

1 **Comparing Two Electrochemical Approaches for**
2 **Measuring Transference Numbers in Concentrated**
3 **Electrolytes**

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15**Abstract**

16 We compare two experimental approaches for measuring the cation
17transference number in mixtures of polyethylene oxide (PEO) and lithium
18bis(trifluoromethanesulfonyl)imide (LiTFSI) salt: the well-established current-
19interrupt method proposed by Ma et al.,¹ and a more recent method based
20on measuring the steady-state current proposed by Balsara and Newman.² In
21electrolytes comprised of high molecular weight PEO, the data from the two
22techniques agree, highlighting the equivalence of these two approaches.
23However, in lower molecular weight PEO electrolytes the values of the two
24approaches diverge at low salt concentrations. We posit this is because the
25approach of Ma et al. requires measurements that are sensitive to the nature
26of the interface between the electrolyte and the electrode. The transference
27numbers measured by the approach of Balsara and Newman for both low
28and high molecular weight samples vary from 0.7 to -0.8 and are within
29experimental error throughout the entire salt concentration window.

30

31Introduction

32 The development of high energy density rechargeable batteries may
33enable the widespread adoption of mass market electric vehicles, thereby
34offering a promising route toward reducing the overall carbon footprint of our
35economy. The industry standard for rechargeable batteries is the lithium-ion
36battery, comprised of a graphite anode, a composite cathode, and an organic
37liquid electrolyte through which lithium ions are shuttled to and from the
38electrodes during charge and discharge. Next generation battery technology
39centers around increasing the energy density by employing novel active
40materials that are generally incompatible with traditional liquid electrolytes.
41Promising alternatives for liquid electrolytes include those based on
42polymers such as mixtures of polyethylene oxide (PEO) and lithium
43bis(trifluoromethanesulfonyl)imide (LiTFSI) salt.³⁻⁶ Complete characterization
44of a battery electrolyte material requires knowledge of three independent
45transport properties: ionic conductivity, σ , salt diffusion coefficient, D , and
46cation transference number, t_+ , in addition to the thermodynamic factor,
47 $(1 + d\ln\gamma_+/d\ln m)$.⁷ The experimental techniques for accurate measurement of
48 σ and D are well established; data of σ from ac impedance spectroscopy and
49 D from restricted diffusion are prevalent in the literature. In contrast, the
50best technique for measuring t_+ remains a topic of discussion.

51 The history of the transference number dates back to the 19th century,
52when Hittorf devised an experimental approach based on passing a known
53amount of charge through a cell with non-blocking electrodes and measuring

the concentration of salt within compartmentalized sections of the electrolyte.⁸ This technique is straightforward for liquid electrolytes and has been applied to a wide variety of systems.⁹ An extension of this approach was later developed for solid electrolytes by Tubandt,¹⁰ where the masses of the electrolyte compartments are measured instead of the salt concentration. Since then, a wide variety of approaches for determining the transference number have emerged. Techniques such as the moving boundary method,¹¹ electromotive force measurement,¹² and electrophoretic NMR¹³ are experimentally rigorous, requiring complex experimental setups, special salts, or unique cell architecture. Other techniques commonly used to measure t_+ such as impedance spectroscopy^{14,15} and pulsed-field gradient NMR^{16,17} rely on assumptions that are invalid for concentrated electrolytes. Due to experimental simplicity, the steady-state current approach outlined by Bruce and Vincent^{18,19} is perhaps the most prevalent technique reported in the literature. In this experiment, a polarization is applied across a symmetric cell with non-blocking electrodes, and the transference number is calculated by the ratio of the steady-state current to the initial current. We refer to this parameter as $t_{+,ss}$, where the subscript is used to denote the experimental approach. Despite its popularity, $t_{+,ss}$ is derived using ideal solution assumptions and thus does not reflect the true transference number of an electrolyte.^{2,20} Values for $t_{+,ss}$ are bounded by zero and one, whereas the transference number has no bounds.

76 A more rigorous electrochemical approach has been recently identified
77by Balsara and Newman.² They use concentrated solution theory to derive
78the relationship between $t_{+,SS}$ and the true transference number of the
79electrolyte, referred to as $t_{+,Ne}$. Experimental determination of $t_{+,Ne}$ requires
80four different electrochemical measurements: σ from ac impedance
81spectroscopy, D from restricted diffusion, $t_{+,SS}$ from the steady-state current
82measurement, and U , the potential of concentration cells. This technique
83has been used by Pesko et al. to obtain the transport properties of
84electrolytes comprised of PEO and LiTFSI salt.²¹ The observed dependence of
85 $t_{+,Ne}$ on salt concentration was complex, exhibiting negative values at
86intermediate concentrations.

87 A similar electrochemical approach has been defined by Ma and
88coworkers and is also based on concentrated solution theory.¹ In this
89approach, data obtained from current interrupt experiments are combined
90with measurements of D and U in order to determine $t_{+,Cl}$. Numerous studies
91have used this approach to measure $t_{+,Cl}$ in polymer electrolytes^{1,22-24} and
92liquid electrolytes.^{25,26} The work of Edman et al., who characterized mixtures
93of PEO and LiTFSI,²⁷ is of particular relevance to the present study. The
94results of Edman et al. suggest that $t_{+,Cl}$ has a simple, monotonic dependence
95on salt concentration and is positive at all concentrations. Thus, the results
96of Pesko et al. and those of Edman et al. for the transference number of PEO/
97LiTFSI electrolytes are not in agreement. One possible reason for this

98discrepancy could be the difference of molecular weight of the PEO polymer
99used in these studies.

100 We set out to resolve this issue by performing a direct comparison of
101 $t_{+,Ne}$ and $t_{+,Cl}$ over a wide range of salt concentrations in two electrolytes: 5
102kg/mol and 275 kg/mol PEO mixed with LiTFSI salt. Our results demonstrate
103the reproducibility of the $t_{+,Ne}$ measurements, and also highlight the
104experimental factors that may lead to discrepancies between the two
105techniques.

106

107**Experimental**

108 The polymers used in this study are 5 kg/mol and 275 kg/mol
109 poly(ethylene oxide) (PEO) with -OH end groups purchased from Polymer
110 Source, and the salt is lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)
111 purchased from Novalyte. We refer to the 5 kg/mol polymer as PEO-5K and
112 the 275 kg/mol polymer as PEO-275K. All sample preparation was performed
113 inside of an argon glovebox where water and oxygen levels remained below
114 1 and 5 ppm, respectively. Both the polymer and salt were dried thoroughly
115 under vacuum (12 hours at 90°C for PEO, 3 days at 120°C for LiTFSI) in the
116 glovebox antechamber before being transferred into the glovebox.
117 Electrolytes were prepared by fully dissolving PEO and LiTFSI in anhydrous
118 tetrahydrofuran (THF) at 60°C, then subsequently evaporating the THF to
119 produce a homogeneous polymer/salt mixture. The PEO/LiTFSI electrolytes
120 were dried under vacuum for 12 hours at 90°C to remove any excess
121 solvent.

122 The salt concentrations of the electrolytes ranged from $0.01 \leq r \leq 0.3$
123 for PEO-5K and $0.005 \leq r \leq 0.3$ for PEO-275K, where r is the molar ratio of
124 lithium ions to ether oxygens, $r = [\text{Li}^+]/[\text{O}]$. We have previously reported
125 measurements of density, ρ , and calculations of molarity, c , over a wide
126 range of r in mixtures of 5 kg/mol PEO and LiTFSI at 90°C.²¹ We use these
127 values for ρ and c in both PEO-5K and PEO-275K. The molality, m , of the
128 electrolytes is calculated according to $m = r / M_{\text{EO}}$, where M_{EO} is the molar

mass of the ethylene oxide repeat unit (44.05 g/mol). Table 1 provides values of ρ , c , and m for all electrolytes in this study.

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Table 1. Values for density, molarity, and molality of PEO-5K and PEO-275K electrolytes based on r . We assume that these values are the same in both electrolytes.

r	ρ (g/L)	c (mol/L)	m (mol/kg)
0.00	1128	0.00	0.00
0.005*	1144	0.13	0.11
0.01	1160	0.25	0.23
0.02	1180	0.47	0.45
0.04	1210	0.87	0.91
0.06	1230	1.20	1.36
0.08	1330	1.59	1.81
0.10	1365	1.87	2.27
0.12	1380	2.11	2.72
0.14	1430	2.38	3.17
0.16	1450	2.58	3.63
0.18	1470	2.76	4.08
0.21 [†]	1516	3.05	4.76
0.24	1580	3.36	5.44
0.27 [†]	1572	3.49	6.12
0.30	1640	3.78	6.80

*only PEO-275K, [†]only PEO-5K

Ionic conductivity was obtained by performing ac impedance spectroscopy on symmetric cells with blocking electrodes. We assembled stainless-steel-polymer-stainless-steel symmetric cells by pressing the PEO/LiTFSI electrolyte into a 508 μm thick silicone spacer and sandwiching between two 200 μm stainless-steel shims. The entire assembly was vacuum

sealed in an airtight pouch material (Showa-Denko) with aluminum tabs serving as electrical contacts. Once the sealing was complete, the sample was removed from the glovebox for electrochemical characterization. Cells were annealed at 110°C prior to the conductivity measurement which was made at 90°C. Ac impedance spectroscopy was performed with a Biologic VMP3 potentiostat, where complex impedance measurements were acquired for a frequency range of 100 mHz to 1 MHz at an amplitude of 80 mV. The high-frequency minimum on the Nyquist impedance plot is taken to be the bulk electrolyte resistance, R_b , which is used along with electrolyte thickness, L , and electrolyte area, a , to calculate the electrolyte conductivity, σ , according to eq. 1.

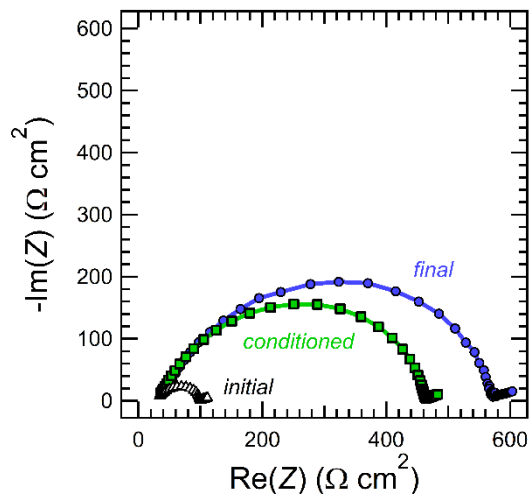
$$\sigma = \frac{L}{aR_b} \quad (0)$$

The inner diameter of the spacer, 3.175 mm, is used to calculate a . Thickness, L , is taken to be the final thickness of the electrolyte, measured after conductivity measurements were completed.

The steady-state current, restricted diffusion, and current interrupt measurements were performed on lithium-polymer-lithium cells. These samples were prepared by pressing the electrolyte into a 508 μm thick silicone spacer and sandwiching between two 150 μm thick lithium foils purchased from the MTI Corporation. Each lithium electrode was backed with a layer of nickel foil to keep the surface of the lithium pristine and a stainless-steel shim to prevent cell deformation. Nickel tabs were secured to

the stainless-steel shims to serve as electrical contacts. The cells were vacuum sealed in pouch material to maintain an air free environment upon removal from the glovebox.

All electrochemical characterization data were obtained using a Biologic VMP3 potentiostat, and the temperature was 90°C. At the beginning of the experiment, cells were annealed for 4 hours to ensure good contact at the lithium-electrolyte interface. Conditioning cycles were performed for 5 charge/discharge cycles at a low current density of 0.02 mA/cm². Each conditioning cycle consisted of a 4 hour charge, 45 min rest, 4 hour discharge, and 45 min rest. Ac impedance spectroscopy was performed before and after the conditioning cycles, and then again at the end of the electrochemical measurements to track the cell resistances over the course of the experiment. Values for the bulk resistance, R_b , and the interfacial resistance, R_i , were obtained by fitting the data in the form of a Nyquist plot to an equivalent electrical circuit appropriate for a symmetric cell with non-blocking electrodes.²¹ Figure 1 shows an example of these data obtained from a lithium-polymer-lithium symmetric cell containing a PEO-5K electrolyte with a salt concentration of $r = 0.06$. In this sample, R_i increased significantly over the course of the experiment with most of the change occurring during the conditioning cycles, whereas R_b was constant throughout the entire experiment. Both the PEO molecular weight and the salt concentration affect the behavior of R_i throughout the experiment.



186

187**Figure 1.** Nyquist plot showing ac impedance measurements from a lithium-
 188polymer-lithium symmetric cell obtained initially, after the cell was conditioned, and
 189at the end of the experiment. This cell contained a PEO-5K electrolyte with $r = 0.06$.
 190The lines between points are a guide to the eye.
 191

192 Steady-state current and restricted diffusion measurements were
 193performed at potentials of $\Delta V = 10$ mV, -10 mV, 20 mV, and -20 mV to
 194ensure the results were independent of the sign and magnitude of the
 195applied potential. Here, we provide a brief description of these experiments;
 196additional details are included in reference 21.

197 The steady-state current experiment was performed by polarizing the
 198cell at constant potential, ΔV , for 4 hours and measuring the current density
 199reached at steady-state, i_{ss} . The resistances of the cell initially ($R_{i,0}$ and $R_{b,0}$)
 200and at steady-state ($R_{i,ss}$ and $R_{b,ss}$) were measured using impedance
 201spectroscopy. The steady-state current transference number, $t_{+,ss}$, derived by
 202Bruce and Vincent^{18,19} is calculated according to the relationship

$$t_{+,SS} = \frac{i_{SS}(\Delta V - i_{\Omega} R_{i,0})}{i_{\Omega}(\Delta V - i_{SS} R_{i,SS})}, \quad (0)$$

where i_{Ω} is the initial current density calculated according to Ohm's law,²⁸

$$i_{\Omega} = \frac{\Delta V}{R_{i,0} + R_{b,0}}. \quad (0)$$

It is important to note that the resistance of the electrode-electrolyte interface is subtracted from the measured data to obtain $t_{+,SS}$.

Restricted diffusion measurements were obtained using the concentration polarization introduced by the steady-state current experiment. Upon removal of the applied potential, the open-circuit voltage, OCV, of the cell relaxed with time, t . The salt diffusion coefficient, D , is calculated using

$$\frac{-d \ln(OCV)}{dt} = \frac{\pi^2 D}{L^2}, \quad (0)$$

where the left side of the equation is the slope from the least-squares linear fit of $-\ln(OCV)$ vs. t from $5 \text{ min} \leq t \leq 2 \text{ hours}$. L is the thickness of the electrolyte, measured by disassembling each cell subsequent to the completion of the electrochemical experiments.

The current interrupt technique was performed following the details outlined in reference 1. A polarization was applied to the lithium-polymer-lithium cell at a constant current density, i , for a short period of time: $5 \text{ seconds} \leq t \leq 2 \text{ min}$. The values of i used in this experiment were $i = 0.1, 0.2, 0.3, \text{ and } 0.4 \text{ mA/cm}^2$. Upon the interruption of the current, the OCV of

the cell was recorded immediately following the discharge of the double layer. A least-squares linear fit of the data plotted in the form of OCV versus $t^{0.5}$ is used to obtain the slope, m_{Cl} , which is the relevant experimental quantity for this technique.

The thermodynamic factor is obtained by measuring the voltage, U , of a concentration cell of the form $Li | PEO/LiTFSI (r_{ref}) | PEO/LiTFSI (r) | Li$. These samples were prepared by creating a channel (approximately 3 cm by 2 mm) in a 508 μm thick silicone spacer, and filling half of the channel with reference electrolyte ($r_{ref} = 0.06$), and the other half with electrolytes at various r . Lithium backed with nickel foil was placed on either end of the channel to serve as electrodes. Nickel tabs were secured as electrical contacts, and the assembly was vacuum sealed in pouch material. Each cell was annealed at 90°C for 20 hours before the value of U was recorded; this length of time ensures the formation of stable interface layers prior to the electrochemical measurement. The diffusion length of 3 cm resulted in a concentration gradient relaxation process that occurred over the course of several days. Two or three concentration cells were prepared for each salt concentration.

For experiments using stainless-steel and lithium symmetric cells (σ , D , $t_{+,SS}$, and m_{Cl}), three samples were prepared, the measurements were averaged, and the standard deviation is reported as the error. The error of $t_{+,Ne}$ and $t_{+,Cl}$ is determined through propagation of these errors, not including that of the concentration cell measurements.

244**Results and Discussion**

245 We measured the ionic conductivity, σ , salt diffusion coefficient, D ,
246 steady-state current transference number, $t_{+,ss}$, and concentration cell
247 potential, U , over a wide range of salt concentrations in 5 kg/mol (PEO-5K)
248 and 275 kg/mol (PEO-275K) PEO electrolytes with LiTFSI salt at 90°C. Here,
249 we use r to denote salt concentration, defined as the molar ratio of lithium
250 ions per ether oxygen on the polymer, $r = [\text{Li}^+]/[\text{O}]$.

251 Figure 2a shows σ as a function of r , obtained by performing ac
252 impedance spectroscopy on symmetric cells with blocking electrodes. The
253 maximum σ in both polymers is approximately 2×10^{-3} S/cm, occurring at r
254 = 0.08 in PEO-5K and $r = 0.06$ in PEO-275K. The dependence of conductivity
255 on the molecular weight of PEO at $r = 0.08$ has been previously established
256 by Teran and coworkers.²⁹ At this concentration, conductivity is independent
257 of molecular weight above 5 kg/mol, consistent with our results (Figure 2a).
258 Both PEO-5K and PEO-275K show a non-monotonic dependence of σ on r . The
259 most prominent difference between the concentration dependence of σ in
260 our electrolytes is that PEO-5K has two local maxima at $r = 0.08$ and $r =$
261 0.18, whereas PEO-275K exhibits one broad peak, ranging from $r = 0.04$ to r
262 = 0.18. At this point, it is not clear from where this difference arises. The
263 data in Figure 2a are largely consistent with previous reports on PEO/LiTFSI
264 electrolytes.³⁰⁻³⁵

265 In Figure 2b, we show D as a function of r , obtained from restricted
 266 diffusion measurements using lithium-polymer-lithium cells. The
 267 concentration dependence of D in our electrolytes shows two peaks in PEO-
 268 5K and one broad peak in PEO-275K, analogous to the concentration
 269 dependence of σ observed in Figure 2a. The values of D in PEO-5K are
 270 greater than those obtained in PEO-275K throughout most of the
 271 concentration range. The maximum D in PEO-5K is $1.3 \times 10^{-7} \text{ cm}^2/\text{s}$ ($r =$
 272 0.06), which is approximately double that observed in PEO-275K, 6.9×10^{-8}
 273 cm^2/s ($r = 0.08$). The molecular weight dependence of the salt diffusion
 274 coefficient in polymer electrolytes is not well understood. Two previous
 275 studies have reported on D in PEO/LiTFSI mixtures with salt concentrations
 276 near $r = 0.08$: Mullin et al. reported $D = 1.1 \times 10^{-7} \text{ cm}^2/\text{s}$ for 27 kg/mol ($r =$
 277 0.085, 90°C)³⁶ and Edman et al. reported $D = 4.6 \times 10^{-8} \text{ cm}^2/\text{s}$ for 5,000
 278 kg/mol ($r = 0.083$, 85°C).²⁷ Our measurements of D in PEO-5K fall close to the
 279 value reported by Mullin et al., while our measurements of D in PEO-275K are
 280 between the values reported by Mullin and Edman. It is clear that D exhibits
 281 a significant dependence on molecular weight above 5 kg/mol, in contrast to
 282 σ which is independent of molecular weight above 5 kg/mol.

283 Figure 2c shows $t_{+,ss}$, the transference number obtained by measuring
 284 the steady-state current in lithium-polymer-lithium cells, as functions of r in
 285 our PEO electrolytes. It has been established that this is not the true
 286 transference number.^{2,20,21} Nonetheless, $t_{+,ss}$ is an important parameter as it
 287 describes the fraction of the initial current that is sustained at steady-state

for a given electrolyte. In Figure 2c, the values of $t_{+,ss}$ of PEO-5K and PEO-275K fall within error of one another, with the exception of $r = 0.3$. In both cases, $t_{+,ss}$ decreases as a function of r until $r = 0.16$, and then increases monotonically. Our data are in excellent agreement with a previous report of $t_{+,ss}$ in PEO/LiTFSI electrolytes by Pożyczka et al.³⁵

Figure 2d shows U as a function of $\ln(m)$, where U is the potential measured in a concentration cell of the form $\text{Li} \mid \text{PEO/LiTFSI}(r_{\text{ref}}) \mid \text{PEO/LiTFSI}(r) \mid \text{Li}$, and m is the molality of the PEO/LiTFSI(r) electrolyte. The reference salt concentration, r_{ref} , was 0.06 in both PEO-5K and PEO-275K. The relevant parameter for our study is $dU/d\ln(m)$; thus the choice of r_{ref} is arbitrary. We take U to be positive when $r < r_{\text{ref}}$ and negative when $r > r_{\text{ref}}$. While there is good agreement between U at high salt concentrations ($\ln(m) > 0$), the values of U in PEO-5K and PEO-275K deviate slightly at lower salt concentrations ($\ln(m) \leq 0$). Following the approach introduced by Ma et al.,¹ each data set is fit to an expression as a function of $\ln(m)$. The polynomial expression thus obtained for PEO-5K is

$$U = 47.50 - 69.88(\ln m) - 32.98(\ln m)^2 - 8.19(\ln m)^3, \quad (0)$$

and for PEO-275K is

$$U = 15.92 - 68.51(\ln m) - 29.61(\ln m)^2 - 6.65(\ln m)^3. \quad (0)$$

These equations are shown as solid curves in Figure 2d. Taking the derivative of eq. 5 and eq. 6 gives us the concentration dependence of

$307 dU/d\ln(m)$ for both PEO polymers, which are consistent with those published
308 by Edman et al. using a 5000 kg/mol PEO/LiTFSI electrolyte.²⁷

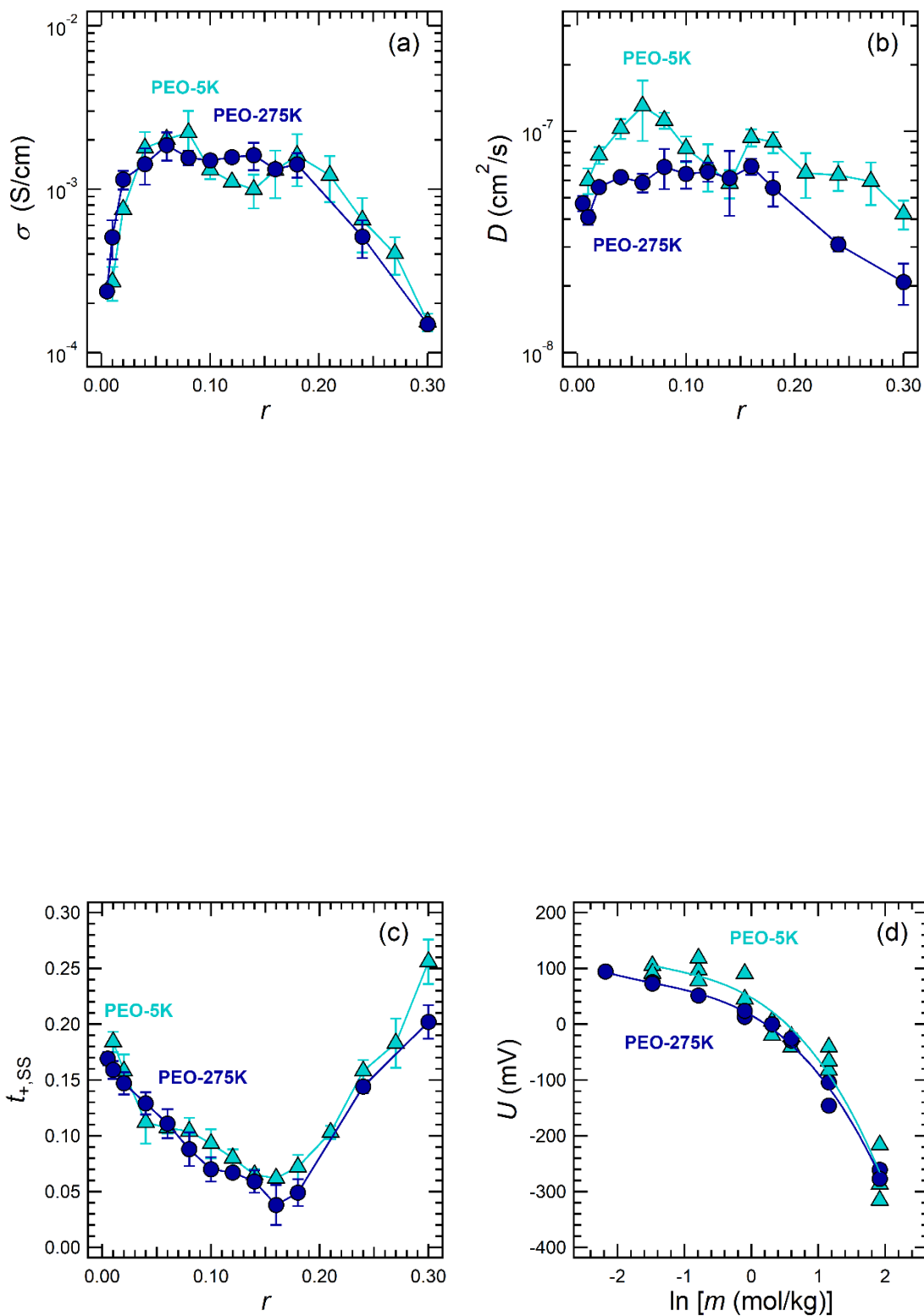


Figure 2. (a) Ionic conductivity, (b) restricted diffusion, (c) steady-state current transference number, and (d) open-circuit potential of concentration cells of 5

313 kg/mol and 275 kg/mol PEO electrolytes as a function of LiTFSI salt concentration at
314 90°C.

315

316 The relationship between the electrolyte characteristics shown in
317 Figure 2 and the cation transference number, $t_{+,Ne}$, has been defined by
318 Newman and coworkers.^{2,21,37}

$$t_{+,Ne} = 1 - \frac{I_{-}}{I_{+} + I_{-}} \quad (0)$$

319 Figure 3a shows $t_{+,Ne}$ as a function of r in PEO-5K and PEO-275K. The
320 concentration dependence of $t_{+,Ne}$ observed in both electrolytes is complex,
321 exhibiting two local maxima at high and low salt concentrations ($r = 0.08$
322 and $r = 0.21$ for PEO-5K, $r = 0.06$ and $r = 0.24$ for PEO-275K) and one local
323 minimum at intermediate salt concentrations ($r = 0.16$). Comparing the
324 values of $t_{+,Ne}$ in both electrolytes, we find that $t_{+,Ne}$ of PEO-275K lies above
325 that of PEO-5K at low salt concentrations ($r \leq 0.06$), but there is excellent
326 agreement at intermediate and high salt concentrations ($r \geq 0.08$). Further
327 work is required to determine the underpinnings of the molecular weight
328 dependence of $t_{+,Ne}$ at low salt concentrations.

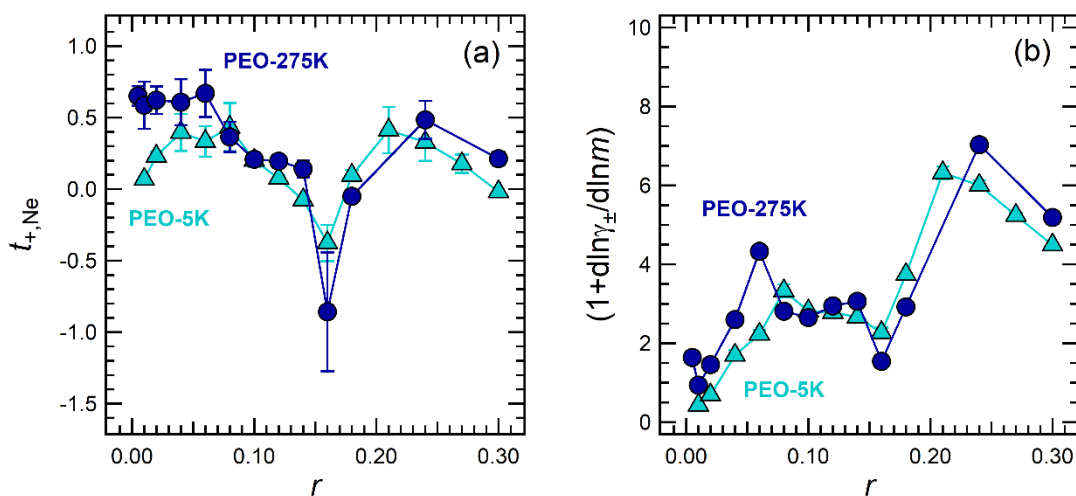
329 The sign of $t_{+,Ne}$ at $r = 0.16$ is negative in both PEO electrolytes. The
330 existence of negative transference numbers in polymer electrolytes has been
331 acknowledged in previous literature,^{1,22,23} and is the topic of recent work from
332 our group.^{31,37} The sign of the transference number provides some insight
333 into the ionic speciation in the electrolyte. If all ions in the system exist as
334 free cations and anions, the transference number must be positive. A

negative transference number suggests that a majority of ions exist as complex species such as negatively-charged triplets or higher-order aggregates.¹ At $r = 0.16$, the concentration at which $t_{+,Ne}$ exhibits a sharp minimum, the ratio of ether oxygens to Li^+ is approximately 6:1. Molecular simulations of PEO/LiTFSI electrolytes indicate that the solvation shell of Li^+ comprises six ether oxygens.^{38,39} Thus, in the vicinity of $r = 0.16$, all solvation sites on the polymer are likely to be saturated, and one might expect that additional salt molecules dissolved into the electrolyte will form aggregates due to the absence of available solvation sites. Our conclusion is in reasonable agreement with previously published spectroscopic studies of PEO/LiTFSI electrolytes, which have concluded that ionic aggregation is present for $r > 0.12$.^{40,41} Further studies are needed to establish the underpinnings of negative transference numbers in polymer electrolytes, as well as the underlying factors that lead to the reemergence of positive transference numbers at high salt concentrations.

The thermodynamic factor, $(1 + d \ln \gamma_{\pm} / d \ln m)$, provides information about how the mean molal activity coefficient, $\gamma_{\pm}$, of the electrolyte changes with m of the solution. This quantity is calculated using the following relationship²¹

$$\left(1 + \frac{d \ln \gamma_{\pm}}{d \ln m}\right) = \frac{-F}{2RT} \quad (0)$$

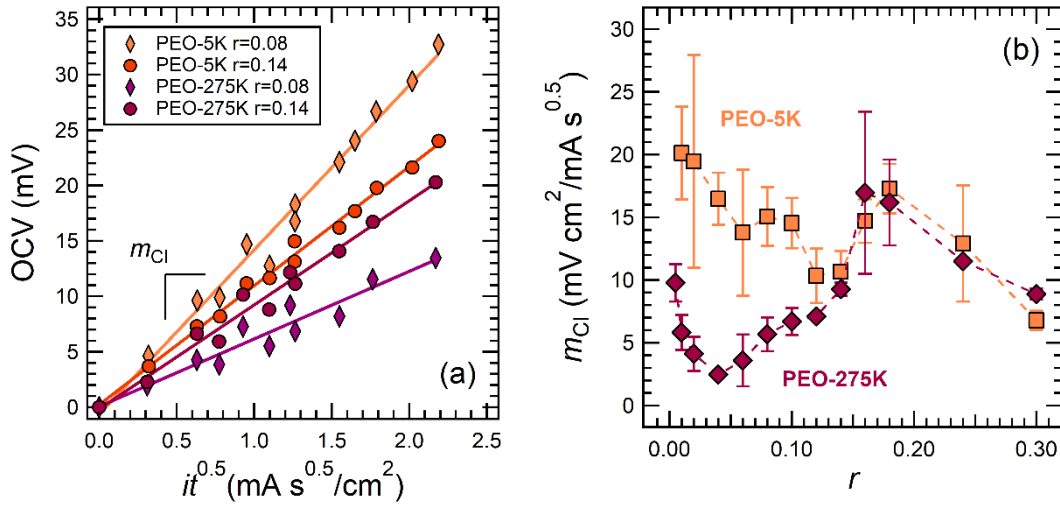
354 where t_+ is the cation transference number that, in principle, can be
 355 determined using a variety of approaches. We use $t_{+,Ne}$ (Figure 3a) and
 356 $dU/d\ln(m)$ (Figure 2d) to calculate $(1+d\ln\gamma_{\pm}/d\ln m)$ as a function of r . In Figure
 357 3b, we report on the thermodynamic factor of PEO-5K and PEO-275K
 358 electrolytes. The value for thermodynamic factor in an ideal solution is unity.
 359 Given that our data for $(1+d\ln\gamma_{\pm}/d\ln m)$ are greater than one throughout
 360 much of the concentration range (Figure 3b), we conclude that our
 361 electrolytes are nonideal at most concentrations ($r \geq 0.04$). It is clear that
 362 the thermodynamic factor in both PEO electrolytes is similar, suggesting that
 363 the activity coefficient of PEO/LiTFSI mixtures is independent of polymer
 364 molecular weight above 5 kg/mol.



365

366 **Figure 3. (a)** Transference number obtained using the Balsara-Newman technique
 367 (eq. 7) and **(b)** Thermodynamic factor (eq. 8) for 5 kg/mol and 275 kg/mol PEO
 368 electrolytes as a function of LiTFSI salt concentration at 90°C.

369 An alternative approach for measuring t_+ using concentrated solution
 370 theory relies on the current interrupt technique. This technique consists of
 371 polarizing a lithium-polymer-lithium cell at current density, i , for time, t , and
 372 measuring the open-circuit potential (OCV) of the cell immediately after the
 373 current is interrupted. Figure 4a shows typical data obtained from this
 374 experiment, plotted in the form of OCV versus $it^{0.5}$ as suggested by Ma et al.¹
 375 These plots are expected to be linear in the limit of small $it^{0.5}$. The important
 376 experimental quantity is the slope, m_{Cl} , of the OCV versus $it^{0.5}$ plot.
 377 Comparing the slopes of the data in Figure 4a, at $r = 0.08$ the slope of the
 378 PEO-5K data is larger than that of PEO-275K, while at $r = 0.14$ the slope of
 379 the data from both electrolytes is approximately the same. It is clear that
 380 the concentration dependence of m_{Cl} is different in PEO-5K and PEO-275K.
 381 Figure 4b shows m_{Cl} as a function of r for both electrolytes. There is a
 382 significant difference between m_{Cl} in our electrolytes at low concentrations (r
 383 ≤ 0.12), where the values of m_{Cl} in PEO-5K are more than double those in
 384 PEO-275K at many concentrations. At high concentrations we observe good
 385 agreement.



386

387 **Figure 4.** (a) Current interrupt data from 5 kg/mol and 275 kg/mol PEO at $r = 0.08$
 388 and $r = 0.14$. Data represent an average of multiple samples; error bars are
 389 excluded for clarity. (b) The slope, m_{Cl} , of the OCV versus $it^{0.5}$ plots at all salt
 390 concentrations in this study. Error bars represent the standard deviation of the data
 391 taken from multiple samples.
 392

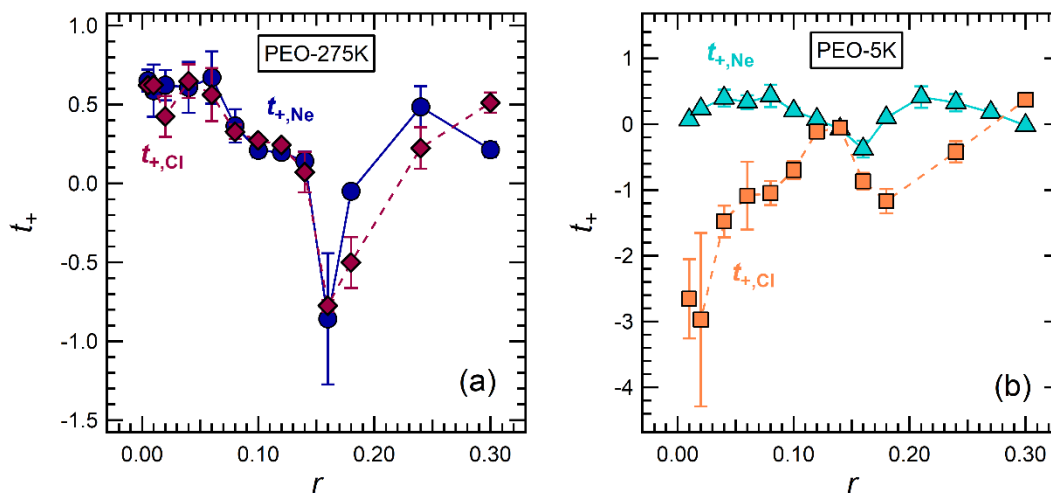
393 We calculate the transference number based on the current interrupt
 394 technique, $t_{+,Cl}$, using an equation derived by Ma et al.,¹

$$t_{+,Cl} = 1 - \frac{m_{Cl} c F (\pi D)^{\frac{1}{2}}}{4} \left(\frac{d \ln c}{dU} \right), \quad (0)$$

395 where m_{Cl} is given in Figure 4b, D is given in Figure 2b, and $d \ln(c)/dU$ is
 396 obtained by fitting the concentration cell data in Figure 2d in terms of $\ln(c)$,
 397 instead of $\ln(m)$. The dependence of m on c in PEO/LiTFSI is given in Table 1.

398 In Figure 5a, we compare our results for $t_{+,Ne}$ and $t_{+,Cl}$ in PEO-275K. The
 399 results from both approaches are in excellent agreement and fall within error
 400 at most concentrations in this study. The maximum value of $t_{+,Cl}$ is $0.65 \pm$
 401 0.06 ($r = 0.04$), while that of $t_{+,Ne}$ is 0.67 ± 0.17 ($r = 0.06$). The minimum

value of $t_{+,Cl}$ is -0.78 ± 0.30 ($r = 0.16$), while that of $t_{+,Ne}$ is -0.86 ± 0.42 ($r = 0.16$). The agreement observed in Figure 5a is noteworthy given the complexity of the dependence of t_+ on r . The comparison of $t_{+,Ne}$ and $t_{+,Cl}$ in PEO-5K electrolytes is given in Figure 5b. Here we observe significant disagreement between these two parameters, particularly at low salt concentrations. The sign of $t_{+,Cl}$ is negative at all values of r with the exception of $r = 0.3$, whereas the sign of $t_{+,Ne}$ is negative only at $r = 0.14$, 0.16, and 0.3. The minimum value of $t_{+,Cl}$ is -3.0 ± 1.3 ($r = 0.02$), while that of $t_{+,Ne}$ is -0.38 ± 0.13 ($r = 0.16$). The reason for this disagreement is an interesting, open question. In theory, both approaches should yield the same results. However, our results show that in some instances experimental factors may lead to a discrepancy between $t_{+,Ne}$ and $t_{+,Cl}$.



414

Figure 5. Comparison between different transference number measurements ($t_{+,Ne}$ and $t_{+,Cl}$) for **(a)** 275 kg/mol and **(b)** 5 kg/mol PEO electrolytes as a function of LiTFSI salt concentration at 90°C.

418

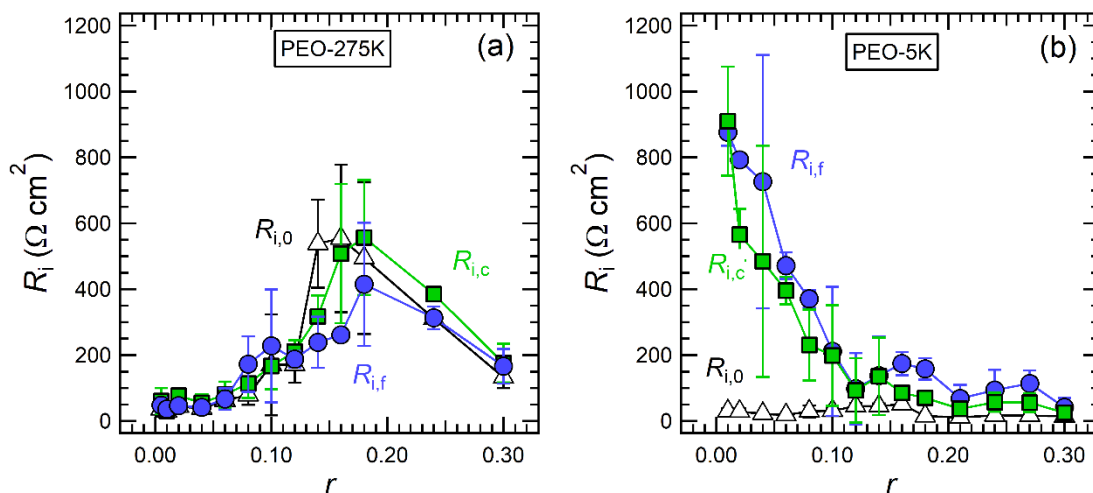
419 We posit that the discrepancy in Figure 5b arises due to differences in
420the electrode-electrolyte interfaces formed in our lithium-polymer-lithium
421cells. At the beginning of our experiments, cells were cycled 5 times using a
422constant current density of 0.02 mA/cm²; we refer to these as conditioning
423cycles. Our objective was to complete the formation of stable solid
424electrolyte interface (SEI) layers prior to making electrochemical
425measurements (D , $t_{+,ss}$, and m_{Cl}). To evaluate the nature of the SEI layers, we
426perform ac impedance spectroscopy on our lithium-polymer-lithium cells
427over the course of our experiments. Examples of these measurements are
428shown in Figure 1. The impedance data exhibited the standard signatures
429seen in symmetric cells with non-blocking electrodes: a bulk resistance, R_b ,
430reflecting the resistance of ion transport in the polymer electrolyte, and an
431interfacial resistance, R_i , reflecting the resistance of charge transfer at the
432polymer-lithium interface. The values of R_b were independent of time and
433consistent with those expected based on our ac impedance measurements
434using blocking electrodes (Figure 2a). In contrast, R_i showed a significant
435dependence on time and salt concentration in some cases. Further analysis
436of R_i provides insight into the disagreement observed between $t_{+,Ne}$ and $t_{+,Cl}$
437in Figure 5b.

438 Measurements of interfacial resistance obtained initially, $R_{i,0}$, post
439conditioning cycles, $R_{i,c}$, and at the end of the experiments, $R_{i,f}$, are reported
440for PEO-275K (Figure 6a) and PEO-5K (Figure 6b). Note that $R_{i,0}$ is measured
441after annealing the cells for 4 hours at 90°C; thus, the system is expected to

442be thermally equilibrated. The dependence of interfacial resistance on salt
443concentration is clearly affected by polymer molecular weight. In PEO-275K,
444 $R_{i,0}$ is a strong non-monotonic function of r , reaching a maximum value of
44554 Ωcm^2 ($r = 0.16$). In contrast, in PEO-5K, $R_{i,0}$ is nearly independent of r ,
446reaching a maximum value of 51 Ωcm^2 ($r = 0.16$). The underpinnings of this
447observation are not well understood. In the case of PEO-275K, $R_{i,0}$, $R_{i,c}$, and $R_{i,f}$
448are within experimental error across the entire salt concentration window
449(Figure 6a). In the case of PEO-5K, only $R_{i,c}$ and $R_{i,f}$ are in agreement at all r ,
450both significantly greater than $R_{i,0}$ at low salt concentrations (Figure 6b). It is
451important to note that the agreement between $R_{i,c}$ and $R_{i,f}$ in Figure 6a and b
452demonstrates that the SEI layer has reached steady-state prior to the point
453where electrochemical measurements are being conducted for both PEO-5K
454and PEO-275K. To our knowledge, the data in Figure 5 represent the first
455report of the effect of salt concentration and polymer molecular weight on
456interfacial impedance.

457 Comparing $R_{i,0}$ and $R_{i,c}$ provides information about the evolution of the
458charge transfer resistance at the lithium-polymer interface over the course of
459the conditioning cycles. In PEO-275K, the charge transfer resistance is stable
460during the conditioning cycles, demonstrated by the fact that there is
461reasonable agreement between $R_{i,0}$ and $R_{i,c}$ in Figure 6a. In PEO-5K however,
462at many concentrations $R_{i,c}$ is significantly larger than $R_{i,0}$ indicating that the
463conditioning cycles lead to the formation of resistive electrode-electrolyte
464interfaces that impede charge transfer. The concentration of chain ends in

465 PEO-5K is significantly higher than that in PEO-275K. The formation of
 466 resistive layers in PEO-5K may be attributed to reactions between the end
 467 groups and Li metal; the reaction between -OH groups and Li metal is well-
 468 established.⁴² The increase in R_i during conditioning cycles in PEO-5K is most
 469 pronounced at low salt concentrations ($r < 0.12$). Perhaps, the presence of
 470 LiTFSI at high concentrations slows down the reaction between -OH groups
 471 and Li metal. We note that $r < 0.12$ is also the concentration range where
 472 the differences between $t_{+,Ne}$ and $t_{+,Cl}$ in PEO-5K are most significant (Figure
 473 5b). Further study is required to determine the influence of interface layers
 474 on the measurements of on $t_{+,Cl}$.

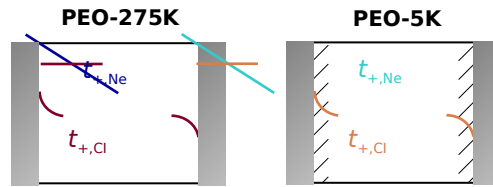


475

476 **Figure 6.** Interfacial resistance taken initially, $R_{i,0}$, after the conditioning cycles, $R_{i,c}$,
 477 and at the end of the experiment, $R_{i,f}$, from lithium-polymer-lithium cells with (a)
 478 275 kg/mol and (b) 5 kg/mol PEO with LiTFSI at 90°C.
 479

480 It is important to recognize that $t_{+,Ne}$ is derived from measurements of
 481 σ , $t_{+,SS}$, D and U (see eq. 7), whereas $t_{+,Cl}$ is derived from measurements of

m_{Cl} , D , and U (see eq. 9). Thus, discrepancies between these two approaches must originate from the effect of interface layers on σ , $t_{+,ss}$ and m_{Cl} ; D and U are used in both approaches and the effect of interface layers on these parameters cannot be the cause of the observed discrepancies. One notable difference is the length scales over which the measurements take place. As impedance spectroscopy and the steady-state current measurement are both techniques that probe the bulk of the electrolyte: σ is obtained by measuring the bulk resistance in a stainless-steel symmetric cell and $t_{+,ss}$ is obtained by polarizing a lithium-polymer-lithium cell for long periods of time generating concentration gradients that span the electrolyte. In contrast, the current interrupt technique is a more surface-sensitive technique, as m_{Cl} is obtained by polarizing a lithium-polymer-lithium cell for short periods of time generating concentration gradients that are localized near the electrode surface. In a perfect system where the electrolyte near the electrode surface is representative of the bulk electrolyte, $t_{+,Ne}$ and $t_{+,Cl}$ should be in agreement. This appears to be true for PEO-275K (Figure 5a). However, if the electrolyte near the electrode surface is more resistive than the bulk, as is suspected to be the case for PEO-5K, then there might be a discrepancy between $t_{+,Ne}$ and $t_{+,Cl}$ (Figure 5b). We believe $t_{+,Ne}$ to be the more robust approach for measuring the transference number of an electrolyte because the measurements required to determine this parameter are not sensitive functions of interfacial impedance.



*Resistive interface
layer*

504

505**Figure 7.** Representation of the length scales over which salt concentration
506gradients form in the electrolyte during our transference number measurements in
507lithium-polymer-lithium cells: $t_{+,Cl}$ probes the electrolyte near the electrode surface
508whereas $t_{+,Ne}$ probes the bulk electrolyte. This may explain the discrepancy between
509 $t_{+,Ne}$ and $t_{+,Cl}$ in PEO-5K (Figure 5b) where a resistive interfacial layer is thought to be
510present at the lithium surface.

511

512

513**Conclusions**

514 We have compared two different electrochemical approaches for
515 measuring the transference number of an electrolyte. A new approach
516 proposed by Balsara and Newman² ($t_{+,Ne}$) is compared against the well-
517 established approach by Ma et al.¹ ($t_{+,Cl}$) using two different electrolytes: 5
518 kg/mol PEO (PEO-5K) and 275 kg/mol PEO (PEO-275K) mixed with LiTFSI.
519 Both approaches are based on concentrated solution theory and require a
520 combination of electrochemical measurements. Many of the measurements
521 involve symmetric cells with lithium electrodes.

522 The complex dependence of $t_{+,Ne}$ on salt concentration in PEO-5K and
523 PEO-275K is similar, both exhibiting two maxima at low and high salt
524 concentrations, and a sharp minimum at intermediate salt concentrations
525 where the value of $t_{+,Ne}$ is negative. For PEO-275K, $t_{+,Cl}$ and $t_{+,Ne}$ are within
526 error across most of the salt concentration window. In contrast, in PEO-5K
527 there is a substantial difference between the $t_{+,Cl}$ and $t_{+,Ne}$, especially at low
528 salt concentrations. We attribute this to the fact that the parameters
529 measured to obtain $t_{+,Cl}$ are sensitive to the nature of the lithium electrode-
530 electrolyte interfaces. In contrast, the parameters measured to obtain $t_{+,Ne}$
531 are insensitive to the nature of the lithium electrode-electrolyte interfaces.
532 Our work thus suggests that $t_{+,Ne}$ is a more robust measure of the
533 transference number.

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544**Notes**

545The authors declare no competing financial interest.

546

547List of Symbols

PEO	polyethylene oxide
LiTFSI	lithium bis(trifluoromethanesulfonyl) imide
THF	tetrahydrofuran
OCV	open circuit voltage (mV)
σ	ionic conductivity (S/cm)
D	salt diffusion coefficient (cm ² /s)
t_+	cation transference number
U	potential of a concentration cell (mV)
$t_{+,SS}$	transference number obtained using stead-state current method
$t_{+,Ne}$	
$t_{+,Cl}$	transference number obtained by the approach of Balsara and Newman ²
r	
ρ	transference number obtained by the approach of Ma et al. ²
c	molar ratio of lithium ions to ether oxygens, $r = [Li^+]/[O]$
m	density (g/L)
M_{EO}	salt molarity (mol/L)
R_b	salt molality (mol/kg)
$R_{b,0}$	molar mass of the ethylene oxide repeat unit (44.05 g/mol)
$R_{b,SS}$	bulk resistance (Ω cm ²)
R_i	initial bulk resistance (Ω cm ²)
$R_{i,0}$	bulk resistance at steady-state (Ω cm ²)
$R_{i,SS}$	interfacial resistance (Ω cm ²)
L	initial interfacial resistance (Ω cm ²)
a	interfacial resistance at steady-state (Ω cm ²)
ΔV	thickness of the electrolyte (μ m)
i_Ω	area of electrolyte (cm ²)
i_{ss}	applied potential (mV)
t	initial current density calculated according to Ohm's law (mA/cm ²)
i	
m_{Cl}	steady-state current (mA/cm ²)
r_{ref}	time (h)
$1+d\ln\gamma_{\pm}/d\ln m$	current density
$\gamma_{\pm}$	slope of the OCV versus $it^{0.5}$ data (mV cm ² /mA s ^{0.5})
z_+, z_-	reference concentration used in concentration cells
v_+, v_-	thermodynamic factor
v	mean molal activity coefficient of the salt
F	charge number of cation and anion
R	the number of cations and anions into which the salt dissociates
T	dissociates
$R_{i,c}$	total number of ions into which the salt dissociates
$R_{i,f}$	Faraday's constant (96485 C/mol)
	gas constant (J/mol K)
	temperature (K)

548

interfacial resistance post conditioning cycles ($\Omega \text{ cm}^2$)
interfacial resistance at the end of the experiments ($\Omega \text{ cm}^2$)

549References

5501. Y. Ma et al., *J. Electrochem. Soc.*, **142**, 1859 (1995)
551<http://jes.ecsdl.org/cgi/doi/10.1149/1.2044206>.
5522. N. P. Balsara and J. Newman, *J. Electrochem. Soc.*, **162**, A2720–A2722 (2015)
553<http://jes.ecsdl.org/content/162/14/A2720.full>.
5543. M. B. Armand, J. M. Chabagno, and M. J. Duclot, in *Fast Ion Transport in Solids*,
555eds. Vashishta, P.M., Mundy, J.N., and Shenoy, G.K., p. 131–136, North-Holland
556(1979).
5574. M. ARMAND, *Solid State Ionics*, **9–10**, 745–754 (1983)
558<http://www.sciencedirect.com/science/article/pii/0167273883900838>.
5595. W. H. Meyer, *Adv. Mater.*, **10**, 439–448 (1998)
560[http://doi.wiley.com/10.1002/%28SICI%291521-](http://doi.wiley.com/10.1002/%28SICI%291521-4095%28199804%2910%3A6%3C439%3A%3AAID-ADMA439%3E3.0.CO%3B2-I)
5614095%28199804%2910%3A6%3C439%3A%3AAID-ADMA439%3E3.0.CO%3B2-I.
5626. B. Scrosati and C. A. Vincent, *MRS Bull.*, **25**, 28–30 (2011).
5637. J. Newman and K. E. Thomas-Alyea, *Electrochemical Systems*, third., John Wiley &
564Sons, (2004).
5658. J. W. Hittorf, *Ann. der Phys. und Chemie*, **160**, 214–220 (1851)
566<http://doi.wiley.com/10.1002/andp.18511601004>.
5679. M. Spiro, in, p. 92–114 (1989) [http://pubs.acs.org/doi/abs/10.1021/bk-1989-](http://pubs.acs.org/doi/abs/10.1021/bk-1989-5680390.ch007)
5680390.ch007.
56910. C. Tubandt and H. Reinhold, *Zeitschrift für Anorg. und Allg. Chemie*, **160**, 222–
570236 (1927) <http://doi.wiley.com/10.1002/zaac.19271600122>.
57111. L. G. Longworth, *J. Am. Chem. Soc.*, **65**, 1755–1765 (1943).
57212. P. B. Taylor, *J. Phys. Chem.*, **31**, 1478–1500 (1926)
573<http://pubs.acs.org/doi/abs/10.1021/j150280a002>.
57413. M. Holz, *Chem. Soc. Rev.*, **23**, 165 (1994) [http://xlink.rsc.org/?](http://xlink.rsc.org/?DOI=cs9942300165)
575DOI=cs9942300165.
57614. P. Ravn Sørensen and T. Jacobsen, *Electrochim. Acta*, **27**, 1671–1675 (1982)
577<https://www.sciencedirect.com/science/article/pii/001346868280162X>.
57815. R. Pollard, *J. Electrochem. Soc.*, **136**, 3734–3748 (1989)
579<http://jes.ecsdl.org/content/136/12/3734.abstract>.
58016. W. S. Price, *Concepts Magn. Reson.*, **9**, 299–336 (1997)
581[http://doi.wiley.com/10.1002/%28SICI%291099-](http://doi.wiley.com/10.1002/%28SICI%291099-2053%281997%299%3A5%3C299%3A%3AAID-CMR2%3E3.0.CO%3B2-U)
5820534%281997%299%3A5%3C299%3A%3AAID-CMR2%3E3.0.CO%3B2-U.
58317. C. Capiglia et al., *J. Power Sources*, **81**, 859–862 (1999).
58418. P. G. Bruce and C. A. Vincent, *J. Electroanal. Chem. Interfacial Electrochem.*,
585**225**, 1–17 (1987)
586<http://www.sciencedirect.com/science/article/pii/0022072887800013>.

58719. J. Evans, C. A. Vincent, and P. G. Bruce, *Polymer (Guildf.)*, **28**, 2324–2328 (1987)
588<http://www.sciencedirect.com/science/article/pii/0032386187903946>.

58920. M. Doyle and J. Newman, *J. Electrochem. Soc.*, **142**, 3465 (1995)
590<http://jes.ecsdl.org/cgi/doi/10.1149/1.2050005>.

59121. D. M. Pesko et al., *J. Electrochem. Soc.*, **164**, E3569–E3575 (2017)
592<http://jes.ecsdl.org/lookup/doi/10.1149/2.0581711jes>.

59322. M. M. Doeff, P. Georèn, J. Qiao, J. Kerr, and L. C. De Jonghe, *J. Electrochem. Soc.*, **594146**, 2024 (1999) <http://jes.ecsdl.org/cgi/doi/10.1149/1.1391885>.

59523. A. Ferry, M. M. Doeff, and L. C. De Jonghe, *J. Electrochem. Soc.*, **145**, 1586
596(1998) <http://jes.ecsdl.org/cgi/doi/10.1149/1.1838522>.

59724. A. Ferry, M. M. Doeff, and L. C. Dejonghe, *Electrochim. Acta*, **43**, 1387–1393
598(1998).

59925. L. O. Valøen and J. N. Reimers, *J. Electrochem. Soc.*, **152**, A882 (2005)
600<http://jes.ecsdl.org/cgi/doi/10.1149/1.1872737>.

60126. S. Zugmann et al., *Electrochim. Acta*, **56**, 3926–3933 (2011).

60227. L. Edman, M. M. Doeff, A. Ferry, J. Kerr, and L. C. De Jonghe, *J. Phys. Chem. B*,
603**104**, 3476–3480 (2000) <http://dx.doi.org/10.1021/jp993897z>.

60428. M. Chintapalli et al., *Macromolecules*, **49**, 3508–3515 (2016) <http://pubs.acs.org/doi/abs/10.1021/acs.macromol.6b00412>.

60629. A. A. Teran, M. H. Tang, S. A. Mullin, and N. P. Balsara, *Solid State Ionics*, **203**,
60718–21 (2011).

60830. S. Lascaud et al., *Macromolecules*, **27**, 7469–7477 (1994).

60931. D. M. Pesko et al., *Macromolecules*, **49**, 5244–5255 (2016)
610<http://pubs.acs.org/doi/abs/10.1021/acs.macromol.6b00851>.

61132. D. M. Pesko et al., *Solid State Ionics*, **289**, 118–124 (2016)
612<http://www.sciencedirect.com/science/article/pii/S0167273815300837>.

61333. Q. Zheng et al., *Macromolecules*, **51**, 2847–2858 (2018).

61434. D. Devaux, R. Bouchet, D. Glé, and R. Denoyel, *Solid State Ionics*, **227**, 119–127
615(2012).

61635. K. Pożyczka, M. Marzantowicz, J. R. Dygas, and F. Krok, *Electrochim. Acta*, **227**,
617127–135 (2017)
618<http://www.sciencedirect.com/science/article/pii/S0013468616327311>.

61936. S. A. Mullin, G. M. Stone, A. Panday, and N. P. Balsara, *J. Electrochem. Soc.*, **158**,
620A619 (2011) <http://jes.ecsdl.org/content/158/6/A619.full>.

62137. I. Villaluenga et al., *J. Electrochem. Soc.* (2018).

62238. O. Borodin and G. D. Smith, *Macromolecules*, **39**, 1620–1629 (2006)
623<http://dx.doi.org/10.1021/ma052277v>.

62439. M. A. Webb et al., *ACS Cent. Sci.*, **1**, 198–205 (2015)

625<http://dx.doi.org/10.1021/acscentsci.5b00195>.

62640. I. Rey, J. C. Lassègues, J. Grondin, and L. Servant, *Electrochim. Acta*, **43**, 1505–1510 (1998) <http://linkinghub.elsevier.com/retrieve/pii/S0013468697100925>.

62841. L. Edman, *J. Phys. Chem. B*, **104**, 7254–7258 (2000).

62942. I. E. Kelly, J. R. Owen, and B. C. H. Steele, *J. Power Sources*, **14**, 13–21 (1985)
630<https://www.sciencedirect.com/science/article/pii/0378775385880046>.

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