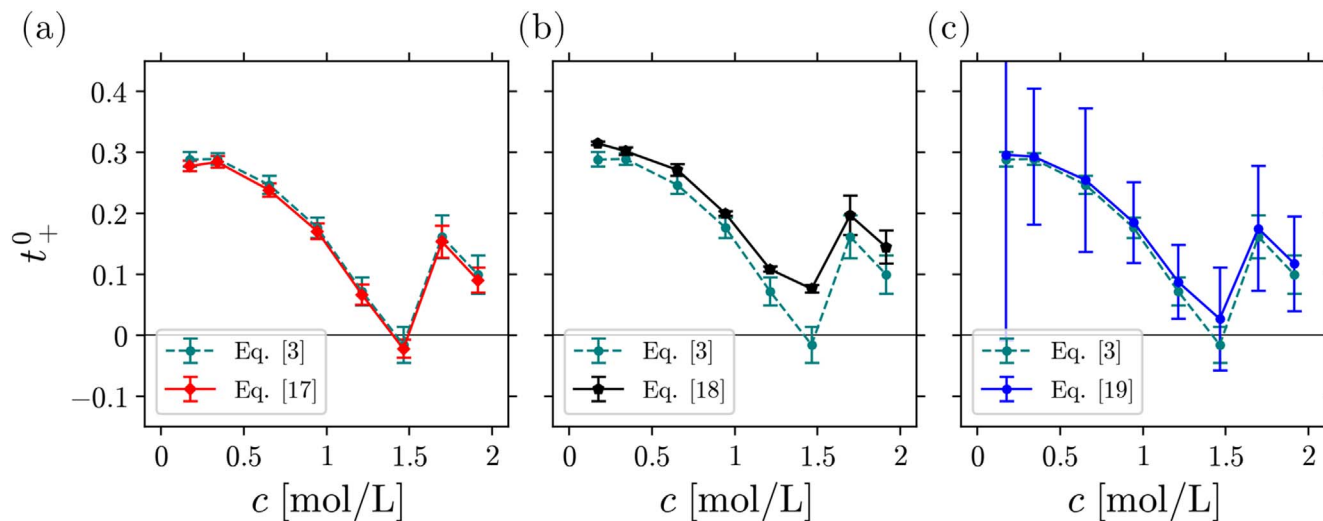
$$v'_{\text{interface}} = (c\bar{V})v'_- + (1 - c\bar{V})v'_0. \quad [23]$$

All of the parameters on the right sides of Eqs. 22 and 23 are known, and thus  $v'_{\text{interface}}$  can be estimated using two independent expressions. The calculated values thus obtained are plotted as a function of concentration in Fig. 5. The agreement between the two independently calculated  $v'_{\text{interface}}$  values lends considerable support to our approach for calculating this parameter. We also show  $v'_{\text{interface}}$  for a reversible lithium metal electrode, calculated using Eq. 4. It is clear that the reactions occurring in our eNMR cell that give rise to motion of the positive electrode electrolyte interface are very different from reversible plating and stripping. Further work is needed to identify the reactions that underlie our measurements of  $v'_{\text{interface}}$ .



**Figure 4.** The dependence of  $t_+^0$  on concentration based on single-species velocity expressions for LiTFSI/tetraglyme electrolytes at 30 °C.  $t_+^0$  is calculated using  $v'_+$  in (a) (Eq. 17),  $v'_-$  in (b) (Eq. 18), and  $v'_0$  in (c) (Eq. 19), assuming  $v'_{\text{interface}} = 0$ . As a reference, we present  $t_+^0$  determined by the standard approach (Eq. 3) in all three plots.





**Figure 6.** The dependence of  $t_+^0$  on concentration based on single-species velocity expressions for LiTFSI/tetraglyme electrolytes at 30 °C.  $t_+^0$  is calculated using  $v_+^0$  in (a) (Eq. 17),  $v_-^0$  in (b) (Eq. 18), and  $v_0^0$  in (c) (Eq. 19), using  $v_{\text{interface}}^0$  values from Fig. 5. As a reference, we present  $t_+^0$  determined by the standard approach (Eq. 3) in all three plots.

We use averaged  $v_{\text{interface}}^0$  values from Fig. 5 with Eqs. 17–19 to obtain a revised estimate of  $t_+^0$ . These estimates are compared with the standard  $t_+^0$  in Fig. 6. Not only do the original three-species equation (Eq. 3) and the single-species expressions (Eqs. 17–19) estimate similar  $t_+^0$ , all of them also capture the minimum value of  $t_+^0$  near  $c \approx 1.5 \text{ mol L}^{-1}$ . The error bars in Fig. 6c are larger as compared to Figs. 6a and 6b because the magnitude of the solvent velocity is smaller than that of the ionic species (see Fig. 3).

It is interesting to note that while Eqs. 17–19 only rely on one species velocity for estimating  $t_+^0$  (in contrast to Eq. 3), we require at least two species velocities,  $v_+^0$  and  $v_0^0$  or  $v_-^0$  and  $v_0^0$ , to underpin the unpredictable flux caused by  $v_{\text{interface}}^0$  (using Eqs. 22 and 23, respectively). The standard method for measuring  $t_+^0$  (Eq. 3) employs differences of velocities in both the numerator and denominator and is thus insensitive to  $v_{\text{interface}}^0$ . Only when employing eNMR velocities on their own such as in Eqs. 17–19 does the need to account for the electrolyte–electrode interface motion become apparent. In that sense, single-velocity estimates of  $t_+^0$  require fewer experiments, but may require either careful consideration of interfacial effects, or potentially more involved experimental setups utilizing non-blocking electrodes where  $v_{\text{interface}}^0$  is well-defined.

### Conclusions

As compared to traditional electroanalytical techniques, electrophoretic NMR (eNMR) is a more straightforward approach for measuring the transference number of electrolytes. In the standard approach, measurements of all three species velocities, i.e., cation, anion and solvent, are used to determine  $t_+^0$  of a binary electrolyte using Eq. 3.<sup>37</sup> Our main purpose is to present new equations that express  $t_+^0$  in terms of individual species velocities (Eqs. 17–19). Our theoretical results (Eqs. 1–19; 21–23) apply to any binary electrolyte, regardless of the values of  $z_+$  and  $z_-$ . We show that a reference frame attached to the electrode electrolyte interface is convenient for solving the governing equations and relating the species velocities to  $t_+^0$ . Interestingly, our work shows that even measurements of the solvent velocity alone can be used to characterize the transference number. In other words, the velocity of the uncharged species can be used to determine a parameter that is related to the fraction of current carried by the cation relative to that of the anion. We tested the validity of the single-species equations using experimentally measured eNMR species velocities in LiTFSI/tetraglyme.<sup>38</sup>

All electrode electrolyte interfaces must move when electrochemical reactions are carried out, and this results in translation of the entire electrolytic phase. Since this motion is unrelated to ion transport within the electrolyte, measurements of species velocities based on a stationary reference frame must be corrected for this translation. Fortunately, the electrode electrolyte interface velocity cancels out in the standard approach for determining  $t_+^0$  from species velocities (Eq. 3). Knowledge of the electrode electrolyte interface velocity is, however, necessary for determining  $t_+^0$  from single species velocities unless these velocities are much larger than  $v_{\text{interface}}^0$ . In the present case of LiTFSI/tetraglyme electrolytes examined using Pt electrodes, eNMR measurements of all species velocities enable quantifying  $v_{\text{interface}}^0$ , a parameter that has hitherto remained unrecognized in the literature.

Our approach is based on concentrated solution theory,<sup>6</sup> and can thus be used to interpret eNMR measurements of transference numbers at any salt concentration. It may be particularly important in the characterization of electrolytes containing species not easily accessible by NMR, such as  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$ . There is no inherent reason to use blocking electrodes such as Pd and Pt in eNMR experiments. These electrodes must participate in irreversible reactions involving the electrolyte and solvent molecules at the electrode electrolyte interfaces. Employing reversible electrodes with well-defined reactions will enable determining the electrode electrolyte interface velocity directly. In Ref. 43, Hayamizu et al. conducted eNMR experiments using reversible Li metal electrodes. Such experiments also enable measurement of current, an important parameter that is rarely discussed in the context of eNMR.

Concentrated solution theory as established in 1965 quantifies ion transport in electrochemical systems.<sup>6</sup> Even today, it provides fertile ground for establishing new approaches for studying ion transport, including the analysis of experiments that were not conceived when the theory was proposed.

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### ORCID

David M. Halat <https://orcid.org/0000-0002-0919-1689>

Aashutosh Mistry <https://orcid.org/0000-0002-4359-4975>

Darby Hickson <https://orcid.org/0000-0002-5133-9755>

Venkat Srinivasan <https://orcid.org/0000-0002-1248-5952>

Nitash P. Balsara <https://orcid.org/0000-0002-0106-5565>

Jeffrey A. Reimer <https://orcid.org/0000-0002-4191-3725>

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