Ion Conducting Polymer Interfaces for Lithium Metal Anodes: Impact on the Electrodeposition Kinetics

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Electrochemical cells that utilize metals (e.g., lithium, sodium, zinc) as anodes are under intense investigation as they are projected to replace the current lithium-ion batteries to serve as a more energy-dense option for commercial applications. In addition, metal electrodes provide opportunities for fundamental research of different phenomena, such as ion transport and electrochemical kinetics, in the complex environment of reactive metal-electrodeposition. In this work, computationally and experimentally the competing effects related to transport and kinetics during the metal electrodeposition process are examined. Using Brownian dynamics simulations, it is shown that slower deposition kinetics results in a more compact and uniform Li morphology. This finding is experimentally implemented by designing ion-containing polymeric coatings on the electrodes that simultaneously provide pathways for lithium-ion transport, while impeding the charge transfer ($\text{Li}^+ + e^- \rightarrow \text{Li}$) at heterogeneous surfaces. It is further shown that these ionic polymer interfaces can significantly extend the cell-lifetime of a lithium metal battery in both ether-based and carbonate-based electrolytes. Through theoretical and experimental investigations, it is found that a low kinetic to transport rate ratio is a major factor in influencing the Li plating morphology. The plating morphology can be further fine-tuned by increasing ionic conductivity.

1. Introduction

Rapid growth of electrochemical energy storage technology is essential to addressing the rising demands for energy-dense batteries and emergent electronic systems. A promising, yet challenging pathway towards high energy storage systems is replacement of the graphitic anode in state-of-art lithium-ion batteries with metallic lithium that can enhance the anode-specific capacity by ten-times and at the same time facilitate the usage of lithium-free and earth-abundant cathodes, such as oxygen or sulfur, for high energy batteries.[1–10] However, lithium metal anodes suffer from several instabilities during the electrodeposition process of battery charging. The low reduction potential and reactive nature of lithium metal leads to electrolyte decomposition at the electrodesurface, forming an insulating layer called the solid electrolyte interphase (SEI). The SEI coverage on the electrode surface is known to be nonuniform, causing uneven electrodeposition. Consequently, these lithium deposits result in concentration of the electric field at sharp tips, which is the cause of dendrite or whisker growth which degrades the battery. The high surface area metal deposition also causes faster parasitic reactions between the lithium metal and organic electrolyte (SEI growth), which is responsible for the rapid fade of battery capacity.

According to conventional understanding, the primary sources of instabilities in electrodeposition is diffusion limitations in ion transport processes both in the bulk electrolyte and at the electrode-electrolyte interfaces.[11,12] In native metals like zinc and copper, this phenomenon occurs only at very high current densities such that the deposition rate is higher than the ion transport rate. However, in reactive metals (like sodium or lithium), growth of whiskers is also observed at low currents due to SEI-related transport barriers. Many previous theoretical efforts have been focused on modeling the dendritic growth in a diffusion-limited condition by varying the transport properties like ion conductivity, relative mobility of anions and cations (transference number), and studying the effects from electrolyte modulus or electrode geometry.[13–21] Likewise, several experimental efforts have reported improved electrodeposition
stability for electrolytes with high transference number, conductivity, or modulus.[14,22–26] While the ion transport and mechanics are important determinants of morphological evolution of the metal electrode, other coupled factors like electrochemical kinetics and the electrostatic potential landscape can play a critical role.[27–29] For example, several experimental findings have reported the observation of fractal structures during electrodeposition even at rates much below the diffusion-limited current density.[11,12,30–32] This further indicates that transport parameters in the electrolyte may not be the sole determinant of morphological stability. The relative effect of the electrochemical kinetics and ion transport is particularly important considering the metal electrode does not have uniform conductivity on the surface (due to the presence of nonuniform SEI), which perturbs the surface morphology even at the earlier stages of deposition.[33] The physical undulations on the metal surface results in abrupt enhancement of local electric field causing the ions to be preferentially directed towards the metal tips, ultimately leading to unstable growth. In addition, a major challenge in understanding this phenomenon is the fact that transport and kinetics essentially rely on the same physical factors as ion concentration, viscosity, and temperature, among others. Past theoretical and experimental studies have discovered the relationship between lower exchange current density and larger Li deposition size.[34,35] While this study focused on just the electron transfer process,[35] our study took both the electron transfer and the ion transport processes into consideration. Specifically, we selected Damköhler number (Da) as the descriptor that unified both processes.

In this work, we leverage ultrafast scanning voltammetry and pulse-field gradient NMR to decouple the effects of kinetics and transport, respectively. Based on these analyses, we design an ionic polymer coating to be used as the electrode-electrolyte interface that stabilizes electrodeposition by enabling a uniform ion flux to the electrode and allows us to tune the Da number. We reveal that low Da number leads to larger Li deposition size in both ether and carbonate electrolyte, and improves short-term and long-term cycling performance both in Li|Cu and Li|NMC configurations.

2. Results and Discussion

2.1. Concept and Theoretical Understanding

The schematic in Figure 1a shows the central hypothesis of this paper. Barton and Bockris[36] previously considered a simple circuit model for the electrodeposition process. It represents the net overpotential ($\eta_{\text{total}}$) as a sum of the activation overpotential ($\eta_{\text{act}}$) and the diffusion overpotential ($\eta_{\text{diff}}$). The activation overpotential is associated with the electrochemical reaction at the electrode, described by the Butler–Volmer equation:

$$i = i_0 \exp \left( \frac{zF\eta_{\text{act}}}{RT} \right) - \exp \left( - \frac{zF\eta_{\text{act}}}{RT} \right)$$

(1)

where $i_0$ is the exchange current density, $a_e$ and $a_c$ are the anodic/cathodic charge transfer coefficient, and $z$, $R$, and $T$ are number of electrons, ideal gas constant, and temperature, respectively. The diffusion overpotential is associated with the transport parameters of the electrolyte, derived from the Nernst Equation:

$$i = i_0 \left( 1 - \exp \left( \frac{zF\eta_{\text{diff}}}{RT} \right) \right)$$

(2)

where $i_0$ is the limiting current density. A nondimensional Damköhler number (Da), can be defined as the ratio between the rate of electrochemical reaction ($i_0$) and the rate of ion transport ($i$). Since the charge transfer process in electrochemical reaction (Li$^+ + e^- \rightarrow Li$) is a surface phenomenon, it is dependent on the local electric field. The resultant electric field on an equipotential surface is understood to be dependent on the surface roughness, such that the ions are directed towards the tips of metal nucleates having high electrostatic potential. On the contrary, the flux due to ion diffusion at low current densities ($i < i_0$) has no preferential directionality either to the tips or valleys of the nucleates. Thus, the ion deposition morphology can be correlated with the Damköhler number:

$$Da = \frac{\text{electrochemical reaction}}{\text{ion transport}}$$

(3)

At small overpotentials, it can be also represented as:

$$Da = i_{\text{act}} / i_0$$

(4)

Increasing Da results in a higher rate of deposition at the tips of lithium nucleates, while reducing Da favors uniform surface morphology.

We use a 3D coarse-grained Brownian dynamics model to simulate lithium deposition under an applied voltage and to explore the effect of the Damköhler number on morphology. This model accounts for both diffusion and drift driven by the electric field. The potential field is obtained by solving the Poisson equation at each simulation step. The boundary conditions are defined by the positions of the existing lithium deposits, to accurately represent the effect of lithium morphology on the local electric field. Further details are available in the Supporting Information. When lithium ions contact a lithium metal surface or the current collector, a probability $p$ is assigned for successful deposition. This probability is closely connected to the exchange current density $i_0$. In the limit of fast kinetics ($p = 1$), growth is dendritic and porous (Figure 1b). This is due to the electrostatic forces attracting ions to growing lithium tips. The uniformity of the deposits can be quantified by the ratio of the deposited volume of lithium within the control volume to ideal close packing for the same volume, defined as the normalized density $\rho$. In the limit of slow kinetics or low Da, growth is uniform, dense, and non-dendritic. Lithium is initially attracted to dendritic tips but diffuses away before the reaction occurs, leading to randomized deposition. The rate of lithium deposition decreases at low Da, as expected. Therefore, decreasing Da can lead to more uniform lithium deposition at the cost of a lower charging rate for the same applied potential.

2.2. Polymer Coating Design

Based on the above discussion, we propose to incorporate an ionic polymer coating at the electrode-electrolyte interface, which
Figure 1. Concept and Brownian dynamics simulations: a) Schematic showing electrodeposition as a function of electrochemical kinetics and ion transport properties. Here, the circuit diagram indicates that the deposition overpotential is a sum of resistances due to diffusion and activation limitations. At a high Damköhler no., the electrodeposition is localized at the heterogeneous regions of electrodes, while deposition is believed to be uniform at lower values. b) Molecular dynamics simulations show the relationship between the rate and morphology with the deposition probability. A lower deposition probability (p) signifies a lower Damköhler no., where the deposited Lithium beads (insets) are seen to be uniformly stacked compared to the higher p.

2.3. Ionic and Electrochemical Properties

The lithium-ion solvation environment and transport properties in these ionic polymer networks in presence of the solvent mixture ethylene carbonate/diethylene carbonate (EC/DEC) were analyzed using NMR. The characterizations of polymers were specifically done in presence of the electrolyte solvent to mimic the conditions of the anodic interface in a battery and to rule out the differences in mechanics and SEI among the polymer samples when in swollen-state. [38] Figure S2, Supporting Information.
shows the $^7\text{Li}$ NMR intensity profiles at different immobilized salt content (here, all crosslinked polymers were soaked in the NMR tubes with excess electrolyte solvent: EC/DEC (1:1 by vol)). There are two important observations as the tethered salt content is varied: the peak intensity increases and there is a downfield (less-negative) shift. The progressive rise in intensity indicates the increase in the amount of tethered salt. We hypothesized that the downfield shift of $^7\text{Li}$-NMR peak is related to increased solvent-uptake of the polymer when the percentage of solvent-blocking PFPE polymer is decreased.

The $^7\text{Li}$-NMR peak is related to increased solvent-uptake of the polymer when the percentage of solvent-blocking PFPE polymer is decreased. The interfacial impedance was measured in a carbonate-based electrolyte (1 M LiTFSI in EC/DEC) when the electrode was coated with polymers of different salt content (Figure S3, Supporting Information). We found a polymer with higher salt content can improve the interfacial ion transport and decreasing the impedance. Although the interfacial impedance for the polymer-coated electrode is lower than that of the uncoated case, the Li diffusivity remain similar for 1.5 moles kg$^{-1}$ polymer swollen in solvent and the electrolyte (discuss in the below section). We note that the exchange current density can be calculated from the slope, such that:

$$i \approx \frac{i_o z_F}{RT \eta} \tag{5}$$

We plot the corresponding $i_o$ for the different samples in Figure 3a. It is observed that for the bare electrode, exchange current density is 15 mA cm$^{-2}$, while that of crosslinked PFPE (no
tethered salts) coated electrode is two orders of magnitudes lower, indicating that the deposition kinetics is significantly slowed down at the electrode. This observation implies that the polymer coating acts as a blocking interface to inhibit the lithium-ion reduction on the anode surface. The presence of grafted salt molecules (Li-SFTFSI) in the network, however, results in increased exchange current density. The progressive rise with increasing immobilized salt content signifies that the Li\(^+\) experiences a loosened solvation shell to undergo faster electrochemical reduction, which also confirms the \(^{7}\)Li NMR, as previously discussed. However, it is important to note that, unlike the significantly high lithium-ion mobility and conductivity in ionic polymer networks, the electrochemical reaction rates (as measured from the exchange current density) are still lower than that in the liquid electrolyte. For example, for the ionic polymer coatings with 1.5 moles kg\(^{-1}\) salts, the exchange current density is \(\sim 6\) times lower than that of bare electrode.

We further measured self-diffusion characteristics of lithium and grafted STFSI ions. Figure S6, Supporting Information shows a representative pulsed field gradient (PFG)-NMR fitting curve for the diffusion measurement of the 1.5 moles/kg salt-containing PFPE network that is soaked in excess EC/DEC solvent. Figure 3b plots the lithium-ion diffusivity in the left axis, measured using PFG NMR, while the right axis reports the Li-transference number \((t_{\text{Li}})\) for the corresponding ionic polymer networks. The Li diffusivities across the different salt concentrations are relatively high compared to the diffusivity values of lithium salts reported in the literature\(^{[12]}\) and also are similar for all concentrations measured in this study. For comparison, the lithium diffusivity using the same method for 1 M LiTFSI in EC/DEC is \(1.41 \times 10^{-6}\) cm\(^2\) s\(^{-1}\). Thus, the mobility of lithium ion in the ionic polymer network is similar to that in the liquid electrolyte, which is essential to enabling unhindered transport when used as a polymer electrolyte or as an electrode coating. The Li transference number in Figure 3b is calculated using \(t_{\text{Li}} = \frac{D_{\text{Li}}}{D_F}\), where \(D_{\text{Li}}, D_F\) are the diffusivities obtained from the pulse field gradient NMR measurements. Owing to the immobilization of the STFSI anions, \(t_{\text{Li}} > 0.5 (\approx 0.7)\) for all the polymer networks as compared to \(t_{\text{Li}} = 0.49\) for the liquid electrolyte (1 M LiTFSI in EC/DEC). The polymer electrolytes with high transference number can essentially eliminate space charge formation due to ion polarization even at relatively high current densities as reported by several theoretical and experimental studies\(^{[16,42]}\).

In our case, the coating significantly reduced the Damköhler number and therefore the charge transfer rate. In the following section, we show that coating with higher salt contents resulted in smoother lithium morphology and higher Coulombic Efficiency (CE), despite slightly higher exchange current densities. In another recent study on correlating kinetics to cyclability and lithium metal morphology in various liquid electrolytes, it was found that Li/Li\(^+\) equilibrium potential and the surface energy—thermodynamic factors modulated by the strength of Li\(^+\) solvation—underlie electrolyte-dependent trends.
Figure 4. Electrochemical performance in ether-based electrolytes: Nyquist diagrams of symmetric lithium cells obtained using impedance spectroscopy measurement without a) and with b) the ionic polymer coating on the lithium. The different results were obtained after varying rest times of the batteries. Electrolyte is 1 M LiTFSI in DME. c) Comparison of Coulombic efficiency measurements in Li||Cu configuration, using a modified Aurbach method, where the copper is coated with or without different ionic polymers and the bulk electrolyte utilized is 1 M LiTFSI in DME (grey) or 2 M LiTFSI in DME (red). d) Comparison of lithium morphology on copper electrode after depositing and stripping 5 mA cm\(^{-2}\) of lithium before re-depositing the same amount, using the electrolyte 1 M LiTFSI in DME. Coulombic efficiency measuring using a Li||Cu electrode for the polymer coated and bare copper cases at two different current densities of 1 mA cm\(^{-2}\) and 3 mA cm\(^{-2}\) f), with the plating time in both cases being 1 hour. The electrolyte utilized here is 1 M LiTFSI in DOL/DME with 1wt% LiNO\(_3\). g) Full cell cycling performance in 4 M LiFSI DME electrolyte with detailed cycling conditions noted in the graph.

Our observations with different salt content are consistent with this finding as we also found a weaker Li solvation environment by Li-NMR with higher salt content.

To appropriately understand the relative effects of the ion transport and electrochemical reaction at the interface, we calculate the approximate Da for all the samples in Figure 3c, where\(^{[17]}\)

\[ i_i = 2zF \frac{D}{(1 - t_{Li})} L \]  

Here, the corresponding concentration, diffusivity, and transference number were utilized for the different samples, and length (L) was taken to be 25 µm which is the typical inter-electrode distance in a battery. The experimental Da for the liquid electrolyte is two orders of magnitude higher than the ionic polymers, and there was no trend observed across different immobilized salt concentrations. This result suggests that the ionic polymers are excellent candidates to serve as artificial interfaces between the electrode and electrolyte to suppress the ion localization at heterogeneous regions of lithium electrode surface.

We also evaluated the Da number in an ether-based (1 M LiTFSI DME) electrolyte. Figure S7, Supporting Information shows the fitting of the exchange current densities from the CV data, while Figure 3d plots the extracted exchange current densities. The layer of salt-containing polymer coating can reduce the exchange current density by an order. The diffusivity of Li\(^{+}\) in either 1 M LiTFSI DME electrolyte or in polymer coating that is soaked in excess DME was shown in Figure 3e. At room temperature, the diffusivity of Li in either the electrolyte or the swollen polymer is similar. The Da number was also calculated for the ether the bare (in the electrolyte) or coated case, and we found the Da number of the coated sample is close to two orders of magnitude lower than the bare case (Figure 3f). This is consistent with our observation in the carbonate-based system. Here the transference number of Li in ether-based electrolyte is estimated to be 0.19, based on past literature.\(^{[44]}\)

Based on our understanding of Da number, we further evaluated our coating’s ability to affect Li deposition and battery cycling performance in both ether and carbonate electrolyte.

2.4. Stability in Ether-Based Electrolytes

We utilized the synthesized ionic polymer networks as an interfacial layer on the lithium metal electrodes in a symmetric cell configuration and analyzed the interfacial impedance using a bulk electrolyte (1 M LiTFSI in DME) after resting the cells. Figure 4a,b shows the Nyquist plots for lithium electrodes either bare or coated with the 1.5 moles kg\(^{-1}\) salt cont. polymer network. The resistance value for the neat electrolyte (without any coating) is lower than that of salt-containing polymer-coated one. We found the interfacial impedance of the polymer-coated sample stabilizes at 16 hours, while the bare electrode’s impedance continues to increase after 16 h. The interfacial impedance increase is attributed to the reaction at the interface and the formation of the SEI. The reaction layer reduces the ion transport rate at the electrode, reflected in the measured increased interfacial impedance. The reaction-based impedance increment is time-dependent and increases over time. For electrodes that are coated with polymer, a coating layer also reduces the ionic conductivity at the interface, which is reflected as the higher initial impedance for the...
ether electrolyte. The elevated impedance is not time-dependent and doesn’t increase over time. On the contrary, this coating layer limits the reaction between the electrode and the electrolyte and reduces the reaction-based impedance growth over time. As a result, impedance increase is slowed down with the coating present. This implies that the coating significantly blocks the liquid electrolyte access to the metal electrode. Yu et al.\textsuperscript{45} previously reported that polymers that limit solvent transport can prevent continuous side reactions between the bulk electrolyte and lithium metal electrode which cause capacity fade in reactive metal batteries. While it is important to prevent or limit the solvent access to the lithium electrode, the electrode-electrolyte interface should maintain unperturbed lithium-ion transport. Our design strategy of incorporating tethered salt molecules in the polymer networks is useful to enable high interfacial ion conduction. As seen in Figure S3, Supporting Information, the interfacial resistance progressively decreases as the salt content in the network increases. As previously observed using the diffusivity measurement from NMR experiments, the ionic polymer networks can maintain high lithium-ion mobility, thus the coatings facilitate transport from the bulk electrolyte to the Li electrode without significantly contributing to the interfacial resistance. The significant reduction in the interfacial impedance for 1.5 moles kg\textsuperscript{−1} salt-containing polymer coatings can also be attributed to the presence of a higher number of ionic (polar) sites on the non-polar PFPE polymer backbone to coordinate with the lithium ions and facilitate ion transport across the interface.

We examined the effect of the synthesized polymer coatings on the electrode in a lithium metal battery. Figure 4c shows the comparison of the coulombic efficiency for the neat electrolyte with that of polymer-coated electrodes. The measurement was done using a modified Aurbach method. The experimental details are provided in Methods. A typical voltage profile for the measurement is shown in Figure S8, Supporting Information. With the electrolyte 1 M LiTFSI in DME, there is successive improvement in the coulombic efficiency of lithium metal plating-and-stripping as the grafted salt concentration is increased in the polymer coating, which indicates that the ionic polymers suppress dendritic growth and chemical side-reactions of the lithium metal. It is further seen that, using a higher salt content in the liquid electrolyte (2 M LiTFSI/DME), the coulombic efficiency is higher, as previously reported in the literature;\textsuperscript{46} however CE of the ionic-polymer-coated electrolyte outperforms the bare electrode. Increasing the salt concentration reduces the amount of free solvent in the electrolyte, since Li salt is solvated by coordinating with the solvent molecule. This reduces the undesirable side reaction between Li metal and the solvent, which in turn increases the cycling performance.\textsuperscript{47} This result denotes the fact that the bulk electrolyte chemistry/conductivity plays an important role in lithium deposition that works in tandem with the polymer interfaces.

We further analyzed the morphology of lithium deposits using scanning electron microscopy (SEM). In this experiment, we plated 25 μm (5 mAh cm\textsuperscript{−2}) of lithium onto a copper electrode with and without the polymer coating and thereafter stripped and re-plated the same amount, before disassembling the battery for the SEM analysis using the electrolyte 1 M LiTFSI in DME. As shown in Figure 4d, the electrodeposits without the polymer coating (bare) are fibrous and comprises of heterogenous shapes. However, in the presence of a polymer coating with 0.9 moles/kg grafted salts, the morphology becomes relatively compact and uniform. Remarkably, the electrodeposition morphology with 1.5 moles kg\textsuperscript{−1} grafted salt is significantly more stable. We find the same observation for a larger area of observation using a lower magnification (as seen in Figure S9, Supporting Information). Previous literature reported a positive correlation between a lowered exchange current density and a more uniform Li deposition morphology in ether-based electrolyte.\textsuperscript{45} In this work, we described the interface with the Da number, which takes both ion transport and electron transfer into consideration, and we found a lowered Da number can result in a more uniform Li deposition morphology. Among the polymers with different salt content, we attributed the improved Li morphology at higher salt content to the elevated ionic conductivity. Past literature has reported on the importance of ionic conductivity on the Li deposition morphology, and argues that a higher ionic conductivity can reduce side reactions and result in a homogenous Li.\textsuperscript{47}

The long-term stability of the polymer coating during electrochemical cycling was evaluated in both the Li||Cu and the Li||NMC cell. At both the current density of 1 mA cm\textsuperscript{−2} (Figure 4e) and 3 mA cm\textsuperscript{−2} (Figure 4f), our polymer coating was able to stabilize the cycling CE in Li||Cu cells (electrolyte: 1 M LiTFSI in DOL/DME (1 wt.% LiNO\textsubscript{3})), while the uncoated cells experienced quick decay in the CE in the first 50 cycles for the 1 mA cm\textsuperscript{−2} current density condition, and 20 cycles for the 3 mA cm\textsuperscript{−2} current density condition. We further characterized our coating in Li||NMC full cell with a 4 M LiTFSI DME ether-based electrolyte. A high salt concentration ether-based electrolyte is chosen for its oxidative stability (Figure 4g).\textsuperscript{46} The polymer-coated full cell can maintain more than 90% of its original capacity after 100 cycles, while the cell with a bare Li electrode lost 10% of its initial capacity at ~30 cycles. The other two repetitions of the cell cycling results are shown in Figure S10, Supporting Information, and a similar trend of coating improving capacity retention was observed.

We also performed XPS (X-ray photoelectron spectroscopy) analysis on copper electrodes which were subjected to the same electrodeposition process of plating, stripping, and re-plating 25 μm (5 mAh cm\textsuperscript{−2}) of lithium in a Li||Cu cell with 1 M LiTFSI in DME electrolyte. The C– and F– XPS spectra in Figure S11 show that the uncoated copper has abundance of Li–F bonds compared to C–F groups, while in the polymer-coated samples, we find that the C–F intensities are stronger (present in PFPE and STFSI moieties). This implies the presence of the polymer coating even after the stripping and plating processes.

### 2.5. Stability in Carbonate-Based Electrolytes

To understand the ion concentration at the interface after soaking in electrolyte, we soaked polymers with different ion content in carbonate electrolytes for an extended period. We found the coating with 1.5 moles kg\textsuperscript{−1} salt concentration has higher ionic conductivity than the 0.9 moles kg\textsuperscript{−1} polymer. The conductivity is similar after 2 and 8 hours of soaking, indicating that we are measuring the steady-state ionic conductivity (Table S1, Supporting Information). We noted that the ion exchange has a limited effect on the ionic conductivity compared to the polymer coating.
The long-term stability of polymer coating was evaluated by monitoring the evolution of the interfacial resistance over time with and without the polymer coating. Specifically, we built symmetric lithium cells using the liquid electrolyte of 1 M LiPF$_6$ in EC/EMC with 10% FEC and measured the interfacial resistance growth over time using impedance spectroscopy. Figure 5a,b shows the Nyquist diagrams from impedance measurements in symmetric lithium cells with and without the ionic polymer coating (1.5 moles kg$^{-1}$ of grafted salts) using the same electrolyte. The presence of polymer coating significantly diminishes impedance growth as a function of time. At the end of 100 h rest, the cell without the coating has doubled the interfacial resistance over time compared with the coated case. The control showed higher interfacial impedance compared to the coated one in the carbonate electrolyte. Carbonate electrolyte can quickly build-up interfacial impedance in the time frame of 10–30 minutes. This short time-period is often hard to capture during the assembling and transportation of the coin cell. For coated symmetric cells in carbonate, the initial interfacial reaction is significantly slowed down, which results in lower initial interfacial impedance. This phenomenon is also observed when other coatings were applied in the carbonate electrolyte environment. The solvent-blocking nature of the coating is then coupled with the low Da number. The fundamental reason why a polymer coating lowers the electron transfer kinetics is the dielectric constant and the dampening of the electric field, as shown in our simulation and theoretical understanding. This reduces the probability of the self-accelerating dendritic Li deposition process. While a coating changes the dielectric environment of the interface, it simultaneously limits solvent access to the electrode surface. Therefore, the additional benefit of a low Da coating is slowing the interfacial reaction rate.

We used SEM to characterize the deposition morphology of Li under the influence of a polymer coating in the carbonate electrolyte environment. We found our polymer coating resulted in more homogenous Li deposition morphology while the uncoated one showed fibrous Li morphology (Figure 5c,d). This is similar to the trend we observed in ether-based electrolyte, and we attributed the improved Li morphology to the lower Da number at the interface.

The cycling stability of the ionic polymer coatings in Li||Cu configuration was analyzed using the same electrolyte of 1 M LiPF$_6$ in EC/EMC with 10% FEC at a current density of 0.5 mA cm$^{-2}$, with each plating cycle comprised of 2 h. The comparison of coulombic efficiency between the control (bare electrode) and polymer coating is presented in Figure 5e. It is seen that the ionic polymer coating shows improved performance for at least 150 cycles in comparison to the control that fails at ≈50 cycles. We have compared the coulombic efficiency of this coating with that reported in the literature in Table S2, Supporting Information. Finally, the polymer coated thin 25 μm lithium metal electrode (N = 5mAh cm$^{-2}$) was paired against a lithium nickel manganese cobalt oxide (NMC-532) cathode with a capacity (P) of 1.7mAh cm$^{-2}$ and the batteries (N/P = 3) were cycled using the electrolyte 1 M LiPF$_6$ in EC/EMC with 10% FEC. The corresponding capacity and coulombic efficiencies for the two different cases (with and without polymer coating) is plotted in Figure S12, Supporting Information, while the overall efficiency, measured by the formula:

$$CE = 100(1-N/n 	imes P)$$

where n is the cycle number until 80% fade, is plotted as bar chart in the inset. We observe that the polymer coating significantly enhances the lifetime of the full cell, in agreement with the findings.
from the electrochemical and electrodeposition results. Here, we
cycled our cells at a harsh condition: only 25 μm Li anode paired
with a standard carbonate electrolyte. Our cycling performance
is commensurate with literature-reported values using similar conditions.[55,56]

In addition to the harsh condition, we also cycled Li∥NMC full
cells with a less stringent condition (50 μm Li with calendared
cathode, Figure 5f). Similar to previous observations in ether-
based electrolyte, cells with our coating can maintain more than
90% of its capacity for more than 100 cycles, while the uncoated
one experienced early capacity fading (less than 90%) around 40
cycles. Other repetitions of the cycling data are shown in Figure
S13, Supporting Information.

3. Conclusion

In conclusion, we have shown that the kinetics of electrodeposition
is an important parameter in addition to ion transport. Using
Brownian Dynamics Simulations, we show that at a lower
rate of deposition kinetics, the deposition is significantly more
uniform, dense and compact, while a fast kinetics promotes den-
dritic growth. We built a physical model using synthesized poly-
mers: it comprises of crosslinked PFPE polymers that block elec-
trolyte solvent mass transport, while ensuring ion transport path-
ways via the tethered STFSI-anions. This coating layer served as
a well-defined interface to decouple ion and electron transfer
processes. The relative rate of kinetics and transport can be
quantified using a non-dimensional Damköhler number, which
was experimentally calculated using the electrochemical reaction
rate (exchange current density) using fast-scan voltammetry as
a well-defined interface to decouple ion and electron trans-
fer processes. The relative rate of kinetics and transport can be
quantified using a non-dimensional Damköhler number, which
was experimentally calculated using the electrochemical reaction
rate (exchange current density) using fast-scan voltammetry as
as well as transport properties (diffusion and transference number)
by NMR measurements. We find that polymer coatings on the
lithium electrode comprising of immobilized salts can promote
interfacial conductivity, while reducing the rate of electrochemi-
cal kinetics. Through tuning the salt content in the polymer, we
found a weaker Li solvation environment contributes to improved
battery performance. Through EIS, we found the additional ben-
efit of a low Da coating, which slows the interfacial reaction rate.
Furthermore, given a low enough Damköhler number, we found
the Li morphology can be further improved by increased interfa-
cial ionic transport. Owing to its unique physical and chemical
properties, this coating is successful in enhancing the morphol-
y of lithium deposition, which results in improved coulombic
efficiency and lifetime of a lithium metal battery in both ether-
based and carbonate-based electrolyte.

4. Experimental Section

Theoretical Calculations: A 3D coarse-grained Brownian dynamics
model was used for simulations of lithium deposition. Lithium cations
were represented as coarse-grained beads in an implicit solvent with uni-
form dielectric properties, moving under a voltage difference applied be-
 tween an anode located at the base of the simulation box and a cathode
at the top of the box. Periodic boundary conditions were applied at lateral
faces. The Poisson equation was solved at each step to determine electro-
static forces on the beads, with deposited lithium metal assumed equipo-
tential with the anode and local electroneutrality assumed. When lithium
cation beads came within a cutoff distance \( r_{\text{cut}} \) of the anode or a previously
deposited lithium metal bead, they deposited with a probability \( p \) as fixed
lithium metal hard spheres, and an additional cation was added at the top
of the box to maintain constant ion concentration. Cationic beads moved
each step due to random diffusion, Coulombic forces, and volume exclu-
sion forces. The Einstein relation was used to relate lithium cation mobility
and diffusivity. Simulations were conducted until a lithium metal bead was
deposited above a cutoff height. The normalized volumetric density of de-
posited lithium was calculated based on the number density and radius of
the lithium metal hard spheres and the box lateral area and cutoff height.

Material Preparation and Characterizations: The detailed synthesis pro-
cedure of the crosslinked polymer with different STFSI-Li content was pro-
vided in the Supplementary Information. Part of the procedure of synthe-
sizing STFSI-Li was adopted from previous work.[57] The NMR measure-
ments were done using \(^1\)H, \(^7\)Li, \(^19\)F NMR on a Varian Mercury 400 MHz
and Varian Inova 300 MHz instruments. In the molecular characterization
analysis using \(^1\)H NMR, the polymer was crosslinked inside the NMR tube
by exposure to UV light, as described in the synthesis section, thereafter
it was washed three times using THF and dried, before the tube was filled us-
ing deuterated Methanol for the measurement. The \(^2\)Li, \(^19\)F measurements
were done using the solvent ethylene carbonate (EC)/ diethylene carbon-
ate (DEC) (1:1 by vol.), instead of the deuterated Methanol. The PFG NMR
measurements for room temperature ion diffusion were done using a pre-
viously reported procedure.[58] The crosslinked polymers inside the NMR
tube was soaked with EC/DEC solvent. A convection-compensated pulse
sequence was used for \(^2\)Li, however, no convection compensation was
utilized for \(^19\)F. The area under the NMR curves was utilized for fitting.
Diffusion constants were obtained using a linear fit with the following
equation,[59]

\[
\frac{I}{I_0} = \exp \left( -\frac{\gamma^2 g^2 D (\Delta - \frac{\delta}{2})^2}{2} \right)
\]

In FTIR measurements using a Nicolet i50 FT/IR Spectrometer (Thermo
Fischer), the preformed crosslinked polymers were utilized. The
1 M LiPF\(_6\) EC/EMC electrolyte was purchased from Gotion. For each 1 mL
of the electrolyte, 100 μL of FEC was added (10% FEC). The 1 M and 2 M
LiTFSI DME electrolytes were prepared by adding 2 M and 2 M LiTFSI salt
into 1 mL DME solution.

Electrochemical Measurements: All electrochemical tests were done
using 2032-type coin cells (MTI). All cell fabrications were done in
Argon-filled glovebox. 750 μm Li foils (Alfa Aesar) were used for
Li∥Li and Li∥copper cells. 25 μm Li foils (Rockwood Chemicals) and
LiN\(_{0.5}\)MN\(_{0.5}\)CO\(_{3}\)O\(_{2}\) having capacity of 1.7 mAh cm\(^{-2}\) (obtained from Ar-
gonne National Lab) were used for Li∥Li∥NMC332 cells. 50 μm Li foil was
obtained from Uniglobe Kisco Inc., and the NMC 811 electrodes were pur-
chased from Targray. Celgard 2400 separators were used for all battery con-
figurations. For the polymer-coated lithium, a solution of 50 mg m\(^{-1}\) of
uncrosslinked polymer components in anhydrous THF was prepared in
an Argon-filled glovebox and it was 20 μL of the solution was drop-coated
on a precut lithium metal disc (dia. = 1 cm\(^2\)), thereafter it was exposed to
UV light (365 nm) for 10 mins. The coated lithium was dried at 70 °C
on a hot plate for at least 48 h inside the glovebox before utilizing for the
battery or electrochemical measurements. For the Li∥Cu measurements,
100 mg m\(^{-1}\) of the uncrosslinked polymer components were spin-coated
on copper discs (dia. = 1 cm\(^2\)) using THF solvent at a rate of 1000 rpm
for 30 s followed by UV light (365 nm) exposure for 10 mins. The coated
copper discs were baked at 70 °C under vacuum for 24 h, before transfer-
ing into the Argon-filled glovebox and re-baked at the same temperature
overnight, before the cell assembly. The thickness of the polymer coating
was obtained as \( \pm 1.2 \) μm, while that of the drop-coated case was reciproc-
cated on a silicon wafer that showed a polymer thickness of \( \pm 1.5 \) μm using
profilometer instrument. Four separate forms for electrolytes were used
for different types of measurements as described in the manuscript: 1 M
LiTFSI (Sigma–Aldrich) in DME (Sigma–Aldrich), 1 M LiTFSI in EC/DEC
(Sigma–Aldrich), 1 M LiPF\(_6\) in EC/EMC (10% FEC) (Gotion) and 1 M
LiTFSI in DOL/DME (1 wt.% LiNO\(_3\)) (Sigma–Aldrich). In all coin cells,
80 μL of electrolyte was utilized. The impedance and cyclic voltammetry
measurements were carried out on a Biologic VMP3 system, while the
cycling tests were done using Arbin Tester. The interfacial resistance of
the
polymer-coated, and uncoated lithium metal electrodes was measured using symmetric lithium cell using impedance spectroscopy in the frequency range of 7 Hz to 0.7 MHz with a sinusoidal voltage with a V_{rms} = 10 mV. The microelectrode-based CV measurements were done according to the procedure described in previous literature.[19,20] The tungsten-based microelectrode was built in-house that has a diameter of 23 μm that is embedded inside borosilicate glass. Before every use, the microelectrode was polished using a 0.1 μm diamond lapping disc and sonicated for 5 min in acetone. The measurement was done in a 20 ml vial bottle, with lithium as counter and a pseudo-reference electrode of Ag/AgCl.

For coulombic efficiency measurements, XPS, and SEM analysis studies, copper discs (1 cm²) were punched out and then coated with the polymers using the process mentioned earlier. The electrodes were thereafter transferred to the glovebox. In the coulombic efficiency (CE) measurements, the coated and uncoated copper electrodes were paired against lithium metal anode with a Celgard-2400 separator. The coulombic efficiency measurements are preceded by 10 charge and discharge cycles at a low current density of 0.02 mA cm⁻² between the voltages 0 to 1 V for preconditioning. In short-term CE tests, 5 mAh cm⁻² was deposited, stripped, and redeposited before 5 cycles of plate-strip using 1 mA cm⁻² capacity, and finally completely stripping the deposited lithium from the copper electrode. A description of this method can be found in previous literature.[20] The XPS (PHI VersaProbe I) and SEM (FEI Sirion) analysis was done on a 5 mA cm⁻² deposited lithium on copper electrode. Specifically, in these measurements, the coin cells were uncrimped inside the glovebox. The electrodes were rinsed using fresh DME before being placed in a sealed transfer vessel. The full cell measurement was done using Li||NMC532 configuration, where a 25 μm lithium metal separator was placed in a sealed transfer vessel. The full cell measurement was done using Li||NMC523 configuration, where a 25 μm lithium metal disc was coated by the drop-casted polymer in the glovebox (as described above). The cathode used was NMC532 with areal capacity of 5 mAh cm⁻². The cells were run between 4.2 and 2.7 V. In all measurements, the initial two cycles were performed at C/10, followed by a rate of C/3, where each charge cycle had a constant voltage step of 4.2 V following the constant current charging. All cycling tests were done at ambient conditions.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
S.C., Z.H., C.V.A., and P.R. contributed equally to this work. S.C., J.Q., Y. Cui, and Z.B. conceived the idea. S.C. designed and synthesized related polymers. S.C. and Z.H. performed and/or coordinated materials characterization and electrochemical cycling. C.V.A. and Y. Chen performed and analyzed NMR data. P.R. performed and analyzed the simulations. D.T.B. contributed to data analysis. All authors discussed and analyzed the data. S.C., Z.H., Y. Cui, and Z.B. wrote and revised the manuscript.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

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