Method of Measuring Salt Transference Numbers in Ion-Selective Membranes

Jonathan T. Vardner, Tie Ling, Sebastian T. Russell, Alexis M. Perakis, Yupeng He, Nicholas W. Brady,* Sanat K. Kumar, and Alan C. West**,*

Department of Chemical Engineering, Columbia University, New York, New York 10027, USA

A technique to measure the cation-transference number of salts in fully hydrated ion-selective membranes has been developed and demonstrated on Nafion 117 for LiCl and Li2SO4. Dilute solution theory is used to identify experimental conditions that reduce the propagation of uncertainties in membrane transference number estimates. This technique has advantages over commonly used methods, including the elimination of the need for the analysis of electrode potentials in approaches that exploit electroanalytical methods or the need for additional information required to reconcile NMR-based methods with the bulk transport property. It additionally allows for numerous measurements per day and offers the possibility to relate trace measurements of either cations or anions to values of transference number. For LiCl both modes of the technique were employed; the anion-tracer method is more precise and gives $t_\text{+} = 0.936 \pm 0.010$. The experimental procedure was repeated using the cation-tracer method for Li2SO4, and $t_\text{+} = 0.95 \pm 0.06$ was estimated.

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Numerical simulations are used to further reduce uncertainties introduced by the tracer ion on the \( t_i \) measurement. The simulations for cation-tracer experiments with Nafion 117 indicate that properties of the tracer ion, specifically its diffusivity and solubility in the membrane, have a small impact on the \( t_i \) measurement. These properties, however, can be estimated by the measurement of flux of the target ion and tracer ion across the membrane to minimize their effect on the estimated transference number. The simulations for anion-tracer experiments with Nafion 117 show that the tracer ion has virtually no impact on the \( t_i \) measurement, and therefore, additional properties of the tracer ion need not be estimated. Consequently, the charge of the tracer ion should have the same sign as the charge of the membrane’s fixed ion for the most accurate \( t_i \) measurements. The values of \( t_i \) of LiCl and Li2SO4 in Nafion 117 were experimentally measured to validate the theory and the method.

**Theory**

In the experimental setup, a dilute solution of each of the electrolytes flows through reservoirs adjacent to the ion-selective membrane, one on each of its two sides. A constant current density applied across the membrane affects the flux of ions across the membrane. The computationally determined fluxes depend on the value of \( t_i \). Table I provides a summary of the subscripts for the three experiments studied. In the first cation-tracer experiment, 0.1 M LiCl is placed in the anode reservoir, and 0.1 M KCl is placed in the cathode reservoir. In the second cation-tracer experiment, 0.05 M Li2SO4 is placed in the anode reservoir, and 0.05 M K2SO4 placed in the cathode reservoir. Lastly, in the anion-tracer experiment, 0.05 M Li2SO4 is placed in the anode reservoir and 0.1 M LiCl placed in the cathode reservoir. Simulations also provide a basis to design experiments to minimize uncertainties in the transference number. The flux of ions is assumed to follow dilute-solution theory,

\[
N_j = c_j \nu - D_j \nabla c_j - F z_j u_j c_j \nabla \Phi \tag{1}
\]

where the velocity \( \nu \) is assumed to be zero in the membrane, and the ionic mobility \( u_j \) is given by the Nernst-Einstein relationship:

\[
D_j = RT u_j \tag{2}
\]

For more concentrated electrolytes, concentrated solution theory, which may account for electro-osmotic water flows for example, may be introduced to further refine the present treatment. The current density across the membrane is carried by the mobile ions within the electrolyte. Consequently, the current density can be related to the flux of ions. The relationship is quantified by the following expression:

\[
i = F \sum_j z_j N_j \tag{3}
\]

It is assumed that the electrolyte is well mixed, so that there are no concentration gradients in the electrolyte (concentration polarization) on either side of the membrane. Consequently, the following boundary conditions for each species are provided:

\[
\begin{align*}
\text{at } x = 0, & \quad c_j = S_j c_j,_{\text{bulk}} \\
\text{at } x = L, & \quad c_j = S_j c_j,_{\text{bulk}}
\end{align*} \tag{4}
\]

The system is constrained to obey electroneutrality, assuming a fixed charge of \( z_j c_j \) on the membrane:

\[
\sum_j z_j c_j = -z c_f \tag{5}
\]

For the present purposes, the reported transference number is defined as if only two species are present. This would be the anticipated value when the tracer ion is removed from the system, as we assume this is of practical interest for the present study.

For cation – tracer studies:

\[
t_j = z_j^2 D_j c_j \left( z_j^2 D_j c_1 + z_j^2 D_j c_2 \right)^{-1} \tag{7}
\]

For anion – tracer studies:

\[
1 - t_j = z_j^2 D_j c_j \left( z_j^2 D_j c_1 + z_j^2 D_j c_2 \right)^{-1} \tag{8}
\]

Code was written in fortran95 using a block tridiagonal matrix algorithm developed by Newman,21 to solve the set of equations and boundary conditions. The solution to the governing expression subject to the boundary-condition constraints is dependent on four dimensionless ratios: \( D_j/D_2, D_j/D_3, S_j/S_2 \) and \( t_j \). These four parameters can be fit to experimental data, or alternatively, the parameters \( D_j/D_2, D_j/D_3, S_j/S_2 \) can be experimentally determined to constrain the measurement of \( t_j \). However, the value of \( t_j \) generally has the most prominent effect in the simulation, and therefore, its value can be estimated even with uncertainty in the other dimensionless parameters. As a means of parameter estimation, a quasi-random search using Sobol sequences in Python was conducted over the 4-dimensional parameter space. The optimal parameter values were determined by searching for a minimum in a weighted least-squares value. One million Sobol points, corresponding to one million sets of parameters, were used, and the standard-deviation of the top 100 results provides an estimate of the precision in the transference number given the uncertainty in the other parameters.

Example results for the concentration profiles within the membrane for zero, intermediate, and high current densities are presented in Figure 1. At zero current density, both cations have significant concentration of \( K \) throughout the majority of the membrane thickness. Electrical migration forces a high concentration of \( Li \) and a low concentration of \( K \) throughout the membrane. Consequently, the flux of \( Li \) as \( i \to \infty \) does not depend on the ratio \( D_j/D_2 \), thereby eliminating a source of uncertainty arising from introduction of the tracer salt.

From the concentration profiles, the mathematical framework calculates the dimensionless flux of each species across the membrane. The flux of species 2 (shown in Table I) is of particular interest because its experimental measurement is used to determine \( t_i \). The theoretical flux of species 2 is presented as a function of current density in Figure 2. The dimensionless flux across the membrane is defined as:

\[
\bar{N}_2 = \frac{N_2}{D_2 c_f} \frac{L}{F} \tag{9}
\]

The quantity \( D_2 c_f \) may not be known, especially for novel materials. However, this value is not required to compare simulations to experiment while estimating the transference number. Specifically, normalization of the applied current density with the zero-current flux of species 2 allows for comparison of simulation to experiment:

\[
\bar{N}_{2,_{\text{exp}}} = i \left( F N_{2,_{\text{exp}}} \right) . \tag{10}
\]

The normalization of the measured flux with the applied current density allows facile comparison of experiment and simulation through \( N_{2,_{\text{exp}}} \cdot i \). This normalization of the flux has the further advantage of reaching an asymptotic value at high current densities.

Figure 3 shows simulation results of a cation-tracer experiment and an anion-tracer experiment for different parameter values.

| Table I. Subscripts for the three experiments of this study. |
|-----------------|-----------------|-----------------|
| Species | Li measurement for LiCl \( t_i \) | Li measurement for Li2SO4 \( t_i \) | Cl measurement for LiCl \( t_i \) |
| Cl | 1 | - | 2 |
| Li | 2 | 2 | 1 |
| K | 3 | 3 | - |
| SO4 | - | 1 | 3 |

The tracer ion’s impact on the \( t_i \) measurement is minimized at high currents.
Table II provides a summary of the impact of the parameters on simulation results for cation-tracer as well as anion-tracer experiments. For anion-tracer experiments, the simulation results are only sensitive to transference number. For cation-tracer experiments, the value of the ratio $D_3/D_2$ is significant at low currents and has virtually no effect at high current. The ratio $D_1/D_2$ has no effect on the simulation results when $S_3/S_2 = 1$; however, when $S_3/S_2$ is not equal to unity, the anion concentration is not constant, and consequently, $D_3/D_2$ is of small importance. These general trends provide guidance on the best means of estimating transference number. The insets of Figure 3 show the range of transference numbers from the top-100 best fit estimates of transference numbers to experiments (discussed below). The spread in the other parameters is relatively larger because they have a much smaller impact on simulation results. The estimated transference number shows low sensitivity to other parameters for the cation-tracer experiments and essentially zero sensitivity for the anion-tracer experiment.

For the cation-tracer experiments (Fig. 3a), the asymptotic value of normalized flux is approximated by the following expression for high values of $t_+ (\geq 0.8)$:

$$\left( \frac{FN_2}{i} \right)_{i \to \infty} \approx t_+ \left[ 1 - z_1 \frac{D_1}{D_2} \left( 1 - \frac{S_3}{S_2} \right) \right]$$

[10]

Figure 1. Simulated concentration profiles of the ions present within the membrane for a cation-tracer experiment for three applied current densities. Simulations assume $D_1/D_2 = 1.0$, $D_3/D_2 = 1.0$, $S_3/S_2 = 1.0$, and $t_+ = 0.90$.

Figure 2. The simulated dimensionless flux of the measured species as a function of normalized dimensionless current density. The values of the three parameters in these models are: $D_1/D_2 = 1.0$, $D_3/D_2 = 1.0$, and $S_3/S_2 = 1.0$.

Figure 3. Simulated normalized fluxes as a function of normalized current density. The solid lines of these plots assume $D_1/D_2 = 1$, $D_3/D_2 = 1$, and $S_3/S_2 = 1$. The dashed lines for the cation-tracer experiments (a) assume $D_1/D_2 = 0.3$, $D_3/D_2 = 0.4$, and $S_3/S_2 = 0.9$. The dashed lines for the anion-tracer experiments (b) assume the same ratios for the species present.
Note that the ratio $D_3/D_2$ is not important. For the anion-tracer experiments (Fig. 3b), the results are insensitive to all parameters except $t_i$. In the high current limit, the anion-tracer flux can be approximated by:

$$i/FN_{2,i} \rightarrow 10$$

Note that for an anion-selective membrane the high current limit is $t_i$. The high current limits are defined as values of $i/FN_{2,i} = 0$ that result in constant values of $FN_{2,i}$, which are approached for cation-tracer studies when:

$$i/FN_{2,i} > 10$$

At high current densities, however, concentration polarization (i.e., concentration variations in the near-membrane diffusion layers of the reservoirs) becomes more likely to interfere with the flux measurement due to the relatively high cationic flux. Values of $i/FN_{2,i} < 10$ may be used to determine $t_i$, but result in some uncertainty in the $t_i$ measurement. For anion-tracer studies, the high current limits can be approximated as:

$$i/FN_{2,i} > 5(1-t_i)$$

### Methodology

An AutoCAD schematic of the microfluidic device used for determination of transference number is presented in Figure 4. The device, consisting of two sections, was constructed by etching a slab of poly methyl methacrylate (McMaster Carr). The two components of the device were symmetrical in shape with dimensions presented in the figure. One component housed the Pt anode and allowed for the flow of lithium electrolyte (either 0.1 M LiCl or 0.05 M Li$_2$SO$_4$), whereas the second component housed the Pt cathode and allowed for the flow of potassium electrolyte (either 0.1 M KCl to 0.05 M K$_2$SO$_4$). In the experiments, the values of $t_i$ for LiCl and Li$_2$SO$_4$ were measured, while KCl and K$_2$SO$_4$ were used as tracer salts. Tube fittings (Mc-Master Carr) were inserted into the inlet and outlet ports to connect the device to external polymer tubing. Pt wire with a diameter of 0.1 cm (Sigma Aldrich) was pierced through the outlet tube fittings, inserted into the microfluidic device, and epoxied to fill the piercing.

Experiments were conducted with Nafion 117 membrane (Sigma Aldrich) since this membrane is fairly well characterized and thus ideal to evaluate the methodology. As in the literature, the Nafion membrane was pretreated by slight boiling in 3% H$_2$O$_2$ at 80°C for one hour, followed by boiling in DI water at 80°C for 2 hours, and subsequent boiling in 0.5 M H$_2$SO$_4$ at 80°C for one hour. Kapton tape was then used to cover a fraction of the membrane, defining the area available for mass transport to be a circle with an area of 0.3 cm$^2$. The Nafion membrane was soaked overnight in lithium salt, either 0.1 M LiCl or 0.05 M Li$_2$SO$_4$, before $t_i$ measurements of the respective salts. The membrane was fixed between the two compartments of the microfluidic device, which was fastened together with four screws. The same membrane was used for all experiments.

The experimental process for cation-tracer experiments is shown in Figure 5. Two Kent Scientific syringe pumps controlled volumetric flow rates of electrolyte through the 1/4” vinyl tubing at a flow rate of 1 mL/min. A µAutolab potentiostat was used to apply a constant current between the electrodes ranging from 0–5.5 mA, corresponding to a current density of 0–17 mA/cm$^2$. Electrode reactions were believed to be hydrogen evolution at the cathode and oxygen evolution at the anode.
the anode, though the measurements do not depend on the electrode-reaction assumptions, as long Li and K are not electrode reactants or products under the present aqueous environment. Since the electrodes were positioned in the outlet ports, the reaction products were purged out of the device, and therefore, had minimal interference with the membrane processes. For each applied current, 55 mL of electrolyte were used. The device-liquid volume, including tubing, was approximately 5 mL on both the cathode and anode sides. Thus, the first 40 mL of sample were discarded and the last 15 mL were collected, and this was estimated to allow a steady-state measurement.

The experimental process for the anion-tracer experiments (Table I) were analogous to the cation-tracer experiments. However, the membrane area for these studies was increased to 1 cm² to increase the concentration of the outlet samples to a measurable range. A 2410 Keithley Sourcemeter DC power supply was used to apply a constant current ranging from 0–16 mA, corresponding to 0–13 mA/cm².

Concentrations of the cationic outlet samples were measured with atomic absorption spectroscopy (AAS) using a Buck Scientific Model 200A spectrometer. Absorbance readings scaled linearly with concentration (R² > 0.99) over a range of 1–5 ppm for both Li and K. For either species, 5-point calibration curves were obtained immediately before concentration measurements of the outlet samples, which were diluted to fall within the calibration range. Higher currents resulted in greater flux of Li and lower flux of K across the membrane, so the dilution step was modified appropriately for each current.

Concentrations of the chloride ion from the anionic outlet samples were measured with Mohr’s method. Sample volumes of 10–12 mL were taken from the outlet samples. Due to water electrolysis, the anode reservoir was acidic, and therefore, the pH was tuned to a value between 7 and 8 with 0–1.8 mL of 0.1M bicarbonate. The indicator solution, 100 uL of 5% potassium chromate, was added to the solution. Lastly, 0.01M silver nitrate was used to precipitate the chloride ion until the indicator produced a change in color of the solution. The concentrations of chloride in solution was related to the volume of silver needed for the titration.

For all experiments, the ionic flux was determined from the concentration measurements using a modified version of Fick’s first law:

\[
N_j = \frac{c_j Q}{A}
\]

where \(c_j\) represents the measured outlet concentration, \(Q\) represents the volumetric flow rate, and \(A\) is the cross-sectional area of the membrane available for transport.

**Results and Discussion**

The measured flux across the Nafion 117 membrane as a function of applied current density for LiCl and Li₂SO₄ is shown in Figure 6. Measurements at current densities greater than 6.3 mA/cm² for LiCl and greater than 9.5 mA/cm² for Li₂SO₄ were characterized by larger scatter, as indicated by the error bars. Furthermore, they begin to deviate from the nearly linear dependence on applied current. Analysis suggests that concentration polarization, i.e., mass transfer resistances within the flowing electrolyte may begin to be important. The flow of Li was equal to or slightly greater for Li₂SO₄ than LiCl for all applied current densities unaffected by concentration polarization, although the difference in flux is small compared to the experimental error of the measurements. The flux of K is only slightly greater for Li₂SO₄ than for LiCl because Nafion is highly cation-selective for both salts. The value of \(t^+\) may be slightly greater for Li₂SO₄ than LiCl, which would be expected because (1) the sulfonate groups of Nafion electrostatically repel the sulfate group more than they repel chloride ions, and (2) sulfate is larger than chloride, suggesting a lower anion diffusion coefficient. The molar flux of Cl was approximately a factor of 10 less than the flux of Li, which is to be expected for a cation-selective membrane.

**Li measurement for LiCl transference number.**—The subscripts 1, 2 and 3 are replaced with Cl, Li, and K, respectively for this section (Table I). To facilitate the analysis of \(t^+\), the current density, Li flux, and K flux of Figures 6 and 7 were normalized and subsequently compared with the outlined multi-ion transport theory. As discussed in the theory, the current density was normalized by the Li flux at zero current, and the Li flux was normalized by the current density. The K

![Figure 6. Experimental flux of species 2 as a function of applied current density for the three experiments of this study. Three trials were conducted for most data points, and the error bar is the standard deviation of the measurement.](https://example.com/figure6)

![Figure 7. Experimental potassium flux at varying applied current density for KCl and K₂SO₄. Three trials were conducted for most data points, and the error bar is the standard deviation of the measurement.](https://example.com/figure7)
The zero current data for Figure 8 and the high current data (Figure 9) were used in the analysis since these data lead to the most reliable values of \( t_i \). The data at \( i/F^{NLi,i} = 0 \sim 1 \), for instance, were not accurately simulated for any parameter estimate, likely because of yet-to-be-identified simplifications in the model. Thus, the influence of this data on the \( t_i \) measurement was eliminated. We hypothesize that the inadequacy in the simulations do not have a significant impact at low currents (diffusion only) and high currents (dominated by electrical migration).

The outlined multi-ion transport theory was compared to the experimental data with one million adjustments in parameter fitting. The average and standard deviations for each of the parameters are presented for the 100 fits that resulted in the smallest sum of squares. The best least-squared-fit value of \( t_i \) was 0.90 ± 0.01, while the best-fit parameters for \( D_k/D_L \), \( D_k/D_L \), and \( S_k/S_L \) were 1.8 ± 1.4, 0.90 ± 0.06, and 0.95 ± 0.04, respectively. From a sensitivity analysis of the impact of \( t_i \) on the simulated \( F^{NLi,i} \) (Figure 2) and additional uncertainty associated with parameter co-variance, we conclude \( t_i = 0.90 \pm 0.03 \). Note that if the parameters \( S_k/S_L \), \( D_k/D_L \), and \( D_k/D_L \) were set to unity then \( t_i \) would be estimated as 0.93 from Figure 9. The measurement of \( t_i \) for LiCl is in agreement with the literature values, which range from 0.82 to 0.988 at varying LiCl concentration.\(^{3,22}\)

The quantity \( L/(D_{L,i}c_f) \) can be determined once the four dimensionless parameters are estimated. The four parameters are inserted into the model to determine the simulated dimensionless flux \( N_L^{i} \). The quantity, \( L/(D_{L,i}c_f) \), is obtained from \( N_L^{i} = N_{L,i} L/(D_{L,i}c_f) \) and was found to be \( 1.5 \times 10^{-8} \text{ cm}^2 \text{s}^{-1} \text{mol}^{-1} \). Assuming \( L = 1.8 \times 10^{-2} \text{ cm} \) and \( c_f = 12 \times 10^{-3} \text{ mol cm}^{-3} \), \( D_{L,i} = 2 \times 10^{-7} \text{ cm}^2 \text{s}^{-1} \). There is relatively small uncertainty in the values of \( L/(D_{L,i}c_f) \) and \( D_{L,i} \) since uncertainties in \( D_k/D_L \), \( D_k/D_L \), and \( S_k/S_L \) result in relatively small changes in \( N_L^{i} \).

**Li measurement for \( \text{Li}_2\text{SO}_4 \) transference number.**—The subscripts 2 and 3 are replaced with \( \text{SO}_4 \), \( \text{Li} \), and \( \text{K} \), respectively for this section (Table 1). The same procedure was used to determine \( t_i \) for \( \text{Li}_2\text{SO}_4 \) as was used for LiCl. The current density, Li flux, and K flux of Figures 6 and 7 were normalized and subsequently compared with the outlined multi-ion transport theory as shown in Figure 10. The top 100 fits in the Sobol regression returned a best-fit value of 0.95 ± 0.004, while the parameters \( D_{SO}_4/D_{L,i} \), \( D_{SO}_4/D_{L,i} \), and \( S_{SO}_4/S_L \) were 1.5 ± 1.3, 0.26 ± 0.02, and 0.99 ± 0.01, respectively. The experimental error was determined with the same method discussed above, and this results in \( t_i = 0.95 \pm 0.06 \). If the parameters \( S_k/S_L \), \( D_k/D_L \), and \( DSO_4/D_L \) were set to unity then \( t_i \) would be estimated to be 0.97 from Figure 11.
Anion-tracer method for LiCl transference number.—The subscripts 1, 2, and 3 are replaced with Li, Cl, and SO₄, respectively for this section (Table I). For the anion-tracer experiment, the parameters: Dₛₒ₄/Dₓₓₓ, Dₛₒ₄/Dₓₓᵧ, and Sₓₓ/Sᵧᵧ have negligible effect on the theoretical model. Since these three parameters have an insignificant impact on simulation results, the measurement of tracer (SO₄⁻) flux is not needed. The complete set of data in Figure 11 was included in the fit. A value of 0.936 ± 0.001 for tₛ resulted in the best fit to the experimental data, while the parameters Dₛₒ₄/Dₓₓₓ, Dₛₒ₄/Dₓₓᵧ, and Sₓₓ/Sᵧᵧ were indeterminate since simulation results were independent of their values. The additional uncertainty associated with experimental limits of anion-concentration detection and parameter co-variance leads to tₛ = 0.936 ± 0.010. Applying Equation 11 to the data at the highest current density yields tₛ = 0.937 ± 0.010, which is in agreement with the value obtained using the numerical simulation. The quantity, L(Dₓₓᵧ/Dₓₓᵧ), was analyzed with the same method discussed above and was determined to be 2.1 × 10⁻⁴ cm² s⁻¹. From this value the diffusion coefficient, Dₓₓᵧ, was estimated to be 1 × 10⁻⁴ cm² s⁻¹, which is in accord with the values measured independently via the cation-tracer experiments. This analysis of Dₓₓᵧ is an order-of-magnitude estimate since the values of L(Dₓₓᵧ/Dₓₓᵧ) and Dₓₓᵧ are sensitive to values of Dₓₓᵧ/Dₓₓᵧ, Dₛₒ₄/Dₓₓᵧ, and Sₓₓ/Sᵧᵧ, which were not well-characterized. The cation-tracer mode and anion-tracer mode of experimentation give tₓₓ = 0.90 ± 0.03 and tₛ = 0.936 ± 0.010, respectively. For the anion-tracer mode, the flux of species 2 is much more sensitive to tₛ, and therefore, its uncertainty should be much less than for the cation-tracer mode. This is suggested in Figure 2, which shows that when tₓₓ = 0.90, a 1% uncertainty in flux leads to an ~1% uncertainty in tₓₓ, for cation-tracer experiments and an ~0.1% uncertainty in tₛ for anion-tracer experiments. In this study, however, the use of Molar’s method to measure chloride ion concentration had greater relative error than the use of atomic absorption spectroscopy to measure lithium ion concentration. Consequently, the anion-tracer mode showed only a factor-of-three reduction in tₛ uncertainty. Nevertheless, one can conclude that 0.936 ± 0.010 is the best estimate for the Li transference number in these Nafion membranes. Generally, it is preferred to measure anion fluxes to characterize cation-exchange membranes and cation fluxes to characterize anion-exchange membranes. It has been shown, however, that the best mode of operation is also impacted by the limits of quantitation of the ion-concentration measurement, and this may impose a practical constraint.

As a final note, the dilute solution theory used for data analysis may be substituted for a concentrated solution theory, with an understanding that additional transport properties arise. While, depending on the application, this may be a warranted next step, the re-examination of present data with concentrated solution theory is expected to result in similar values of tₛ. It is also possible, however, that the re-examination of the present data with concentrated solution would lead to a revised estimate of tₛ that reconciles the small discrepancies between the anion and cation-tracer experiments. Furthermore, the underlying theory can be readily modified to account for complicated chemical interactions, such as the formation of ionic clusters in high salt concentrations that lead to apparent negative transference numbers.33

Conclusions

A technique to measure tₛ in ion-selective membranes has been shown to be a reliable and easy-to-implement methodology that does not require any analysis of electrode processes for interpretation. Simulations allow for the identification of experimental conditions (zero current data coupled with data at large dimensionless current) that allow for determination of tₛ, even with incomplete knowledge of transport properties for the ions. Measuring the cation or the anion flux have been demonstrated to yield accurate measurements of tₛ, although there are significant advantages in measuring the anion flux for tₛ measurements with Nafion 117. More generally, there are advantages to measuring the flux of the ion with the same sign charge as that of the membrane’s fixed ion.

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List of Symbols

| Symbol | Definition |
|--------|------------|
| A      | Cross-sectional area of membrane, cm² |
| cₓₓ     | Fixed concentration on membrane, mol cm⁻³ |
| cₓᵧ     | Concentration of component j in membrane, mol cm⁻³ |
| cₓᵧ, bulk | Concentration of component j in flowing electrolyte mol cm⁻³ |
| Dₓₓᵧ    | Diffusion coefficient of component j in membrane, cm² s⁻¹ |
| F       | Faraday’s constant, 96485 C mol⁻¹ |
| i       | Current density, A cm⁻² |
| i’      | Dimensionless current density: iL/(FDₓₓᵧcₓᵧ) |
| Nₓₓᵧ    | Molar flux of component j, mol cm⁻² s⁻¹ |
| Nₓᵧ     | Dimensionless flux of component j: NₓᵧL/(Dₓₓᵧcₓᵧ) |
| Q       | Volumetric flow rate, cm³ s⁻¹ |
| R       | Gas constant, 8.314 kg m² s⁻² K⁻¹ mol⁻¹ |
| Sₓₓᵧ    | Solubility factor of component j in membrane |
| T       | Temperature, K |
| tₓₓ     | Cationic transference number |
| uₓᵧ     | Mobility of component j in membrane, cm² s⁻¹ volt⁻¹ |
| v       | Velocity, cm s⁻¹ |
| x       | Position, cm |
| zₓᵧ     | Fixed charge on membrane |
| zₓᵧ     | Charge of component j |
Greek

\( \Delta t_+ \) Uncertainty in transference number

\( \sigma \) Standard deviation

\( \Phi \) Potential, volt

Subscripts

1 Ion present on both sides of membrane
2 Measured ion of target salt
3 Tracer ion

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