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Interfacial Effects on Transport Coefficient Measurements in Li-ion Battery Electrolytes

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Development of Li⁺-containing electrolytes with improved transport properties requires reliable, reproducible, and ideally low volume techniques to rigorously understand ion-transport with varying composition. Precisely measuring the complete set of transport coefficients in liquid electrolytes under battery-relevant operating conditions is difficult and the reliability of these methods are sparsely described in electrolyte transport literature. In this work, we apply a potentiostatic polarization-based transport characterization approach typically used for polymer electrolytes to liquid electrolyte systems in an attempt to fully measure all transport coefficients (conductivity, total salt diffusion coefficient, thermodynamic factor and transference number) for the model system of LiPF₆ in an ethylene carbonate—ethyl methyl carbonate (EC:EMC) mixture. Using systematic timescale and statistical analyses, we find that transport coefficients measured using potentiostatic polarization of Li-Li symmetric cells exhibit strong correlation to Li electrode interfacial resistance, indicating that such methods are probing both bulk and interfacial phenomena. This reveals a major roadblock in characterizing electrolyte systems where the interfacial resistance is significantly larger than ohmic electrolyte resistance. As a result, we find that methods that rely on potentiostatic Li metal stripping/plating do not readily result in reliable liquid electrolyte transport coefficients, unlike similar methods for solid polymer electrolytes, where interfacial resistances are typically smaller than electrolyte resistances at the elevated temperatures typically of interest for such electrolytes.

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Over the last decade, advances in Li-ion battery (LIB) technology have enabled significant development of portable electronics, electric vehicles (EVs), and distributed energy storage. However, despite their ubiquity, improvements in Li-ion battery performance are still sought, with enhanced charging rates, increased energy density, and reduced safety risks all being essential topics of ongoing research.¹ Current state-of-the-art Li-ion batteries make use of dissociated binary lithium salts, typically lithium hexafluorophosphate (LiPF₆) in a blend of liquid carbonate solvents. Ionic conductivity in these systems is largely driven by the movement of the anion rather than the electrochemically active Li⁺ ion due primarily to lithium's bulky solvation shell. The resulting ionic concentration gradients in the electrolyte extend into the porous electrode and generate overpotentials that limit the rate and efficiency of charging, limit material utilization, and increase the risk of short-circuiting through Li plating and dendrite growth.^{1–3} The severity of these concentration gradients is directly influenced by the Li⁺ transference number (*t*₊), which describes the ratio of current carried by the electrochemically active Li⁺ ion to the total current passed.

In general, rigorously measuring the complete set of transport properties of concentrated liquid electrolytes under battery-relevant operating conditions is difficult and until recently sparsely explored in non-aqueous liquid electrolyte literature. Nyman et al. fully characterized a blend of LiPF₆ in an ethylene carbonate (EC)—ethyl methyl carbonate (EMC) blend using a combination of concentration cells and galvanostatic polarization, where transport coefficients were extracted using a finite element optimization routine.⁴ While this procedure is impressive, it does not guarantee a global solution for each independent transport property, and the authors noted it yielded more precise determination of diffusion coefficients than transference numbers. More recently, the Gasteiger group has fully characterized LiPF₆ in carbonate blends across a wide range of temperatures using concentration cells, restricted diffusion, and the current interrupt method pioneered by Ma and

Newman.^{5–7} Their data is in reasonable agreement with findings from Nyman at room temperature, however deviates significantly at low temperatures from the transference numbers predicted from solvation-based chemical physics models.⁸ In 2020, the Monroe group fully characterized transport of LiPF₆ in propylene carbonate and ethyl methyl carbonate using a combination of Hittorf cells, concentration cells, and restricted diffusion.^{9,10}

An alternative method that has been widely used to characterize electrolyte transport is the Balsara-Newman method which combines conductivity, restricted diffusion, potentiostatic polarization, and concentration cells to fully and rigorously characterize electrolyte transport.¹¹ One of the essential experiments used in the Balsara-Newman method is a Bruce-Vincent type polarization measurement of the current ratio which in the limit of an ideal solution is equal to the transference number.^{12,13} This method has been widely used for polymer systems^{13,14} but only limited data exists for liquid electrolytes,^{15,16} and even then not traditional Li-ion battery carbonate electrolytes which suffer from additional Li metal-related complications including significant Li metal corrosion,¹⁷ large and unstable interfacial impedance, and complexities related to compounding error from inter-related measurements. These limitations are not unique to the Balsara-Newman method, and are present in most lithium metal-liquid electrolyte polarization measurements. Our goal is to evaluate the transport properties of a common Li-ion battery electrolyte using lithium polarization techniques, specifically the Balsara-Newman method, and identify any relevant shortcomings that liquid electrolytes may possess that limits the reliability of such analysis.

Herein, using techniques amenable to small electrolyte volumes, we rigorously measured liquid electrolyte transport properties, including the ideal solution Bruce-Vincent transference number (also known as the current ratio¹³), total salt diffusion coefficient, thermodynamic factor, and the true transference number under battery-relevant conditions using Newman's concentrated solution theory framework.^{11,15,18} In order to validate methodologies that rely on polarization techniques, we use the well-studied liquid electrolyte system of LiPF₆ in an 3:7 by weight EC:EMC blend. We begin with a discussion of the governing equations used to relate transport

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properties to accessible parameters during electrochemical measurements e.g. current density, open circuit voltage, cell resistances. Next, we present measurements for LiPF₆ in EC:EMC over a range of concentrations along with a rigorous statistical analysis of the transport coefficients obtained via these measurements. We then discuss the discrepancy of these values from those reported in the literature, the influence of data-fitting methodology, and highlight the impact of parasitic corrosion reactions and large interfacial resistances at the lithium electrode on electrochemical transport measurements. We support these experimental findings with COMSOL Multiphysics modeling studies. This work reveals a major roadblock in characterizing non-aqueous liquid electrolyte systems that form high impedance Li metal interfaces, as is common for most liquid electrolytes, because the high interfacial impedance severely hinders the reliability of polarization methods during Li metal stripping/plating.

Theoretical Background for the Electrochemical Measurement of Transport Properties

Using the framework of non-equilibrium thermodynamics and entropy production we can derive the governing equations for transport in electrochemical systems.^{18,19} The electrochemical potential of a species ($\hat{\mu}_i$) can be split into electrical and chemical potential contributions according to

$$\hat{\mu}_i = \mu_i^0 + RT \ln(C_i f_i) + z_i F \phi_{el} \quad [1]$$

where μ_i^0 is the standard state chemical potential of species i , R is the gas constant, T is the temperature, C_i , f_i , z_i are the concentration, activity coefficient, and formal charge respectively on species i , F is Faraday's constant, and ϕ_{el} is the potential in the electrolyte. Analyzing fluxes in response to electrochemical potential gradients in the electrolyte we can relate current (i) to the gradient in potential with respect to a lithium metal reference electrode according to

$$i = -\kappa \nabla \phi_{el} + \frac{\nu}{z_+ \nu_+} \frac{RT}{F} \kappa (1 - t_+) \left[\frac{\partial \ln f_{\pm}}{\partial \ln C} + 1 \right] \nabla \ln C \quad [2]$$

where ν is the overall salt stoichiometry, ν_+ is the cation stoichiometry, κ is the solution conductivity, t_+ is the cation transference number, $f_{\pm}$ is the mean molar salt activity coefficient, and C is the salt concentration.¹⁸ The term $\left[\frac{\partial \ln f_{\pm}}{\partial \ln C} + 1 \right]$ is often referred to as the thermodynamic factor (TDF) and allows interconversion between gradients in chemical potential and concentration. Writing mass conservation equations for the electrolyte we can relate the cation reaction rate (r_+) to convective, diffusive and migratory fluxes according to

$$\frac{r_+}{\nu_+} = \frac{\partial C}{\partial t} + \nabla \cdot \left(C \mathbf{v} - D_{\pm} \nabla C + \frac{i}{\nu_+ z_+ F} t_+ \right) \quad [3]$$

where $D_{\pm}$ is the total salt diffusion coefficient with reference to concentration, and $\mathbf{v}$ is the electrolyte velocity. By invoking conservation of charge and assuming constant charge density we can write from the theory of electromagnetism that $\nabla \cdot \mathbf{i} = 0$. Assuming no reaction in the bulk electrolyte, and no convection due to suppression from a microporous separator we can simplify Eq. 3 to

$$\frac{\partial C}{\partial t} - \nabla \cdot (D_{\pm} \nabla C) + \frac{i}{\nu_+ z_+ F} \nabla t_+ = 0 \quad [4]$$

Because ion concentration is difficult to measure in situ under standard battery operating conditions, it is convenient to use Eq. 2 to

relate changes in concentrations across the cell (ΔC) to the potential drop across the cell. Under conditions where the electrode radius (r) is significantly larger than the separation distance between electrodes (1) such that $r_{\text{electrode}}/l \gg 1$, we can assume 1-dimensional transport and express the potential drop according to

$$\Delta \phi_{el} = \int_{x_c}^{x_a} \left(\frac{\nu}{z_+ \nu_+} \frac{RT}{F} (1 - t_+) \left[\frac{\partial \ln f_{\pm}}{\partial \ln C} + 1 \right] \frac{\partial \ln C}{\partial x} - \frac{i}{\kappa} \right) dx \quad [5]$$

where subscripts "a" and "c" denote the anode and cathode respectively. Typically, integration of Eq. 5 requires the assumption that concentration perturbations across the cell (δC) are sufficiently small compared to the bulk concentration, C , such that the transport properties can be reasonably assumed to locally have zero order dependence on concentration, i.e. $\kappa(C_0 + \delta C) \approx \kappa(C_0)$, $t_+(C_0 + \delta C) \approx t_+(C_0)$, and $f_{\pm}(C_0 + \delta C) \approx f_{\pm}(C_0)$. Under special circumstances, such as open-circuit relaxation or steady state operation, $\Delta \phi_{el}$ can be directly related to the cell voltage (ΔV) measured across the electrodes.

Restricted diffusion measurements.—The restricted diffusion techniques - originally pioneered by Harned and French for dilute electrolytes and later expanded by Newman to concentrated solutions - is used to measure diffusion coefficients by monitoring concentration gradient relaxations after polarization inside the bulk electrolyte.^{20,21} Polarization (either galvanostatic or potentiostatic) is used to induce a concentration gradient within the electrolyte. Upon current interruption the concentration profile relaxation can be described using Eq. 4, which can be further reduced to

$$\frac{\partial C}{\partial t} + \nabla \cdot (-D_{\pm} \nabla C) = 0 \quad [6]$$

If we assume that $\nabla \cdot D_{\pm} = 0$, Eq. 6 reduces to

$$\frac{\partial C}{\partial t} - D_{\pm}(C_0) \nabla^2 C = 0 \quad [7]$$

This assumption is valid only if variations in the concentration within the electrolyte are small compared to the bulk electrolyte concentration such that $D_{\pm}(C_0 + \delta C) \approx D_{\pm}(C_0)$. This boundary value problem can be solved using 2 Neumann no-flux boundary conditions at the electrodes such that $\nabla C = 0$ at the anode and cathode. The solution to this boundary value problem in 1-dimension takes the form of

$$C(t, x) = C_0 + \sum_{n=1}^{\infty} A_n \exp\left(\frac{-n^2 \pi^2 D_{\pm}(C_0) t}{l^2}\right) \cos\left(\frac{n \pi x}{l}\right) \quad [8]$$

where the spectral coefficients A_n are dependent on the initial conditions and can be solved for using the orthogonality of cosines. Evaluating the concentration drop across the cell we obtain

$$\Delta C(t) = -2C_0 \sum_{n=1}^{\infty} A_{2n-1} \exp\left(\frac{-(2n-1)^2 \pi^2 D_{\pm}(C_0) t}{l^2}\right) \quad [9]$$

The concentration profile characteristic decay time can be expressed as

$$\tau_{\text{diff}} = \frac{1}{\pi^2} \frac{l^2}{D_{\pm}(C_0)} \quad [10]$$

To relate the concentration profile to the open circuit voltage (OCV) we can invoke Eq. 5, again assuming that concentration variations are sufficiently small such that transport properties are not concentration dependent.²²

$$\Delta\phi_{el} = \frac{\nu}{z_+ \nu_+} \frac{RT}{F} (1 - t_+(C_0)) \left[\frac{\partial \ln f_{\pm}}{\partial \ln C}(C_0) + 1 \right] \ln \frac{C_a}{C_c} \quad [11]$$

For small concentration drops and point symmetric profiles, the logarithmic term can be approximated using a Taylor series expansion²³ yielding

$$\Delta\phi_{el} = \frac{\nu}{z_+ \nu_+} \frac{RT}{F} (1 - t_+(C_0)) \left[\frac{\partial \ln f_{\pm}}{\partial \ln C}(C_0) + 1 \right] \frac{\Delta C}{C_0} \quad [12]$$

Under open circuit conditions, there are no surface or kinetic overpotentials (i.e., $\Delta\phi_{el} = \Delta V$), we can directly relate the open circuit potential, $U(t)$, to the potential drop across the electrolyte as expressed in Eq. 12. Plugging Eq. 9 into Eq. 12 we now obtain the relationship between $U(t)$ and $D_{\pm}$.

$$U(t) = -\frac{2\nu}{z_+ \nu_+} \frac{RT}{F} (1 - t_+(C_0)) \left[\frac{\partial \ln f_{\pm}}{\partial \ln C}(C_0) + 1 \right] \sum_{n=1}^{\infty} A_{2n-1} \exp\left(\frac{-(2n-1)^2 \pi^2 D_{\pm}(C_0)}{l^2} t\right) \quad [13]$$

At long times, of which an estimate will be provided below, we can neglect the influence of higher order terms yielding,

$$U(t) \approx \alpha \exp\left(\frac{-\pi^2 D_{\pm}(C_0)}{l^2} t\right) \quad [14]$$

where all terms in the exponential prefactor are constants and therefore lumped together in α . Because the diffusion coefficient is measured inside a porous separator, it represents the effective diffusion coefficient. In order to convert the effective diffusion coefficient into an electrolyte phase diffusion coefficient, we simply multiply by the separator tortuosity (τ_s) such that

$$D_{\pm}^{el} = \tau_s D_{\pm}^{eff} \quad [15]$$

Current ratio from polarization measurements.—Potentiostatic polarization techniques were built upon the work by Bruce and Vincent for measuring the transference number in polymer electrolyte systems assumed to follow ideal solution behavior.^{12,23} This measurement technique was later extended for use in concentrated non-ideal electrolytes by Balsara and Newman.¹¹ By comparing the resistance of the electrolyte under the condition of no concentration gradients to the resistance of the electrolyte when concentration gradients are fully developed, we can obtain information about the selective transport of lithium ions. In the absence of any concentration gradients, such as just when current starts to flow upon polarization, Ohm's law can be invoked to relate the potential drop in the electrolyte to the ohmic current (I_{Ω}) according to

$$\Delta\phi_{el,0} = \frac{I_{\Omega} l}{\kappa} \quad [16]$$

Ohm's Law is no longer valid as concentration gradients begin to form and we must consider both diffusive and migratory fluxes. The flux of the anion, J_- , can be expressed in terms of convection, diffusion and migration as

$$J_- = C v - D_{\pm} \nabla C + \frac{i}{\nu_- z_- F} (1 - t_+) \quad [17]$$

Because anions do not participate in any electrode reaction in a lithium-ion system, as the concentration profile reaches a steady state, there is no net anion flux. Assuming no net convection, the anionic diffusive flux is equal and opposite to the anionic migratory flux.

$$D_{\pm} \nabla C = \frac{i}{\nu_- z_- F} (1 - t_+) \quad [18]$$

Rearranging and again assuming that concentration variations in the electrolyte are one dimensional and small relative to the bulk concentration such that electrolyte properties are concentration independent, we can integrate Eq. 18 across the length of the cell yielding

$$\begin{aligned} \Delta C &= \frac{I_{ss} l}{\nu_- z_- F D_{\pm}(C_0)} (1 - t_+(C_0)) \\ &= -\frac{I_{ss} l}{\nu_+ z_+ F D_{\pm}(C_0)} (1 - t_+(C_0)) \end{aligned} \quad [19]$$

where I_{ss} is the current at steady state. As in our analysis for Eq. 12, we can use a Taylor series approximation to write

$$\ln \frac{C_a}{C_c} \approx \frac{\Delta C}{C_0} = \frac{I_{ss} l}{C_0 \nu_+ z_+ F D_{\pm}(C_0)} (1 - t_+(C_0)) \quad [20]$$

To find the potential drop in the electrolyte, we can use Eq. 5 again assuming constant transport properties. Upon replacing the concentration at the cathode and anode with the expression for concentration difference found in Eq. 20 we obtain

$$\Delta\phi_{el,ss} = \frac{I_{ss} l}{\kappa(C_0)} + \frac{\nu}{z_+ \nu_+} \frac{RT I_{ss} l}{F^2 C_0 D_{\pm}(C_0)} (1 - t_+(C_0))^2 \left[\frac{\partial \ln f_{\pm}}{\partial \ln C}(C_0) + 1 \right] \quad [21]$$

Since $\Delta\phi_{el,ss}$ is not directly accessible experimentally during the polarization experiment, we must relate it to the cell voltage such that $\Delta V = \Delta\phi_{el} + I R_{eff}$ where R_{eff} is an effective resistance that captures the cathodic and anodic overpotentials at the electrodes due to SEI resistance. R_{eff} can be measured using impedance spectroscopy before and during polarization.¹² Writing the potential drop in the electrolyte in terms of ΔV and R_{eff} we obtain

$$\Delta\phi_{el,0} = \frac{I_{\Omega} l}{\kappa} = \Delta V - I_{\Omega} R_{eff,0} \quad [22]$$

and

$$\begin{aligned} \Delta\phi_{el,ss} &= \frac{I_{ss} l}{\kappa} + \frac{\nu}{z_+ \nu_+} \frac{RT I_{ss} l}{F^2 C_0 D_{\pm}(C_0)} (1 - t_+(C_0))^2 \left[\frac{\partial \ln f_{\pm}}{\partial \ln C}(C_0) + 1 \right] \\ &= \Delta V - I_{ss} R_{eff,ss} \end{aligned} \quad [23]$$

Now comparing the resistances due to the electrolyte in the absence and presence of concentration gradients we obtain the current ratio (ρ_+) which is equivalent in form to the Bruce-Vincent ideal solution transference number (t_+^{BV})

$$\begin{aligned} \rho_+ &= t_+^{BV} = \frac{\frac{I_{ss}}{\Delta\phi_{el,ss}}}{\frac{I_{\Omega}}{\Delta\phi_{el,0}}} = \frac{I_{ss} (\Delta V - I_{\Omega} R_{eff,0})}{I_{\Omega} (\Delta V - I_{ss} R_{eff,ss})} \\ &= \left[1 + \frac{\nu}{z_+ \nu_+} \frac{RT \kappa}{F^2 C_0 D_{\pm}(C_0)} (1 - t_+(C_0))^2 \left(\frac{\partial \ln f_{\pm}}{\partial \ln C}(C_0) + 1 \right) \right]^{-1} \end{aligned} \quad [24]$$

Here $R_{eff,0}$ is the interfacial resistance prior to polarization, $R_{eff,ss}$ is the interfacial resistance at steady state during polarization, and I_{Ω} is calculated by dividing the applied voltage by the total cell resistance measured by EIS before polarization. Thus one can calculate ρ_+ by

comparing the ohmic or initial current in a symmetric cell to the steady state current obtained upon applying a constant polarization potential after appropriately subtracting out potential drop within the SEI.^{12,13} As shown below, ρ_+ is important in the calculation of the thermodynamic factor (TDF) and transference number (t_+).

Concentration cells.—The change in open circuit potential with respect to the logarithm of concentration $\frac{\partial U}{\partial \ln C}$ can easily be obtained by manipulating Eq. 2 yielding

$$\frac{\partial U}{\partial \ln C} = \frac{\nu}{z_+ \nu_+} \frac{RT}{F} (1 - t_+) \left[\frac{\partial \ln f_{\pm}}{\partial \ln C} + 1 \right] \quad [25]$$

Equivalently, the TDF can be expressed in terms of mean molal salt activity coefficients ($\gamma_{\pm}$) and molality (m), such that the open circuit potential with respect to the logarithm of molality can be similarly expressed

$$\frac{\partial U}{\partial \ln m} = \frac{\nu}{z_+ \nu_+} \frac{RT}{F} (1 - t_+) \left[\frac{\partial \ln \gamma_{\pm}}{\partial \ln m} + 1 \right] \quad [26]$$

This quantity can then be used in combination with ρ_+ obtained from a polarization experiment to independently isolate the TDF from t_+ .

Isolating the transference number and thermodynamic factor.—Having obtained expressions that can be used to fit experimental data to extract our three transport properties and the thermodynamic factor (see Eqs. 14, 15, 16, 24, 26), we can isolate the transference number and thermodynamic factor.¹⁵ Plugging Eq. 26 into Eq. 24 and solving for the transference number in terms of measured quantities we obtain

$$t_+ = 1 - \frac{FD_{\pm}C\left(\frac{1}{\rho_+} - 1\right)}{\kappa \frac{\partial U}{\partial \ln m}} \quad [27]$$

Plugging Eq. 26 back into Eq. 27 we obtain the thermodynamic factor

$$\frac{\partial \ln \gamma_{\pm}}{\partial \ln m} + 1 = \frac{z_+ \nu_+}{\nu} \frac{\kappa \left(\frac{\partial U}{\partial \ln m} \right)^2}{RTD_{\pm}C\left(\frac{1}{\rho_+} - 1\right)} \quad [28]$$

Experimental

Materials.—Battery grade lithium hexafluorophosphate (LiPF₆), ethyl methyl carbonate (EMC), fluorinated ethylene carbonate (FEC), vinyl carbonate (VC), and ethylene carbonate (EC) were purchased from Gotion Inc. and directly transferred under inert atmosphere to an argon glove box (Vacuum Atmospheres) kept below 5 ppm water and oxygen. Electrolytes were prepared inside the glove box on a moles per kg solvent basis. All electrolyte concentrations were made using a 3:7 EC:EMC ratio by weight. In order to convert to per volume concentration, densities for each solution were obtained by weighing 100 μ l of each solution as dispensed by a positive displacement capillary pipette (Rainin). Each density measurement was performed in triplicate. Viscosity measurements were performed in triplicate in an electromagnetically spinning viscometer (EMS-1000s, Kyoto Electronics) spinning at 1000 rotations per minute at 30 °C. Metallic lithium (FMC Corp., 100 μ m) was mechanically brushed with a nylon brush prior to use in concentration cells and coin cells. Celgard 2500 (polypropylene, 55% porosity) was used as received as a microporous separator for coin cells.

Conductivity.—Solution conductivity (κ) was measured using a Mettler Toledo InLab 751-4 mm conductivity probe with blocking

platinum electrodes inside the glove box. The conductivity probe was calibrated using 84 μ S/cm, 1413 μ S/cm, and 12.88 mS/cm aqueous standards (Mettler Toledo) prior to bringing it inside the glove box. Samples were maintained at 30 °C using a dry block (Torrey Pines). Solution temperatures were verified using a temperature sensor inside the cell and were always within ± 0.5 °C of the set point. A 5% error is estimated for probe measurements based on replicate measurements. Conductivity within the porous separator was also measured against non-blocking lithium metal electrodes in coin cells using AC impedance spectroscopy on a Bio-Logic VMP3 potentiostat in the frequency range from 1 MHz to 100 mHz with a 5 mV AC amplitude. Impedance data was tested for linearity using a Kramers-Kronig analysis and fit to R-RQ equivalent circuit using the open-source Py-EIS package for Python.²⁴ Assignment of the electrolyte resistance was confirmed by varying the cell thickness by varying the number of porous separators used. The conductivity in the separator (κ_s) can thus be calculated according to

$$\kappa_s = \frac{l}{R_{hf}A} \quad [29]$$

where l is the separator thickness, R_{hf} is the high frequency resistance, and A is the geometric electrode area. Conductivity within the separator can be converted to a bulk electrolyte phase conductivity using the tortuosity (τ_s) and porosity (ϵ_s) of the Celgard 2500 separator according to

$$\kappa = \kappa_s \frac{\tau_s}{\epsilon_s} \quad [30]$$

For Celgard 2500 separators, a porosity value of 0.55 was used as specified by the manufacturer and a tortuosity value of 2.5 ± 0.2 was obtained from literature.²⁵

Concentration cells.—Concentration cells were constructed inside a custom fabricated low-volume glass U-cell with a P4 glass frit (Adams & Chittenden).¹⁵ Concentration cell measurements were performed inside the argon glove box with cell temperature maintained using a dry block with each U-cell equilibrated at 30 °C prior to electrolyte addition. For each measurement, one side of the U-cell contains 0.5 m LiPF₆ in EC:EMC as a reference electrolyte while the other side contains electrolyte of varying concentration. U-cells were constructed using 750 μ l of electrolyte added on each side of the glass frit before brushed lithium metal electrodes were immersed in the solution on each side. The open-circuit potential, $U(t)$, was recorded over the course of 1 h using a Bio-Logic VMP3-potentiostat with a 0.5 s sampling rate. Concentration cell measurements were constructed for 10 concentration combinations ranging from 0.03 m to 1.75 m with approximate logarithmic spacing.

Polarization experiments and restricted diffusion measurements.—Polarization experiments and restricted diffusion experiments were performed sequentially in the same lithium symmetric coin cells. 10 layers of 19mm disks of Celgard 2500 impregnated with electrolyte were sandwiched between 12.7 mm brushed lithium electrodes inside a CR2032 coin cell (cell components from MTI Corporation and Hohsen Corporation were both used). To ensure good wetting of the electrode and separator, 5 μ l of electrolyte was added in between each layer for a total added electrolyte volume of 55 μ l. Each electrode stack was finished with a 0.5 mm thick stainless steel spacer and wave spring before crimping. Three replicate cells were made for each concentration. Cells were run inside an environmental chamber (Thermotron Inc.) maintained at 30 °C. In order to ensure a stable solid-electrolyte interphase (SEI) is formed, each cell was preconditioned for 6 cycles of ± 20 μ A/cm² for 4 h per polarization.^{14,15} Impedance measurements were made after each polarization using the interfacial resistance to monitor the development of the SEI. After preconditioning, cells were allowed to

sit at open circuit voltage (OCV) for 1 h. A polarization potential (ΔV) was then applied for 60 min with current recorded every second. EIS spectra were collected every 20 min from 1 MHz to 100 mHz with a 5 mV AC amplitude overlaid. After 60 min of polarization the cells were allowed to relax at OCV, $U(t)$, for one hour with $U(t)$ recorded every 0.5 s. This procedure was then repeated with a reverse bias. For each cell at least 6 polarization and relaxation experiments were performed in the following order of applied voltage: 5 mV, -5 mV, 10 mV, -10 mV, 15 mV, -15 mV. All impedance data was tested for linearity using a Kramers-Kronig analysis prior to analysis. Spectra were truncated to a range of 100 kHz to 10 Hz and fit to R-RQ equivalent circuit using the open-source Py-EIS package for Python.²⁴ The current ratio was calculated according to Eq. 24. Diffusion coefficients were obtained by fitting the open-circuit voltage decay signal according to Eq. 14. Each average reported in the results and discussion is an average of 2 measurements per applied voltage on 3 replicate cells.

Coulombic efficiency.—Coulombic efficiency was measured in lithium || copper cells. Two layers of Celgard 2500 (19 mm diameter) soaked with 22.5 μ l of electrolyte were sandwiched between a Lithium metal (100 μ m, 1/2" diameter, brushed) and a copper foil (25 μ m, 1/2" diameter). Stacks were topped with a 0.5 mm thick spacer and wave spring and sealed in a CR2032 coin cell inside the inert glove box. Cells were tested at 30 °C and allowed to sit for 1 h at OCV prior to testing. Lithium plating and stripping was performed at 0.1 mAh/cm² for 1 mAh/cm². For stripping a 1 V cutoff potential was applied. All measurements were performed in triplicate.

Finite element transport modeling.—A 1-D Newman isothermal battery model was created for a lithium symmetric cell using the Batteries and Fuel Cells Module in COMSOL Multiphysics. Cell dimensions were made to match those in coin cells with two 0.1 mm thick lithium metal electrodes separated by a 250 μ m porous separator/electrolyte region. Tortuosity and porosity of the separator reflected that of Celgard 2500. Electrolyte properties for LiPF₆ in 3:7 EC:EMC as a function of concentration were used directly from the COMSOL Materials library which draws these values from Nyman et al. (2008).⁴ Electrode kinetics were modeled using a reference exchange current density of 10 A/m². In order to account for resistance due to the SEI a 184 Ω -cm² film resistance was added at each electrode/electrolyte interface. As shown in the results and discussion, this value reflects the average interfacial resistance at each electrode measured in our experimental coin-cells. Both the potentiostatic polarization and restricted diffusion experiments were simulated as described above.

Results and Discussion

Electrochemical characterization experiments were performed on LiPF₆ in 3:7 EC:EMC across concentrations ranging from 0.05 to 1.5 mol/kg. The density and viscosity of all compositions characterized are provided in Table I. Ionic conductivity values extracted from AC Impedance Spectroscopy with non-blocking lithium according to Eq. 29 are in good agreement with those obtained from conductivity probe measurements with blocking platinum electrodes (see Fig. 1). The non-monotonic trend in conductivity

Figure 1. Conductivity (mS/cm) for LiPF₆ in 3:7 EC:EMC at 30°C as measured with platinum (blocking) and lithium (non-blocking) electrodes.

across the range of concentrations can be explained by a mix of increasing viscosity and increased ion-pairing at higher electrolyte concentrations. At the highest measured salt concentrations we observe a deviation between the conductivity measured with blocking and non-blocking electrodes, with lithium metal electrodes resulting in a 30% lower ionic conductivity for a 1.5 mol/kg electrolyte. We believe that this difference can be attributed to concentration changes in the electrolyte during SEI formation cycles performed prior to measuring conductivity in our electrolyte-lean lithium metal cells. Across all concentrations, ionic conductivity was in good agreement with values reported in the literature.^{4,5}

In Fig. 2a we plot the OCV across a lithium concentration cell composed of an electrolyte of reported concentration in one chamber, and an electrolyte with a reference concentration of 0.5 mol/kg in the other. We see that at higher salt concentrations, the measured cell potential deviates significantly from the Nernst potential calculated assuming a constant activity coefficient of 1. Ueno and Tatara et al. attribute this steep increase in potential away from the Nernst potential to depletion of free solvent molecules as almost all solvent molecules become part of the Li⁺ solvation shell.²⁶ Tatara et al. demonstrated there is negligible free solvent LiPF₆ in EC:EMC electrolytes for concentrations above 2.4 M.²⁷ Fitting the experimental data to a 3rd order polynomial and taking the derivative, we obtain $\frac{\partial U}{\partial \ln m}$ which is equivalent to the product of the anion transference number and the thermodynamic factor as noted in Eq. 26. We note the obtained value of $\frac{\partial U}{\partial \ln m}$ can be highly dependent on fitting if insufficient data points are taken and that while a 3rd order polynomial fit is often used in the literature there is

Table I. Properties of LiPF₆ in 3:7 wt:wt EC:EMC electrolyte compositions examined.

Molality (mol kg ⁻¹)	wt.% salt	Density (g L ⁻¹)	Molality (mol L ⁻¹)	Viscosity (mPa·s)
0.051	0.8	1040.6 ± 1.9	0.053	1.21 ± 0.02
0.101	1.5	1054.6 ± 2.5	0.105	1.33 ± 0.02
0.500	7.1	1143.3 ± 4.6	0.531	1.97 ± 0.03
1.001	13.2	1200.4 ± 2.3	1.043	3.04 ± 0.02
1.500	18.6	1248.3 ± 3.5	1.525	7.03 ± 0.01

Figure 2. Concentration cell experiments. (a) Experimentally obtained open-circuit voltage (mV) and theoretical Nernst potentials vs $\ln(m)$ (m in mol/kg) for concentration cells with a reference electrolyte concentration of 0.5 mol/kg. (b) Derivative of open circuit voltage with respect to natural logarithm in molality as calculated from a 3rd order polynomial fit of concentration cell data.

no physical reason for the dependence to be 3rd order in nature. We thus caution that it is prudent to take sufficient data points with logarithmic spacing such that $\frac{\partial U}{\partial \ln m}$ converges within $\sim 10\%$ whether a finite difference approach, 2nd order polynomial fit, or 3rd order polynomial fit is used to calculate the derivative.

To verify that the concentration differences were sufficiently small such that transport properties could be estimated as constant across the cell throughout polarization and relaxation experiments and the Taylor series approximations in Eqs. 12 and 20 are valid, the concentration difference upon polarization was modeled in COMSOL. Figure 3a shows the maximum normalized concentration polarization experienced across a wide range of concentrations as a function of applied voltage. We observe that concentration variations across the cell are never more than 10% of the bulk concentration for a 15 mV polarization and for concentrations over 0.5 M are less than 2% of the bulk concentrations. This confirms that assuming constant transport properties for each measurement is valid.²⁸ We note that in systems with significantly different interfacial to electrolyte resistance ratios, a larger concentration gradient could form and therefore we recommend this condition is validated

for new systems. This model also suggests that larger polarization potentials could be used for higher concentration solutions, however we found that the interfacial resistance is typically not stable for applied voltages above ~ 20 mV and is certainly not stable for applied voltages of 100 mV. In Fig. 3b we can observe that across the range of concentrations modelled, all concentration gradients should fully dissipate within 240 s of current interruption which would indicate that the OCV should decay to a steady value within this time window.

When fitting voltage relaxation data according to Eq. 14, we found a strong dependence of the resulting diffusion coefficient on the time window over which data is fit, with values differing by an order of magnitude between fit methods (see Fig. 4). At short time, the concentration profile is poorly estimated using a single exponential, however we calculate that truncating the solution to a single exponential for times greater than $0.2\tau_{\text{diff}}$ introduces less than 2% error in calculated diffusion coefficients. Newman and Thompson suggest fitting data for times greater than $0.05l^2/D$ or about $0.5\tau_{\text{diff}}$ in order for Eq. 13 to converge regardless of the initial concentration profile shape.²² Steady-state potentiostatic polarization should result

Figure 3. Finite element modeling of Li symmetric cells. (a) Maximum electrolyte concentration drop normalized to bulk concentration (%) vs applied voltage (mV) for a Li symmetric cell under polarization modeled in COMSOL across range on electrolyte concentrations. (b) Normalized electrolyte concentration drop (%) vs time (s) during relaxation after steady state polarization at 15 mV. (c) Steady-state applied voltage breakdown vs ratio of interfacial resistance to electrolyte resistance for Li symmetric cell polarized at 15 mV for 1 h assuming transport properties of a 1 mol/kg LiPF₆ in EC:EMC. Gray shading indicates resistance ratios typical for our experiments. **Note for figures a, b an interfacial resistance of 184 $\Omega\cdot\text{cm}^2$ is assumed at each electrode to be consistent with our experimental observations.

Figure 4. Restricted diffusion measurements. Salt diffusion coefficient (cm^2/s) vs concentration (mol/kg) (a) fit according to $0.2\tau_{\text{diff}} < t_{\text{fit}} < 4\tau_{\text{diff}}$, (b) all fit methods $0.2\tau_{\text{diff}} < t_{\text{fit}} < 4\tau_{\text{diff}}$ (pink), $0.2\tau_{\text{diff}} < t_{\text{fit}} < 120 \text{ s}$ (blue), and conditions suggested by Newman & Thompson $t_{\text{fit}} > 0.05l^2/D$ (orange). (c) Example experimental relaxation data for a lithium symmetric cell after 1 h of polarization at 15 mV. Data fitting regions are indicated by the color bars along the x-axis with colors corresponding to fit method in b.

in a symmetric linear profile, therefore the $0.2\tau_{\text{diff}}$ lower fitting limit should be sufficient. However, $0.5\tau_{\text{diff}}$ is a more conservative limit if the initial concentration profile is unknown. While fitting relaxation data for times greater than $0.2\tau_{\text{diff}}$ reduces truncation error in using Eq. 14, it does not guarantee that fitting only captures open-circuit voltage decay due to diffusive phenomena. In addition to concentration differences, interfacial phenomena such as SEI formation or reorganization and electric double layer relaxation can influence the voltage profile. Electric double layer relaxation is suggested to occur with a characteristic time, $\tau_{\text{EDL}} = \frac{\lambda_D l}{D_{\pm}}$ where λ_D is the Debye screening length, and l is the electrode separation distance.²⁹ For LiPF_6 in 3:7 EC:EMC electrolytes, τ_{EDL} is significantly smaller than τ_{diff} and is on the order of 1 ms.³⁰ Changes in the SEI likely occur over a number of time scales. We observe small changes in interfacial resistance over the course of minutes and hours sitting at open circuit.

In order to ensure that we only fit regions of our voltage decay that are primarily due to diffusive phenomena we propose an additional constraint for using Eq. 14, such that the upper fitting bound of $U(t)$ is proportional to τ_{diff} . We suggest restricting fitting to times $0.2\tau_{\text{diff}} < t < 4\tau_{\text{diff}}$ where $4\tau_{\text{diff}}$ was chosen because 98% of the concentration difference should decay within this period. An iterative fitting protocol implemented in Python was used to ensure these criteria are met. Because the concentration decay is measured within the separator, for our analysis we use $D_{\pm}^{\text{eff}}$ to calculate τ_{diff} . Electrolyte phase diffusion coefficients obtained using our newly suggested criteria are plotted in Fig. 4a. Initially we see an increase in the total salt diffusion coefficient with salt concentration from $3.5 \times 10^{-6} \text{ cm}^2/\text{s}$ at 0.05 mol/kg until a maximum around $5 \times 10^{-6} \text{ cm}^2/\text{s}$ at 0.5 mol/kg after which the diffusion coefficient decreases. This phenomenon was previously observed by Nyman et al. who attribute the maximum in diffusion coefficient to an increasing thermodynamic factor as concentration increases.⁴ If the diffusion coefficient with respect concentration gradients is converted to a diffusion coefficient with respect to chemical potential gradients, Nyman observed the thermodynamic diffusion coefficient decrease with increasing concentration due to increasing solution viscosity. Both the magnitude and trend in diffusion coefficient as a function of concentration are in good agreement with values obtained in the literature.^{4,5,31}

The importance of restricting the fit of our OCV to a time scale relevant to diffusion (~ 2 – 3 min in our cell configuration) is apparent in Fig. 4b, where we plot diffusion coefficients obtained if the entire OCV decay after times $t_{\text{fit}} > 0.5\tau_{\text{diff}}$ as suggested by Thompson and Newman.²² If we do not restrict our fit at long times, we obtain diffusion coefficients on the order of $10^{-8} \text{ cm}^2/\text{s}$, which is 2 orders

of magnitude smaller than expected. This is indicative of other processes occurring in the cell that impact the open circuit voltage at longer time scales. One possible explanation for this behavior is the continued reformation of the SEI on freshly plated lithium that could influence the local ion concentration within the direct vicinity of the electrode interface. Further studies of the interface would be required in order to confirm this.

In the lithium symmetric cells used for polarization experiments to calculate ρ_+ via Eq. 24, we observe large total interfacial resistances, R_{int} , ranging from ~ 130 to $730 \Omega\cdot\text{cm}^2$ in comparison to the small series resistances due to electrolyte ionic conductivity, R_s , which ranges from ~ 10 – $50 \Omega\cdot\text{cm}^2$ across the measured concentrations. The average interfacial resistance across concentrations was $368 \Omega\cdot\text{cm}^2$, or $184 \Omega\cdot\text{cm}^2$ at each electrode. While the polarization experiment is intended to probe transport resistances in the bulk electrolyte, the large difference in interfacial and bulk resistance is concerning because reproducibly isolating the series resistance becomes challenging if the interfacial resistance changes even slightly during the polarization measurement. In fact, at Li electrodes, which are highly reactive, the interfacial resistance changes during polarization can be larger than the series resistance itself. This is not the case for conventional polymer electrolytes where the conductivity is significantly smaller than in liquid electrolytes and therefore electrolyte resistances can be significantly larger than the interfacial resistance. Furthermore, interfacial resistances are further reduced at the elevated temperatures (60°C – 100°C) at which polymer electrolyte transport properties are typically measured. As a result, an interfacial to electrolyte resistance ratio of less than 1 is typical for polymer electrolytes.¹³ Though not studied here, we also note for highly concentrated solvent-in-salt electrolytes it may be possible to achieve smaller interfacial to electrolyte resistance ratios through both lower ionic conductivity and more conductive inorganic-rich SEIs.³² LiPF_6 in EC:EMC electrolytes have been studied at concentrations as high as 3.1 M ²⁷ and various other carbonate-based electrolytes to concentrations $> 5 \text{ M}$.³³ However, based on available lithium impedance data from the literature it does not appear that interfacial-to-electrolyte resistance ratios are significantly smaller than those studied here.³² To understand the interplay of different sources of resistance in the cell, we quantify the contribution of these resistances to the potential difference during polarization using a 1-D COMSOL model of the lithium symmetric cell. From this model, we calculate the applied voltage breakdown as a function of time, interfacial vs electrolyte resistance, and applied potential by extracting out the kinetic ($\Delta V_{\text{kinetic}} = \eta_c - \eta_a$) and concentration ($\Delta V_{\text{conc}} = \Delta E_{\text{Eq}}$) overpotentials at each electrode and the ohmic potential drop across the electrolyte ($\Delta V_{\text{ohmic}} = \Delta \phi_{\text{liq}}$) and SEI layers. We can calculate the potential drop across the SEI by multiplying R_{int}

by the local current density ($\Delta V_{\text{SEI}} = 2iR_{\text{SEI}}$). The steady state applied voltage breakdown for a hypothetical symmetric cell containing a 1 molal electrolyte subjected to a 1 h polarization at 15 mV is plotted in Fig. 3c as a function of the ratio of the interfacial resistance to series resistance.

We observe that for an interfacial to electrolyte resistance ratio of 30, which approximately corresponds to an interfacial resistance of $180 \Omega\text{-cm}^2$ per electrode for a cell with 1 molal electrolyte, 92% of the potential drop occurs at the electrode-electrolyte interface—81% through SEI resistance and 11% from kinetic overpotential. Only ~8% of the 15mV applied voltage actually contributes to polarization of the electrolyte and only 1% of the applied voltage is due to concentration overpotentials. This is the first indication that small changes in the interface throughout the polarization experiment can dramatically impact the reliability of the current ratio measurement. It should be noted while the absolute voltage contribution from the electrolyte would increase at higher applied voltages, the percent contribution would remain the same.

Returning to our experimental analysis, from potentiostatic polarization, we calculated the current ratio, ρ_+ , according to Eq. 24, which is plotted in Fig. 5a. The current ratio is less than 0.3 for all measured concentrations and has a minimum around 0.04 for 1 mol/kg, which is significantly smaller than expected based on current ratios calculated from the data of Nyman et al. and Landesfeind and Gasteiger.^{4,5} In order to understand the experimental variables driving the measured current ratio, we performed a statistical effect screening analysis. We built a multiple linear least-squares regression model in JMP 15 statistical software³⁴ with the current ratio as our response variable and all measured parameters including the standard deviations of interfacial and series resistances throughout polarization included. After running an initial predictor screening model to identify relevant predictors, we refined the analysis to a standard least squares model.³⁴ We calculated the variance inflation factor (VIF) for all effect variables to screen for multi-collinearity, and we sequentially removed any variables with a VIF of over 4 and reran the model to avoid overfitting.³⁵ The distribution of residuals from the model were found to belong to the normal distribution using an Anderson-Darling test. We were able to construct a predictive linear model for the measured current ratio response with using only R_s , R_{int} , and the standard deviation in R_{int} throughout the measurement. Model parameters, p-values for corresponding effect F-tests and VIFs can be found in Table II. Two things should be emphasized from this finding. First, interfacial resistance has a statistically significant impact on the measured current ratio, as noted by the small p-values. Second, the current ratio response is statistically dependent only on the series and

interfacial resistance and not the steady state current. This is an artifact of the measurement. Both of these findings emphasize that the current ratio measurement is not exclusively characterizing transport in the bulk electrolyte, as it was originally intended, and instead is probing a mixture of interfacial and electrolyte properties that are not possible to deconvolute. We have repeated these studies with a different cell geometry, higher voltages up to 100 mV, higher current density cell formation protocols and different electrolyte composition see Figs. S1 and S2 (available online at stacks.iop.org/JES/168/060543/mmedia). We found through using larger electrodes and higher stack pressures (achieved by using additional spacers) we could modify the average interfacial resistance of our cells however not significantly enough to eliminate the influence of the interface. At higher applied polarization voltages we observed that the lithium-SEI interface is even more unstable with interfacial resistance changing significantly throughout the experiment (see Fig. S1c). Higher current density formation protocols were not found to stabilize the interface more than the standard formation protocol. We also repeated experiments with a LiTFSI in a 3:7 EC:EMC blend and found interfacial resistances and current ratios in line with those presented here for LiPF₆ in EC:EMC. For all conditions tested we still find that interfacial resistance is a significant factor driving ρ_+ .

In order to understand if improving coulombic efficiency, which is related to the reactivity of Li metal with the electrolyte, would allow appropriate deconvolution of interfacial and bulk electrolyte effects, we repeated current ratio measurements on solutions of LiPF₆ in 3:7 EC:EMC with 2 wt.% VC and 10 wt.% FEC added to improve coulombic efficiency.³⁶ For a 1 molal electrolyte, we see coulombic efficiency increase from 74% to 97% with the inclusion of the VC and FEC, in agreement with Fang et al. Prior to polarization experiments, cells with additives were pre-conditioned under the same manner described previously. We observe no statistically significant difference between the interfacial resistance of cells containing stabilizing additives and those without additives (see Fig. S1b). We observe that the addition of FEC and VC does not significantly impact the measured current ratio, with ρ_+ still well below the expected values of 0.45–0.35 based on the data previously reported in the literature (see Fig. S2a).^{4,5} Two interesting conclusions can be drawn from this experiment. First, improving the coulombic efficiency of lithium plating/stripping through the addition of VC and FEC does not significantly reduce the size or stability of interfacial resistance in lithium cells. Second, the effect of the SEI on current ratio measurements cannot be eliminated by simply increasing coulombic efficiency. These conclusions are in line with the findings of Fang et al. that showed that lithium loss in the SEI is not responsible for the majority of coulombic efficiency

Figure 5. (a) Current ratio (ρ_+) vs concentration (mol/kg) measured using potentiostatic polarization at 15 mV. (b) Calculated transference number vs concentration (mol/kg) with reference to solvent (pink) and the center of mass (blue) velocities as calculated according to Eq. 27 using conductivity from blocking electrodes, diffusion coefficients extracted using fitting restricted by $0.2\tau_{\text{diff}} < t_{\text{fit}} < 4\tau_{\text{diff}}$, concentration cell data and current ratio. Note that we do not actually believe the true transference number is negative for these solutions. Instead these results are due to interfacial interference in polarization experiments. (c) Calculated thermodynamic factor vs concentration (mol/kg) as calculated according to Eq. 28. Like the transference number we believe the thermodynamic factor calculated here is skewed due to interfacial effects.

Table II. Effects screening model parameters for current ratio measurement at 15 mV.

Factor	p-value	VIF
R_s	<0.0001	3.26
$R_{int} \cdot R_s$	0.0002	2.50
R_{int}	0.001	1.95
St.dev. (R_{int})	0.0047	1.64
I_{ss}	0.740	1.00

difference in carbonate based electrolytes with and without FEC. They attribute the large coulombic efficiency difference to significant formation of electronically isolated “dead” lithium in carbonate electrolytes without FEC.³⁶ Our impedance data supports this finding.

To show the impact of the errors in the polarization measurement on the calculation of transport coefficients, we calculate the transference number and thermodynamic factor according to Eqs. 27 and 28 (see Fig. 5b, 5c), both of which depend on ρ_+ calculated from polarization measurements. For all concentrations tested, we calculate a negative transference number ranging from -0.01 to -9.3 with respect to the solvent velocity or -0.001 to -8.0 with respect to the center of mass velocity, with a minimum in transference number around 1.0 m LiPF₆. While a negative transference number has been observed for many polymer systems and could be explained by the presence of negatively charged ion aggregates that cause the lithium ion to migrate in the “wrong” direction with respect to the electric field, we do not believe that this phenomenon is actually present in this system.^{14,15,37,38} Previous studies of this electrolyte in the literature involving alternate polarization methods for transference number measurements have obtained positive transference numbers ranging from 0.12 to 0.4 across this range of concentration.^{4,5,31} While we believe that some of these methods likely also suffer from interfacial effects that interfere with accurate extraction of transport properties, our group has determined transference numbers with reference to the center of mass velocity for a 1 molar LiPF₆ in 3:7 EC:EMC systems using molecular dynamics (MD) simulations and electrophoretic nuclear magnetic resonance spectroscopy (eNMR) and observe only positive transference numbers on the order 0.25–0.30.^{19,39,40}

We believe that the calculated negative transference numbers are actually due to errors in the current ratio measurement that resulted from the analysis unsuccessfully decoupling interface and bulk electrolyte processes. The sensitivity of the measurement to ρ_+ can be easily demonstrated by replacing ρ_+ as calculated in Eq. 24 using the ohmic current, I_Ω , with the current ratio calculated using the first measured current density in the cell, I_0 . This results in a transference number that is positive for all concentrations and ranges from 0.57 to 0.25. We note that the I_0 and I_Ω should be exactly equal and result in the same ρ_+ if the interface were perfectly stable and no concentration gradients form within the short response time of the potentiostat upon applying voltage.

We observe the same compounding effect of ρ_+ on the thermodynamic factor with the calculated thermodynamic factor ranging from 0.058 to 0.32 across the range of concentrations with a minimum around 1 M (see Fig. 5c). Again, this trend does not match previous results or physical intuition which would dictate a thermodynamic factor of 1 in the ideal dilute concentration limit, an initial decrease below 1 in the thermodynamic factor for dilute solutions, and an increase in thermodynamic factor above 1 for solutions in the semi-concentrated regime.⁴¹

Conclusions

In this study, we demonstrate that voltage polarization measurements limit the reliability of measuring physically meaningful

transference numbers and thermodynamic factors for Li-metal-liquid electrolyte systems where interfacial resistances are typically at least an order of magnitude larger than electrolyte resistances. Using impedance spectroscopy, concentration cells, restricted diffusion, and potentiostatic polarization, we characterized the conductivity, binary salt diffusion coefficient, derivative of open circuit voltage with respect to concentration, and current ratio of LiPF₆ in 3:7 EC:EMC across a range of concentrations from 0.01 mol/kg to 1.5 mol/kg. We found conductivity ranged from 2–10 mS/cm and salt diffusion coefficients from 1×10^{-6} to 5×10^{-6} cm²/s. Current ratios were obtained from steady-state polarization experiments and ranged from 0.27 to 0.034. While we found our conductivity, diffusion coefficients, and concentration cell data in good agreement with previous reports, we calculated transference numbers and thermodynamic factors that deviate significantly from those found in the literature. Calculated transference numbers with respect to the solvent ranged from -0.01 to -9.3 , with a minimum in transference number around 1.0 m. We do not believe that this system actually has a negative transference number and instead attribute this to artifacts in polarization experiments used to measure the current ratio.

We demonstrate through a combination of finite element modeling and statistical analysis that polarization experiments primarily capture interfacial effects in these systems when interfacial resistance is an order of magnitude larger than resistance due to bulk conductivity. Through a rigorous statistical analysis, we demonstrated that the current ratio measurement is statistically dependent on the interfacial resistance, indicating that the interfacial and bulk electrolyte effects cannot be properly deconvoluted. We observe that this finding holds true even in different cell geometries and upon addition of stabilizing additives that increase coulombic efficiency. In our system, this results in artificially low current ratios which propagates significant error into calculated transference numbers and thermodynamic factors.

We developed best practices for analyzing restricted diffusion measurements and extracting information from concentration cell experiments. We demonstrate the importance of restricting the fitting window for voltage relaxation profiles using the characteristic diffusion time so as not to include regions of the voltage relaxation due primarily to double layer and interfacial phenomena. We suggested the fitting window of $0.2\tau_{diff} < t_{fit} < 4\tau_{diff}$ for relaxation after steady state polarization experiments. We show that without this restriction on the fit window salt diffusion coefficients can differ by one or more orders of magnitude.

These findings highlight the importance of interfacial resistance and stability throughout the course of full transport property measurements, yet interfacial resistances (and their standard errors) are seldom reported in transport measurement literature.¹³ This work also calls into question the validity and reliability of Bruce-Vincent type transference number measurement for carbonate-based liquid electrolytes and other electrolytes where the interfacial resistance is significantly larger than the bulk resistance. Hence, we urge caution when interpreting transport coefficients obtained through these methods. If these methods are used, we recommend that experimentalists report interfacial resistances as well as a statistical analysis of the correlations between these resistances and the measured current ratio or Bruce-Vincent transport number. While not specifically studied here, we believe that other methods for measuring liquid electrolyte transport properties that rely on lithium metal polarization, such as the current interrupt method, also suffer from these severe interfacial effects and should therefore be scrutinized. From a materials perspective, there is also a clear need to develop substantially lower impedance planar electrodes that allow reversible Li⁺ insertion/alloying to facilitate accurate measurements of transport properties when using polarization techniques to characterize liquid electrolytes.

Our findings also underscore the significant contribution of the lithium solid-electrolyte interface to the overall cell resistance.

While much of the electrolyte engineering literature focuses on electrolytes with improved transport properties or high coulombic efficiency, developing electrolytes with low interfacial resistance is often overlooked. This work highlights how insignificant concentration overpotentials can be to the overall cell voltage in the presence of highly resistive SEIs that form on lithium metal. This is of particular importance for anode-free and lithium metal cell architectures and could be a major limiting factor to performance in these systems.

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