Insights into the Transport and Thermodynamic Properties of a Bis(fluorosulfonyl)imide-Based Ionic Liquid Electrolyte for Battery Applications

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ABSTRACT: Ionic liquid electrolytes (ILEs) have become popular in various advanced Li-ion battery chemistries because of their high electrochemical and thermal stability and low volatility. However, because of their relatively high viscosity and poor Li⁺ diffusion, it is thought that large concentration gradients form, reducing their rate capability. Herein, we utilize operando Raman microspectroscopy to visualize ILE concentration gradients for the first time. Specifically, using lithium bis(fluorosulfonyl)imide (LiFSI) in N-propyl-N-methylpyrrolidinium FSI, its “apparent” diffusion coefficient, lithium transference number, thermodynamic factor, ionic conductivity, and resistance of charge transfer against lithium metal were isolated. Furthermore, the analysis of these concentration gradients led to insights into the bulk structure of ILEs, which we propose are composed of large, ordered aggregates.

As lithium-ion batteries (LIBs) approach their theoretical energy limit, high-energy alternatives are required for the increasingly high-energy applications society now depends on. Popular strategies to improve energy density include utilizing high-voltage cathodes, conversion cathodes, or lithium metal anodes. Conventional electrolyte compositions used in LIBs, such as 1 M LiPF₆ in EC:DMC (1:1 v/v), have proven to be unsuitable because of the unfavorable solid (or cathodic) electrolyte interphase (SEI or CEI) that forms. In recent years, researchers have shown that using ionic liquid electrolytes (ILEs) improves the cyclability because of the stable SEI/CEI on the respective electrode surface. However, with multiple ions in solution and an often high viscosity, ILEs exhibit particularly poor transport properties. This limits their rate performance, as ohmic resistance and concentration gradient formation lead to increasing overpotential with increasing current density. Furthermore, in lithium metal batteries (LMBs), the depletion of Li⁺ at the lithium metal surface has been proven to induce lithium dendrite growth and short-circuiting.

Common ILEs used for battery applications contain 3 or 4 ionic species, and because of the lithium diffusion coefficient ($D_{Li^+}$) frequently being the lowest and Li⁺ often being present in low concentrations, the transference number of Li⁺ ($t_{Li^+}$) in ILEs has shown to be very low.

The most popular method for determining $t_{Li^+}$ in ILEs is via (electrophoretic) pulsed-field gradient nuclear magnetic resonance (pfg-eNMR) studies, which explicitly measures the self-diffusion coefficient of each ion in solution ($D_i$). Without an electric field (i.e., pfg-NMR), the transference number can be estimated by calculating the fraction of current carried by Li⁺ using the product of $D_i$ and $c_i$ of each component. However, this method includes an electrolyte field, and the depletion of Li⁺ at the lithium metal surface has been proven to induce lithium dendrite growth and short-circuiting.

Published: February 16, 2022
Accepted: February 8, 2022
Received: December 31, 2021

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Cite This: J. Phys. Chem. Lett. 2022, 13, 1734–1741
Read Online

https://doi.org/10.1021/acs.jpclett.1c04246
J. Phys. Chem. Lett. 2022, 13, 1734–1741
formed concentration gradient has been formed.\textsuperscript{16–20} Although the mentioned pfg-NMR and Warburg methods for determining $t_{Li}^+$ are equivalent in “ideal” conditions, using electrochemical methods like Hittorf provides the most rigorous definition of transference in nonideal or concentration electrolytes; therefore, measuring $t_{Li}^+$ via electrochemical means provides the best predictor of performance in nonideal electrolyte conditions. Although the pfg-(e)NMR and EIS techniques have shed some light on the complexities and intricacies of ILE transport, there is yet to be a complete experimental study that monitors both $D_{app}$ and $t_{Li}^+$, with added thermodynamic understanding provided through a value such as the molar thermodynamic factor ($\chi_M$).

For a comprehensive understanding of binary electrolyte transport, researchers have utilized operando magnetic resonance imagining (MRI) and Raman techniques to visualize concentration gradients.\textsuperscript{21–24} These studies have not yet been extended to ternary systems or ionic liquid systems. Herein, we use operando Raman microspectroscopy to measure Li$^+$ concentration gradients in an IL-based electrolyte system. We focus on 0.5, 1, and 2 m LiFSI in Pyr1,3FSI, a three-component, common electrolyte system used in high-energy cells.\textsuperscript{25} To be explicit, this is the first time ILE concentration gradients have been visualized. Concentration gradient formation is regarded as ILEs’ primary weakness in LIBs and LMBs, so the visualization of the gradient is of particular importance for the understanding and progression of ILEs. Moreover, key electrolyte properties including the “apparent” diffusion coefficient ($D_{app}$), lithium transference number ($t_{Li}^+$), thermodynamic factor ($\chi_M$), ionic conductivity ($\kappa$), and resistance of charge transfer ($R_{ct}$) are isolated. This is also the first time a full suite of electrolyte properties has been measured for a promising ILE for use in battery applications.

Concentration Gradient Visualization. Concentration gradients were visualized using operando Raman microspectroscopy (Figure 1), specifically, a time-series of one-dimensional (1D) Raman scans across a custom-built optical LiLi symmetric cell while current is passed.\textsuperscript{25} Importantly, the cell was placed vertically on the stage, with stripping occurring at the bottom and plating at the top, to avoid natural convection from density differences of the bulk concentration. The line-scan was performed every 4 h for 36 h. Electrolyte solutions were prepared gravimetrically (molal) to increase reliability and accuracy of preparation (for density measurements and molarity equivalents, see Supporting Methods).

$$\Delta \chi_M = \frac{\Delta \chi_M_{app}}{\Delta \chi_M_{Li}^+}$$

$$\kappa = \frac{\Delta \chi_M_{app}}{\Delta \chi_M_{Li}^+}$$

$$R_{ct} = \frac{\Delta \chi_M_{app}}{\Delta \chi_M_{Li}^+}$$

Figure 1. Method for visualizing ILE concentration profile and obtaining $D_{app}$, $t_{Li}^+$, $\chi_M$, $\kappa$, and $R_{ct}$ values. The asymmetry in the concentration gradient is a result of accumulation of Li$^+$ species at the bottom of the cell.

$\Delta \chi_M$ was calculated by correlating it with the 730 cm$^{-1}$ FSI$^−$ peak shift. Representing the S–N–S bending mode,\textsuperscript{26} the 730 cm$^{-1}$ peak shifts to higher wavenumbers monotonically with increasing $t_{Li}^+$ because of the continuing formation of high-energy bonding in Li(FSI)$^−$ structures.\textsuperscript{27} The calibration curve used is shown in Figure 2a, illustrating the nonlinearity of wavenumber increase with $t_{Li}^+$ as the LiFSI concentration approaches saturation. An alternative method involved using area ratios FSI$^−$ 730 cm$^{-1}$ and Pyr$^+_1$,3 900 cm$^{-1}$ peaks. Because of the increased spectral noise using this method, we selected the former method; further analysis is shown in Supporting Discussion 2.1.

Using the 730 cm$^{-1}$ peak shift method, we checked the mass-balance of the system by integrating each concentration-distance profile, noting if there was any change in the measured profiles over time. Each measurement was within 1.2% of the highest and lowest profile integral over the 36 h experiment. We therefore concluded this is a valid method for calibrating concentration in ILEs.

Asymmetry and Structural Implications. Figure 2b shows a concentration profile of Li$^+$ in 1 m LiFSI in Pyr1,3FSI at 100 $\mu$A cm$^{-2}$ after 12 h. Surprisingly, the profile had an asymmetry, with both bulk concentration change and dc/dz being larger on the stripping side compared to the plating side. This seemed unique to ILE systems, with other systems not showing this phenomenon.\textsuperscript{22}

Prior to the application of current, the cell rested for 4 h and a line-scan was recorded. We noticed an increase in concentration at the bottom of the cell, which indicated an accumulation of $c_{Li}^+$ before any current was applied (see Figure 3a). This accumulation suggested distinct Li$^+$-containing species of higher density were falling because of gravity. To investigate this further, we measured the open-circuit voltage (OCV) of the cell while changing the cell’s orientation. Figure 3b shows how the OCV changed with time, labeled with the orientation of the cell.

It was clear that the OCV was dependent on the orientation of the cell, with it rising from 0 V to $\sim$4 mV after the first few hours and dropping to approximately $\sim$5 mV when the cell was inverted. The cell was then placed horizontally, which led to the OCV reverting back to 0 V. Using 4 mV as the OCV, the thermodynamic activity ratio calculated from the Nernst equation was 1.16, in good agreement with the 1.11 measured for a promising ILE for use in battery applications.\textsuperscript{31,32} (See Supporting Discussion 2.2 for further discussion.) However, further studies are required to confirm this value.
The Raman spectra required for Li\(^{+}\) calibration provided information on electrolyte structural changes with increasing LiFSI content. The peak at 1200–1240 cm\(^{-1}\) represents the S=O stretching mode of FSI\(^{-}\). In the neat IL there was a single peak at 1215 cm\(^{-1}\), and with increasing LiFSI addition a new, defined peak appeared at 1225 cm\(^{-1}\) (Figure 3c). A defined 1225 cm\(^{-1}\) peak is unique to ILEs.\(^{27,36}\) This suggested the ILEs have distinctive structures or domains that are not present in organic-based electrolytes. As has been mentioned in other works, the 1215 cm\(^{-1}\) peak was speculated to be free FSI\(^{-}\) and 1225 cm\(^{-1}\) was thought to be a bound Li-FSI\(^{-}\) species. The solvation number of the Li\(^{+}\) can be calculated, as shown in Supporting Discussion 2.4, and we concluded it remained constant at 2 (i.e., Li\(^{+}\) is solvated by two FSI\(^{-}\)).

With FSI\(^{-}\) experiencing two separate environments, it is at ∼1.1 m that [FSI\(^{-}\)] < [Li(FSI)\(^{2-}\)]. As the concentration increased past 1.25 m, the 1225 cm\(^{-1}\) peak became less defined and more broad (Figure 3d), which we speculate could be due to the fusing of the [Li(FSI)\(^{2-}\)]-derived aggregates forming a homogeneous, percolating network. Indeed, McEldrew et al. predict using MD simulations a “critical threshold” or gelation point where these extended networks form.\(^{37}\) Our data agrees with the hypothesis of McEldrew et al., providing experimental evidence to support their claims.

**Li\(^{+}\) Transport Properties.** The 1 m electrolyte was used as a model system to describe the process of fitting and transport property isolation. Equation 1 is a solution to the diffusion equation in a symmetric cell setup, using the interfacial...
concentration gradient as a spatial boundary condition. Each gradient was fitted to this equation, elucidating information on the transport properties of the electrolytes. Because of the gradients’ asymmetry, each side of the cell was fitted separately with different diffusion length and interfacial gradient values, with p and s indicating the plating and stripping sides respectively:

$$c_{Li^+}(z, t) = c_{Li^+}^* + a(s) \left\{ \frac{b(s)}{d^{1/2}} \exp\left( -\frac{z^2}{b(s)} \right) - 2\text{erfc}\left( \frac{z}{b(s)} \right) \right\} - c(p) \left\{ \frac{d(p)}{d^{1/2}} \exp\left( -\frac{(-z + L)^2}{d(p)} \right) + (-z + L)\text{erfc}\left( \frac{-z + L}{d(p)} \right) \right\}$$

(1)

$$a, d \left. \frac{dc_{Li^+}}{dz} \right|_{z=0,L} = f(1-t_{Li^+})$$

(2)

$$b, d \left( = L_d \right) = 2(D_{app(s,p)} t)^{1/2}$$

(3)

where $c_{Li^+}^*(z, t)$ is the concentration of $Li^+$ at time t in the vertical z-direction; $c_{Li^+}^*$ is the initial lithium concentration; L is the interelectrode distance; $J$ is the applied current density; $F$ is the Faraday constant; $b$ and $d$ are equal to $L_d$ defined as the diffusion length; and $a$ and $\epsilon$ are equal to $\left. \frac{dc_{Li^+}}{dz} \right|_{z=0,L}$, which is the interfacial concentration gradient at each electrode surface, $z = 0, L$.

Figure 4a shows $c_{Li^+}$ gradients of the 1 m electrolyte at different times. As expected, the gradients were large across the electrolyte, with the stripping electrode showing a significant interfacial concentration ($dc/dz_{app}$) gradient of $5.3 \pm 0.20 \times 10^6$ mol m$^{-2}$ at 100 $\mu$A cm$^{-2}$. We also performed the measurement at 50 $\mu$A cm$^{-2}$ showing $dc/dz_{app}$ as $2.8 \pm 0.10 \times 10^6$ mol m$^{-2}$. As is expected, $dc/dz_{app}$ was directly proportional to the current applied, with $dc/dz_{app}$ being almost exactly double when a 100 $\mu$A cm$^{-2}$ was applied compared to 50 $\mu$A cm$^{-2}$. The plating interfacial gradient ($dc/dz_{app}$) at 100 $\mu$A cm$^{-2}$ was lower at $3.5 \pm 0.60 \times 10^6$ mol m$^{-2}$, presumably because of the accumulated aggregates at the bottom of the cell.

Diffusion. By monitoring the diffusion length ($b$ and $d$) over time, one can calculate $D_{app}$ on both sides of the cell. Figure 4b shows b and d versus time (t), with the slope being proportional to $D_{app}$. Also plotted is the 95% confidence band, which highlights the uncertainty especially on the plating side of the cell. The fitting on the stripping side is much more accurate, which is reflected in the error of the $D_{app}$ calculation. On the stripping side, $D_{salt} = 1.77 \pm 0.06 \times 10^{-11}$ m$^2$ s$^{-1}$, and on the plating side $D_{app} = 2.5 \pm 0.50 \times 10^{-11}$ m$^2$ s$^{-1}$, with an inverse-variance weighted average of $1.78 \pm 0.09 \times 10^{-11}$ m$^2$ s$^{-1}$. Pulsed field gradient (pfg)-NMR measurements were performed to compare against these values: using the harmonic mean, $D_{salt}$ was calculated as $1.77 \times 10^{-11}$ m$^2$ s$^{-1}$ (see Supporting Discussion 2.5), very similar to $D_{app}$ calculated using concentration visualization. The magnitude of the diffusivities would suggest transport is occurring primarily via an ion-hopping mechanism as opposed to sedimentation of the aggregates identified in the previous sections. However, sedimentation is proposed to be the reason for the asymmetric concentration gradient that was visualized.

Transference Number. $t_{Li^+}$ was calculated from the fitted concentration gradient. Conventionally, $t_{Li^+}$ is measured via
Table 1. pfg-NMR Diffusivities and Transference in 0.5, 1, and 2 m at 25 °C

| cLi+ (M) | cFSI− (M) | cPyr+ (M) | DLi+ (×10^{-11} m^2 s^{-1}) | DFSI− (×10^{-11} m^2 s^{-1}) | DPyr+ (×10^{-11} m^2 s^{-1}) | Dab (×10^{-11} m^2 s^{-1}) | tLi+ |
|---------|-----------|-----------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------|
| 0.62    | 4.38      | 4.08      | 2.04                          | 2.79                          | 2.47                          | 2.58                          | 0.053 |
| 1.19    | 5.06      | 3.87      | 1.42                          | 1.88                          | 1.76                          | 1.77                          | 0.094 |
| 2.14    | 5.63      | 3.46      | 0.81                          | 0.97                          | 0.92                          | 0.92                          | 0.169 |

Figure 5. LiFSI in Pyr13FSI concentration-dependent transport and thermodynamic properties: (a) Ionic conductivity (κ), fitted by exponential decay. (b) Resistance of charge transfer (Rct) showing a marginal increase at 1 m, then a decrease again at 2 m. (c) Fickian diffusion coefficient (Dab), showing a change moving from 1 to 2 m. (d) Transference number of lithium (tLi+), initially very low but showing a marked increase from 1 to 2 m. (e) (dc/dz)_t=0 at 100 μA cm^{-2}, which was initially constant but showed an increase moving to 2 m. (f) Δκ showing values below 1 for concentrations below 1 m, but increasing to ~2.5 at 2 m. Values below 1 indicate increased association between Li+ and FSI−, and values above 1 indicate the decreasing amount of free FSI− present and thus an increase in “effective concentration” of Li+. The error bars represent the standard deviation of the inverse-weighted mean of the stripping and plating sides from the fitting of the asymmetric gradient. Experimental inconsistencies such as dendrite formation and small temperature variations explain some differences between the calculated property values for repeated experiments.

The Hittorf method, which looks at calculating the change in concentration on either the plating or stripping side of the cell after a known amount of current is passed. This was particularly straightforward when utilizing concentration gradient visualization techniques, as one can monitor the concentration on each side of the cell by integrating under the concentration curve. Moreover, those using a conventional Hittorf setup would not notice the initial gradient from the concentration on either the plating or stripping side of the cell after a known amount of current is passed. Using the pfg-NMR, we used an “external” reference, namely, the center-of-mass reference. tLi+ was calculated:

\[ t_{Li^+} = \frac{\Delta n_{Li^+}}{n_{charge}} = \frac{A \cdot F \left( \Delta \int_{0}^{2\pi/\omega} c_{Li^+} dz \right)}{Q} \]  

where \( n_{charge} \) is the number of moles of charge passed; \( \Delta n_{Li^+} \) is the molar difference between the two sides of the cell before and after time; \( t \); Q is the charge passed over time; and A is the area of the electrode.

Figure 4c shows how the concentration changed for the stripping and plating side; note the change in area is linear, indicating the movement of the aggregated structures remained constant, and so did \( t_{Li^+} \). Using the initial concentration profile prior to application of current, \( t_{Li^+} \) was calculated for each scan over time, and the average \( t_{Li^+} \) was calculated from the inverse-variance weighted mean. On the stripping side \( t_{Li^+} \) was calculated as \( -0.088 \pm 0.024 \) and on the plating side, \( 0.114 \pm 0.062 \), with a weighted average of \( -0.062 \pm 0.070 \). Again, the lower value on the stripping side was likely due the accumulation of higher-density aggregates on oxidation of Li.

By using the pfg-NMR diffusivities and measured concentrations, \( t_{Li^+} \) via pfg-NMR was 0.0941, but without an electric field (like in pfg-eNMR), migration was not taken into account.

**Thermodynamic Factor.** γ_M correlates the electrolytes’ thermodynamic activity with concentration. To our knowledge, no room-temperature Li-ion ILEs’ γ_M values have been...
reported, but the activity of various LiNO₃-AgNO₃ melt compositions (at 260 °C) were measured by Richter a few decades ago.⁴⁶ χₘ was calculated as

$$\chi_M = 1 + \frac{\text{d} n f_x}{\text{d} n c} = \frac{-F}{2RT (1 - t_{Li^+})} \frac{\text{d} t_{Li^+}}{t_{Li^+}^{2 - \delta M}}$$  

(6)

where $f_x$ is the molar activity coefficient. Using the potentiostatic electrochemical impedance spectroscopy (PEIS) data prior to each line scan, $\eta_i$ was calculated by $\eta_i = \eta_{total} - \eta_{[LiF]} + \eta_{[Li^{2+}]}$, where $\eta_{total}$ is measured from the chronopotentiometry data and the resistances are from PEIS.

$\chi_M$ was measured as 0.906 ± 0.064 (Figure 4d), which is reasonable if one were to compare against Richter’s findings, which showed values of between 0.95 and 1.7 as the mole fraction changed between 1 and 0 of AgNO₃.

**Ionic Conductivity and Resistance of Charge Transfer.** From PEIS, prior to current being passed the ionic conductivity ($\kappa$) and resistance of charge transfer ($R_\eta$) were calculated from fitted Nyquist plots (Figure 4e). $\kappa$ was calculated as 3.52 ± 0.01 mS cm⁻¹, which agreed well with previous literature values. Using the pfg-NMR data, the inverse Haven ratio was calculated as 0.520, showing a significant amount of ion–ion correlation. $R_\eta$ was calculated as 44 ± 4 Ω·cm⁻², which is assumed to be a combination of classical charge-transfer and SEI resistance. ILEs containing FSI⁻ in particular have been shown to have fast charge-transfer kinetics, as illustrated by their low $R_\eta$ value.³⁷⁻⁴⁸

**Dependence on Concentration.** To understand transport changes with a varying amount of Li⁺ present, we performed operando Raman experiments on two other ILE concentrations, namely, 0.5 and 2 m. Like the measurements performed with the 1 m electrolyte, 100 µM cm⁻² was applied. With 0.5 m, we also performed a measurement at 50 µM cm⁻² because at the higher current $c_{Li^+}$ dropped very quickly at the plating side. Two measurements were run per concentration. Each $D_{app}$ and $t_{Li^+}$ value can be compared to the pfg-NMR values in Table 1.

Figure 5 shows how electrolyte transport and thermodynamic properties were affected by concentration. $D_{app}$, $t_{Li^+}$, and $dc/dz_{vol}$ were taken from the inverse-variance-weighted average of the stripping and plating sides. Most strikingly, 0.5 m ILE showed many transport and thermodynamic values similar to those of 1 m. For instance, 0.5 m showed $dc/dz_{vol}$ equal to $5.50 \times 10^5$ mol m⁻³ cm⁻¹, like that of 1 m. $t_{Li^+}$ for both these concentrations was very low, although because of the error involved it is difficult to report whether the values were negative or positive. Values of $\chi_M$ were lower than 1 for both 0.5 and 1 m, indicating their activity is lower than their concentration because of a high amount of association.

For 2 m, there was a noticeable change in many of the transport and thermodynamic properties. For example, there was a marginal increase in $dc/dz_{vol}$ from $5.50 \times 10^5$ to $6.50 \times 10^5$ mol m⁻³ cm⁻¹ because of changes of $D_{app}$ and/or $t_{Li^+}$. There was a drop in $D_{app}$ versus 1 and 0.5 m. Most certainly there was an increase in $t_{Li^+}$, which indicated a structural change perhaps correlated to the broadening of the 1200–1240 cm⁻¹ peak. An increase in $\chi_M$ at high concentrations is common among electrolyte solutions and is noticeable here too. Furthermore, results from Richter showed a similar behavior. We speculate that as more LiFSI was added there were fewer free FSI⁻ to stabilize Li⁺ via extended [Li(FSI)₂]⁻ structures; $\chi_M$ then began to rise. There was no noticeable trend in $R_\eta$ with a clear anomaly for one of the 0.5 m samples, which did not appear to affect the other bulk electrolyte property values described.

This reported data suggested there was a transport mechanism change moving from 1 to 2 m. We also speculated above that between these concentrations there was a structural change, as illustrated from the Raman data. We speculate that when [Li(FSI)₂]⁻ > (FSI)⁻, ordered networks form, increasing $t_{Li^+}$.

In summary, by combining spectroscopic and electrochemical techniques with concentration visualization we have presented particularly valuable findings not yet reported in the ILE literature. Specifically, the Li⁺ concentration gradient in ILEs has been visualized for the first time, along with the isolation of key transport and thermodynamic properties. With ILEs’ main weakness being their transport properties, understanding fully the origin of this is paramount for their continuing development. Moreover, this is the first time a thermodynamic understanding of promising battery ILEs has been measured through $\chi_M$. Additionally, the sedimentation of clustered aggregates have been detected, which has not yet been experimentally measured in the academic literature until now. We anticipate this work to further promote concentration visualization’s unique ability to fully understand electrolyte properties, and specifically, we hope our findings regarding ILEs’ properties and structure will inform their ongoing progress.

### METHODS

**Electrolyte Description.** Lithium bis(fluorosulfonyl)imide (LiFSI) (battery grade, 99%) was purchased from Fluorchem Ltd. N-Propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (Pyr1,3FSI) (99.9%) was purchased from Solvionic. Handling of LiFSI and Pyr1,3FSI was always performed in an argon-filled glovebox (MBraun) with low H₂O content (<1 ppm) and low O₂ content (<1 ppm). LiFSI was dried further under high vacuum at 70 °C for 48 h. Pyr1,3FSI was dried under high vacuum at 70 °C for 24 h, with a stirrer bar. The H₂O content of the electrolyte solutions was determined by Karl Fischer titration, which was also performed in an argon-filled glovebox, and recorded to be below 15 ppm of H₂O.

**Calibration.** Using a confocal Renishaw inVia Reflex laser confocal Raman microscope equipped with a near-IR 785 nm laser, a 5X magnification objective (Leica, 0.12 NA, 14 mm WD), leading to a 4.8 µm spot size, along with a 90° mirror (Renishaw) was used to collect Raman spectra of the prepared solution. An even distribution of calibration electrolytes was prepared, between 0.1 and 3 M, inside an Ar-filled glovebox. For each calibration solution, the spectra were recorded with an 800 cm⁻¹ center, at 5% laser power, one second exposure, and 20 acquired spectra. Using Renishaw WiRE 5.5 software, the background of each spectrum was removed and normalized. Each 730 cm⁻¹ peak was fitted with an exponentially modified Gaussian (EMG) function, and the wavenumber number (x-axis) at maximum height was calculated. The calibration curve is shown in Figure 2a.

**Cell Construction.** The custom-designed cell was constructed in an Ar-filled glovebox. Two Li discs of 8 mm diameter were cut and placed onto two stainless steel pistons of the same diameter. One piston was placed into a fused quartz tube; electrolyte was added, and the second piston was added to seal the cell, being careful not to introduce any bubbles into the
system. Once sealed, the cell was placed onto the Raman stage vertically and connected to a Biologic SP150 potentiostat.

Line Scan. 100 μA cm⁻² was applied to the cell, and a 1D line scan in the z-direction was performed every 4 h for 36 h. The same laser settings used for calibration were used for the line scan too. A point-by-point line scan was taken, with equal spacing between the 1.5 cm interelectrode distance. The confocality of the instrument allowed us to measure the line scan in a precise plane of focus; each measurement was 0.5 cm inside the ID of the quartz tube. Using Renishaw's WiRE5.5 software, the background was removed, and each spectrum was compared to the calibration using a Python script. The resulting concentration gradient was fitted with eq 1. The Python scripts used in this work are available at github.com/JFawd.

PEIS. Before any line scan, potentiostatic electrochemical impedance spectroscopy (PEIS) was performed on the cell. It was also performed between line scans to provide an estimation of $\eta_b$. A voltage amplitude ($V_0$) of 100 mV was used, which allowed for linearity. The frequency was scanned from 100 kHz and 1 Hz. The Nyquist plot was used, which allowed for linearity. The frequency was scanned using Biologic EC-lab V11.26 software.

$pfg$-NMR. All pulsed field gradient (PFG) nuclear magnetic resonance (NMR) measurements were completed at 9.45 T ($\omega(1H) = 400.20$, $\omega(19F) = 376.58$, and $\omega(7Li) = 155.53$ MHz) on a Bruker Avance III HD spectrometer using a 5 mm single-axis diffusion probe with exchangeable $^1H$, $^19F$, and $^7$Li ceramic heads. A stimulated echo pulse sequence was utilized with an effective gradient pulse duration (δ) of between 1 and 2 ms, a diffusion time (Δ) of 43–46 ms, with the gradient amplitude varied between 0.1 and 5 T/m. All samples were sealed in a J-Young valve NMR tube; the temperature was stabilized at 298.1 K, and a 5 s recycle delay was used throughout.

Associated Content

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcl.1c04246.

Experimental setup and densitometry measurements; comparison between calibration methods; estimation of aggregate size with Stokes’ Law; description of gradient formation with blocking electrodes; solvation number calculation of Li$^+$ using Raman; description of $D_{app}$ calculation using $pfg$-NMR (PDF)

Transparent Peer review report available (PDF)

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Notes

The authors declare no competing financial interest.

Acknowledgments

The authors acknowledge the ISCF Faraday Challenge projects SOLBAT (Grant Number FIRG026) and LiSTAR (Grant Number FIRG014) as well as the Henry Royce Institute (through UK Engineering and Physical Science Research Council Grant EP/R010145/1) for capital equipment. We also thank Giulia Galatolo for her drawings of the cell in Figures 1 and 2. We thank Dr. Johannes Ihli for his help with the initial operando Raman experiments and conversations regarding the analysis. We also thank Dr. Liyu Jin for his help with the initial pfg-NMR experiments.

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