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# Decoupling interfacial processes in the formulation of fluorine-free lithium metal batteries

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## Abstract

Fluorine additives in lithium metal batteries are often correlated with improved performance, yet lead to challenges associated with cost, health, and safety. In this work, we formulate a series of electrolytes that allow us to interrogate the physical and electrochemical properties of non-fluorinated and fluorinated anions (nitrate, bis(oxalato)borate, and hexafluorophosphate) on the reversible electrodeposition of Li metal via traditional surface characterization methods, spectroscopy, and electroanalytical techniques. When the salts are used in the moderate concentration regime (0.5 M Li), the solid electrolyte interphases (SEIs) generated during cycling are primarily solvent-derived and are statistically similar in terms of ionic transport properties. Nuclear magnetic resonance (NMR) in conjunction with transient voltammetry measurements indicate that Li metal CE is correlated with charge transfer, which is strongly influenced by Li<sup>+</sup> solvation structure. Specifically, we find that the nitrate anion displaces solvent molecules in the Li<sup>+</sup> solvation sphere, leading to tunable solvation/desolvation dynamics. We demonstrate that these metrics can be utilized to construct fluorine-free electrolytes containing lithium nitrate and lithium bis(oxalato)borate for high performance lithium metal anodes.

## Introduction

Modern electrolyte design for Li metal batteries (LMBs) requires controlling Li<sup>+</sup> solvation structure to improve Coulombic efficiency (CE).<sup>1-3</sup> Successful efforts to tune the solvation sphere around Li<sup>+</sup> rely heavily on fluorinated salts and solvents (e.g., high concentrations of lithium bis(fluorosulfonyl)imide (LiFSI), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), fluoroethylene carbonate (FEC), fluorinated ether diluents),<sup>4-8</sup> leading to a long-standing correlation between the properties imparted by fluorine in both the liquid electrolyte and the solid electrolyte interphase (SEI) on CE. For example, weakly coordinating solvents often contain fluorine atoms (e.g., FEC and fluorinated ethers, especially in combination with LiFSI) that do not strongly coordinate to Li<sup>+</sup> thus increasing the concentration of contact-ion pairs



(CIPs) and aggregates (AGGs) in solution compared to solvent-separated ion pairs (SSIPs).<sup>3,9-11</sup> These species shift the equilibrium potential of Li/Li<sup>+</sup> upward, minimizing electrolyte decomposition, thinning the SEI, and improving CE.<sup>12,13</sup> Likewise, altering the solvation structure within the electrolyte changes the chemical species that are delivered to the surface of Li metal during electrochemical cycling, allowing for chemical- and spatial-tuning of SEI structures.<sup>14</sup> Ultimately, this allows the CIPs and AGGs to enrich the SEI with inorganic phases within the “inner” portion of the SEI (i.e., closest to the electrode),<sup>15,16</sup> leading to a strong correlation between the amount of LiF in the SEI and CE.

However, the use of fluorinated electrolyte components (e.g., LiFSI, LiTFSI, fluorinated ethers) presents several issues, including cost,<sup>17</sup> toxicity,<sup>18</sup> and thermal instability.<sup>19</sup> For example, differential scanning calorimetry (DSC) measurements show that the thermal decomposition of LiFSI releases about twice as much heat as lithium hexafluorophosphate (LiPF<sub>6</sub>), presenting serious safety risks. In addition, many of these compounds and their degradation products are perfluoroalkyl substances (PFAS), (i.e., compounds that contain at least one perfluorinated carbon),<sup>20</sup> that are hazardous to the environment and human health. Further, their specific role and necessity for overall LMB performance has recently been called into question.<sup>21-23</sup> The correlation between LiF in the SEI and high CE is counterintuitive because LiF is a poor Li<sup>+</sup> conductor (bulk conductivity = 10<sup>-14</sup> S/cm),<sup>24</sup> suggesting that other features may be responsible for improved performance. For instance, recent work from Hobold and coworkers found a stronger positive correlation between Li<sub>2</sub>O vs LiF content in the SEI and CE, which is a more ionically conductive phase.<sup>22</sup> Further, additional spectroscopic work suggests that in high performance LMBs the LiF phase in the SEI undergoes structural changes (e.g., nanosizing, compositional doping).<sup>25,26</sup> These structural alterations result in superior interphasial transport properties, indicating that morphology and non-fluorinated chemistries may also benefit Li cyclability. Taken together, these data indicate that alternative low- to no-fluorine electrolyte systems may achieve similarly high cycling efficiencies for Li without the associated cost, health, and safety challenges.<sup>27-29</sup>

In this work, we formulate a series of fluorinated and non-fluorinated electrolytes to examine the role that non-fluorinated anions play in determining Li metal CE. We perform these experiments in the moderate concentration regime (0.5 M Li salt), which improves the cost- and density-related shortcomings of more concentrated electrolytes while still allowing us to tune Li<sup>+</sup> solvation environment. We use LiPF<sub>6</sub> to benchmark our systems and compare to various mixtures of lithium bis(oxalato)borate (LiBOB) and lithium nitrate (LiNO<sub>3</sub>), which offer the ability to passivate Al and achieve high ionic conductivity in the SEI, respectively.<sup>30-32</sup> Through a combination of nuclear magnetic resonance (NMR), electrochemistry, and surface analysis we find that the role of solvation and subsequent stripping/plating dynamics in moderately concentrated electrolytes dominates CE performance over SEI composition. Specifically, we find that the addition of NO<sub>3</sub><sup>-</sup> in electrolytes expedites the rate of lithium stripping, but that NO<sub>3</sub><sup>-</sup> alone results in poor plating, likely due to strong solvation sphere interactions. Thus, a balance in



solvation strength that properly weighs both solvation and desolvation needs must be met. We leverage this balance to formulate high CE ( $\sim 97.8 \pm 0.2\%$ ) fluorine-free Li||Cu half cells for LMB applications.

## Results

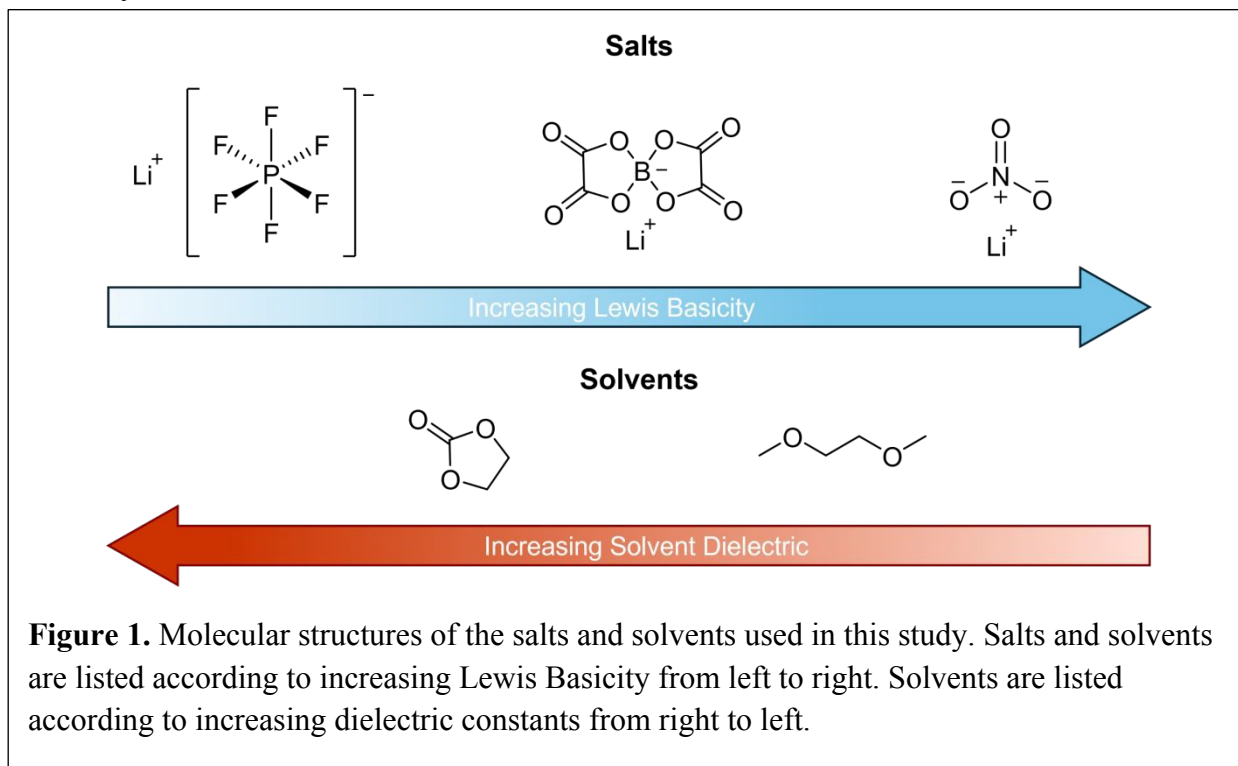
### *Electrolyte formulations*

We first prepared six electrolyte formulations that contain different molar ratios of 0.5 M (total salt concentration) LiBOB, LiPF<sub>6</sub>, and LiNO<sub>3</sub> in 1:1 (vol%) of ethylene carbonate (EC):1,2-dimethoxyethane (DME) (Figure 1). Herein, single salt formulations will be referred to based on their anion identity, e.g., LiBOB/LiPF<sub>6</sub> combinations will be referred to as PB, LiBOB/LiNO<sub>3</sub> combinations will be referred to as BN, and LiPF<sub>6</sub>/LiNO<sub>3</sub> combinations will be referred to as PN. Number ratios preceding a combination nomenclature correspond to the relative ratio of each salt (e.g., 1:4 BN represents a 1:4 LiBOB:LiNO<sub>3</sub> electrolyte).

At 0.5 M total Li salt concentration in EC:DME, we avoid solubility limitations associated with these salts, allowing us to systematically tune the Li<sup>+</sup> solvation environment. Due to the large donor number<sup>33</sup> associated with the anion, LiNO<sub>3</sub> displays poor solubilities in standard carbonate-based electrolytes, requiring ether-based solvents like DME for ion dissociation.<sup>34</sup> Beyond solubility constraints, DME displays low dielectric capabilities due to low polarity. Accordingly, we incorporate EC into our solvent mixture for its high dielectric constant ( $\epsilon \sim 90$ )<sup>35</sup> and enabling high ionic conductivity.



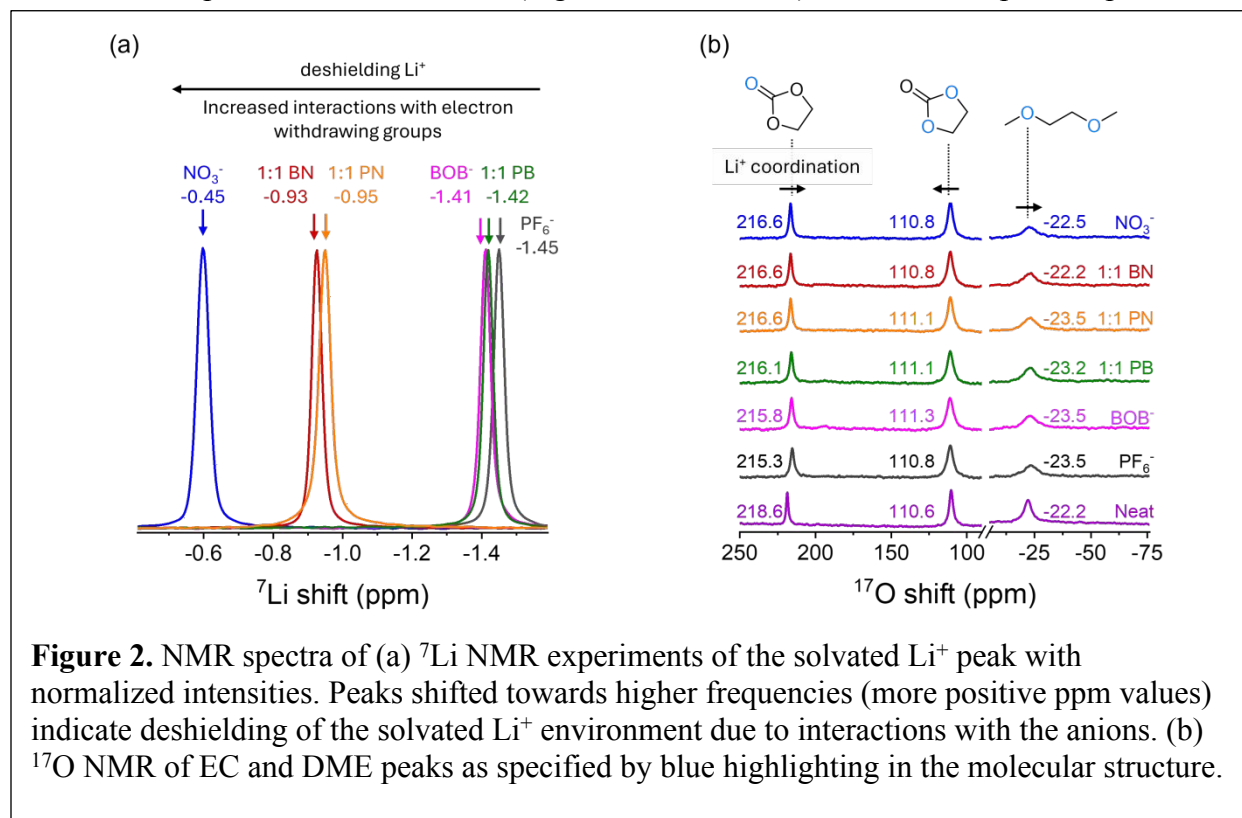
For our salts, we targeted mixed systems that we anticipated would exhibit different solvation environments about  $\text{Li}^+$ . Following Lewis basicity trends, we expect  $\text{PF}_6^-$  to weakly coordinate to the  $\text{Li}^+$  cation, favoring a solvent-rich  $\text{Li}^+$  inner solvation sphere. In contrast,  $\text{NO}_3^-$  is a strong Lewis base, and even at 0.5 M, may displace solvent molecules surrounding  $\text{Li}^+$  to form contact-ion pairs that alter SEI compositions and Li plating behavior.<sup>36</sup>  $\text{BOB}^-$  represents a midpoint in anion Lewis basicity, and may disrupt solvent and  $\text{NO}_3^-$  interactions in multicomponent systems. We theorize two possible outcomes for resultant SEI composition from this electrolyte series. Firstly, SEIs constructed from  $\text{BOB}^-$ -based decomposition products are known to have high structural stability but low ionic conductivity,<sup>30,32</sup> while conversely  $\text{NO}_3^-$ -based decomposition products are known to have comparatively high ionic conductivity.<sup>34</sup> Thus, BN compositions may result in structurally robust and highly ionically conductive SEIs, favorable characteristics for LMB performance. Alternatively, due to the moderate concentration of our electrolytes, we expect solvent molecule coordination to dominate the  $\text{Li}^+$  solvation shell, consequently leading to dominant solvent decomposition and thus a primarily organic SEI regardless of specific electrolyte formulation.



*Using  $^7\text{Li}$  and  $^{17}\text{O}$  Liquid-State NMR to Characterize  $\text{Li}^+$  Solvation Environment*



To probe  $\text{Li}^+$  solvation structure, we conduct a series of  $^7\text{Li}$  and  $^{17}\text{O}$  NMR experiments that measure the local structure around the  $\text{Li}$ -ion and the solvent molecules. Figure 2a shows the  $^7\text{Li}$  NMR spectra of 0.5 M  $\text{LiPF}_6$ ,  $\text{LiBOB}$ ,  $\text{LiNO}_3$ , 1:1 PB, 1:1 PN, and 1:1 BN. When these salts dissolve in EC:DME, electron donors on the solvent molecules (e.g., oxygen atoms from carbonyl and ether groups) interact with  $\text{Li}^+$ . Upon coordination, the  $\text{Li}^+$  environment is populated with more electron density, resulting in a chemical shift towards values lower than 0 ppm for all solvated  $\text{Li}^+$  species. We see the most negative shift for the  $\text{LiPF}_6$  electrolyte at -1.45 ppm, indicating that the  $\text{Li}^+$  cation environment is highly shielded with electron density from electron donating solvent molecules, and likely spends most of its time solvent-separated from the  $\text{PF}_6^-$  anion. The presence of solvent-separated  $\text{Li}^+$  cations is further supported by analysis of the  $^{17}\text{O}$  NMR spectrum of 0.5 M  $\text{LiPF}_6$  (Fig. 2b, S3, Table S2). In  $^{17}\text{O}$  NMR, peaks represent a



**Figure 2.** NMR spectra of (a)  $^7\text{Li}$  NMR experiments of the solvated  $\text{Li}^+$  peak with normalized intensities. Peaks shifted towards higher frequencies (more positive ppm values) indicate deshielding of the solvated  $\text{Li}^+$  environment due to interactions with the anions. (b)  $^{17}\text{O}$  NMR of EC and DME peaks as specified by blue highlighting in the molecular structure.

population-weighted average of the oxygen groups from free solvent and the oxygen atoms coordinated to  $\text{Li}^+$  due to rapid exchange between those two environments.<sup>37</sup> The magnitude of the chemical shift compared to that of the neat solvent (here, EC:DME) is related to the population difference between free and coordinated solvent molecules. In the case of the  $\text{LiPF}_6$  electrolyte solvent, we see the largest negative shift for the EC carbonyl ( $\Delta = -3.3$  ppm, Table S2) and the next largest for the DME ether ( $\Delta = -1.2$  ppm, Table S2), suggesting more coordination of  $\text{Li}^+$  to the EC carbonyl than the DME ether.

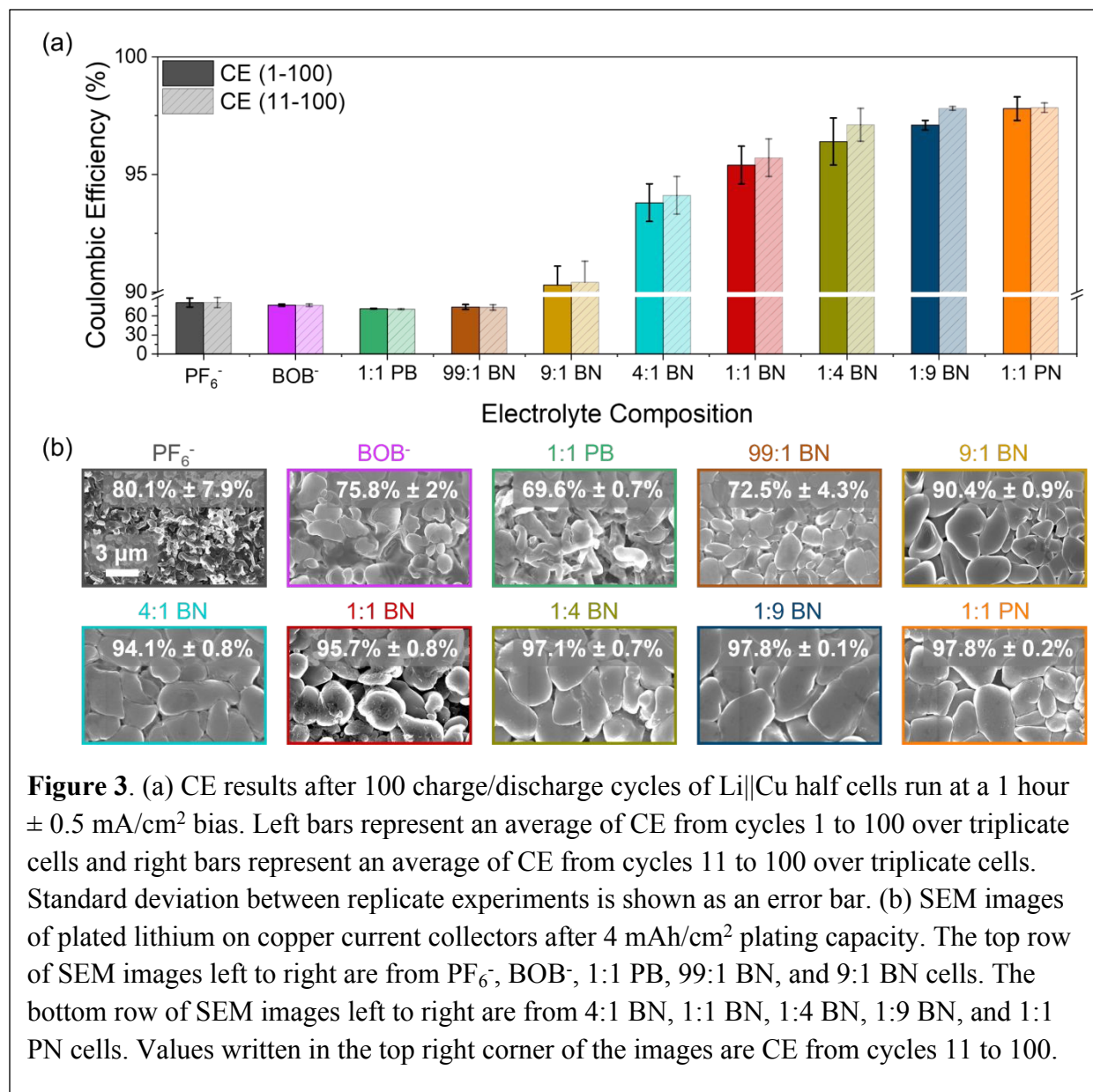
We see similar trends in  $^7\text{Li}$  NMR and  $^{17}\text{O}$  NMR for pure  $\text{LiBOB}$  and 1:1 PB electrolytes with large negative shifts to lower frequency upon solvation, which suggests that solvents are



coordinating to the  $\text{Li}^+$  ions. Compared to the pure  $\text{LiPF}_6^-$  electrolyte, pure LiBOB and 1:1 PB electrolytes show slightly more positive shifts in  $^7\text{Li}$  NMR and slightly more positive EC carbonyl shifts in  $^{17}\text{O}$  NMR, suggesting that the  $\text{BOB}^-$  anion may displace some small molecules in the  $\text{Li}^+$  solvation sphere. This change in peak shift magnitude upon addition of the  $\text{BOB}^-$  anion is less than 1 ppm in reference to the pure  $\text{LiPF}_6^-$  electrolyte for the  $^7\text{Li}$  NMR spectra. A minor change in chemical shift compared to the spectrum of the  $\text{PF}_6^-$  anion indicates that while more  $\text{BOB}^-$  interacts with  $\text{Li}^+$ , the solvation sphere is still primarily solvent dominated.

Upon addition of the  $\text{NO}_3^-$  anion (pure  $\text{LiNO}_3$ , 1:1 BN, and 1:1 PN), we see comparatively large deshielding towards higher frequency for the  $\text{Li}^+$  peak in  $^7\text{Li}$  NMR and the primary coordinating solvent oxygen peaks in  $^{17}\text{O}$  NMR. This deshielding effect is strongest in pure  $\text{LiNO}_3$  with a  $^7\text{Li}$  shift of +1 ppm when compared to that of  $\text{LiPF}_6$ , and an EC carbonyl shift of +1.3 ppm (again, when compared to the EC carbonyl resonance in  $^{17}\text{O}$  NMR for the  $\text{LiPF}_6$  electrolyte). In  $^7\text{Li}$  NMR, both 1:1 PN and 1:1 BN display slightly more modest shifts of +0.5 ppm and +0.7 ppm, respectively, with a similar value of +1.3 ppm for the EC carbonyl peak in  $^{17}\text{O}$  NMR. These results suggest that the  $\text{NO}_3^-$  anion is displacing solvent molecules about the  $\text{Li}^+$  cation at a larger fraction than any other probed anion. This interpretation is also supported by an analysis of the full-width at half maximum (fwhm) of the  $^{17}\text{O}$  NMR data (see Supplemental Note 1). Thus, even at low salt concentration values of 0.5 M, the  $\text{NO}_3^-$  displays strong coordination and primary solvation sphere occupation with  $\text{Li}^+$ .





**Figure 3.** (a) CE results after 100 charge/discharge cycles of Li||Cu half cells run at a 1 hour  $\pm 0.5$  mA/cm<sup>2</sup> bias. Left bars represent an average of CE from cycles 1 to 100 over triplicate cells and right bars represent an average of CE from cycles 11 to 100 over triplicate cells. Standard deviation between replicate experiments is shown as an error bar. (b) SEM images of plated lithium on copper current collectors after 4 mAh/cm<sup>2</sup> plating capacity. The top row of SEM images left to right are from PF<sub>6</sub><sup>-</sup>, BOB<sup>-</sup>, 1:1 PB, 99:1 BN, and 9:1 BN cells. The bottom row of SEM images left to right are from 4:1 BN, 1:1 BN, 1:4 BN, 1:9 BN, and 1:1 PN cells. Values written in the top right corner of the images are CE from cycles 11 to 100.

### Evaluating Li cyclability and deposition morphologies

To probe the impact this solvation trend has on LMB performance and surface chemistry, we evaluate Li metal CE in Li||Cu cells, examine the resulting plating morphology with SEM, and characterize the SEI with X-ray photoelectron spectroscopy (XPS). For electrochemical testing and morphological evaluation, we expand to ten different electrolyte formulations, including five additional BN formulations of ratiometrically increasing NO<sub>3</sub><sup>-</sup> content. Data for average CE values for Li||Cu cells over the course of 100 cycles are shown in Figures 3a, Figures S5-S15, and Table S5. We find that cells that incorporate little to no NO<sub>3</sub><sup>-</sup> (e.g., those with only PF<sub>6</sub><sup>-</sup>, BOB<sup>-</sup>, 1:1 PB, and 99:1 BN) exhibit lower CE values of 80.1%  $\pm$  7.9%, 75.8%  $\pm$  2%, 69.6%  $\pm$  0.7%, and 72.5%  $\pm$  4.3%, respectively, when averaged across cycles 11-100 (Figure 3a). When we increase the relative ratio of NO<sub>3</sub><sup>-</sup> while holding total salt concentration the same, we



consistently see an improvement in CE, with the 1:9 BN formulation reaching one of the highest average CE values of  $97.8\% \pm 0.08\%$  for cycles 11-100. This value is similar to the performance of 1:1 PN where the average CE across cycles 11-100 is also equal to  $97.8\% \pm 0.2\%$ . While we attempted to collect CE data on a cell containing only  $\text{LiNO}_3$  salt in the electrolyte, we repeatedly saw test-ending short circuiting at around the half-way mark of the 100-cycle measurement (Fig. S15).

SEM images of the ten different electrolytes taken after  $4 \text{ mAh/cm}^2$  plating capacity show differences in lithium plating morphologies (Figs. 3b, S16, S17). All BN formulations and 1:1 PN show well-packed boulder-like deposits. These boulders appear to grow in size as CE increases, with the high CE 1:1 BN and 1:1 PN morphologies showing large boulders of  $> 3 \mu\text{m}$  lateral size while the lower CE 99:1 BN morphology shows smaller boulders of  $< 3 \mu\text{m}$  lateral size. Pure LiBOB and 1:1 PB show markedly less uniform growths, with regions of high shape irregularity. The pure  $\text{LiPF}_6$  electrolyte shows the most dramatic morphological differences from the rest of the electrolyte series displaying granular filaments with plated regions of  $< 1 \mu\text{m}$  in lateral size. While large boulder-like morphology can be indicative of high CE in these formulations, plated lithium deposits alone cannot be used as a definitive predictor for cell performance. For example, both 99:1 BN and 9:1 BN cell types show boulder-like plating at  $< 3 \mu\text{m}$  lateral size but display vastly different average CE at  $72.5\% \pm 4.3\%$  and  $90.4\% \pm 0.9\%$  from cycles 11-100, respectively.

With a suite of electrolyte formulations that exhibit different electrochemical behavior, we next investigate (i) the impact on SEI compositions and (ii) charge-transfer kinetics to understand their correlation with reversible Li deposition.

#### *Using XPS to compare SEI compositions emerging from different solvation environments*

XPS analysis of the residual SEI remaining on Cu after 20 stripping/plating cycles shows that the SEI for all electrolyte formulations is dominated by solvent decomposition products (Table S6 shows that carbon and oxygen make up more than 50% of the total atomic composition). Based on our low salt concentration (0.5 M) and the predominance of SSIPs seen in NMR, we expect solvent molecules, particularly EC, to electrochemically decompose over salt anions like  $\text{NO}_3^-$ ,  $\text{PF}_6^-$ , and  $\text{BOB}^-$  during cycling. Even in the case of  $\text{NO}_3^-$  where the  $\text{Li}^+$  solvation sphere contains fewer organic molecules than the other electrolytes, the high concentration of free solvent molecules over solvated inorganic anions still results in a solvent-derived SEI.

From the high resolution C 1s scans we see the presence of C-C, C-O, C=O, and  $\text{Li}_2\text{CO}_3$  bonding environments at 285 eV, 287 eV, 288 eV, and 290 eV, respectively (Fig. S18, Table S7). In the 1:1 PN cell (CE 97.8%), the compositional breakdown falls between 5-8% for all four carbon environments. Conversely, for the other high performing cell, 1:1 BN (CE 95.7%), the  $\text{Li}_2\text{CO}_3$  environment dominates at 25%. Further, although nitrogen is an added component in the 1:1 BN



and 1:1 PN cells, the high resolution N 1s scan reveals similarly low nitrogen percent composition for all cells (Fig. S19, Table S8). Analysis of the high resolution O 1s data shows that for both 1:1 BN and 1:1 PN cells, the C=O bonding environment at 532 eV is the highest oxygen component at 32.6% and 15.3% total composition, respectively. However, the C=O environment is also the dominating oxygen component for the low CE BOB<sup>-</sup> cell (CE 75.8%) at 25.1%, and a large percentage of the low CE 1:1 PB cell (CE 69.6%) at 22.0% (Fig. S20, Table S9). Additional compositional features such as boron and phosphorus are not present in both high-performance cells (e.g., 1:1 PN shows phosphorus but no major boron environments, while 1:1 BN shows no major phosphorus but some boron environments), so we cannot point to any obvious overlap between high CE from high resolution XPS (Fig S21, S22, Table S10, S11). As expected, high resolution F 1s reveals that the BOB<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and 1:1 BN cells do not contain any fluorine, confirming that cross-contamination does not play a role in the observed electrochemical properties (Fig. S24, Table S13).<sup>38</sup>

We statistically rate the relationship between SEI atomic compositions for different electrolyte formulations and CE via a cosine similarity analysis. In this test, a calculated value of 1 indicates perfect similarity, and a calculated value of 0 indicates no similarity (Fig. S25, see Supporting Information for further discussion on the statistical method). We find that two high CE cells, 1:1 PN and 1:1 BN at 97.8% and 95.7%, have a low cosine similarity score of approximately 0.55, indicating low similarity for SEI composition. Additionally, two low CE performing cells, 1:1 PB and PF<sub>6</sub><sup>-</sup> at 69.9% and 80.1% CEs, show a low cosine similarity score of approximately 0.65. These low similarity scores indicate low correlation between performance and total SEI composition. In fact, a relatively high cosine similarity score of approximately 0.85 is found between 1:1 BN and 1:1 PB, two cells displaying opposite performances. Overall, these data indicate that there is minimal statistical correlation between the primarily solvent-based SEI atomic composition and CE for these electrolytes. Instead, we suspect that decreased solvent content in the solvation shell (where systems with less EC in the Li<sup>+</sup> solvation sphere, such as 1:1 PN show higher CE than cells with higher EC solvation content such as 1:1 PB) impacts charge-transfer processes at the interfaces that may be mechanistically probed via electroanalytical methods.

### *Measuring exchange current density in the presence of an SEI*

First, we measure stationary potentiostatic electrochemical impedance spectroscopy (PEIS), one of the most utilized electrochemical protocols in Li battery literature,<sup>39-41</sup> in the presence of a native SEI (we denote these measurements nPEIS). We collect nPEIS measurements at 5-hour intervals immediately after cell assembly over the course of a 65 hour rest period (Fig. S27). In general, all cells display an increase in resistance over time that we ascribe to native SEI formation and wetting (Fig. S28). Following the low-overpotential Butler-Volmer approximation,<sup>42</sup> this resistance increase corresponds to a decrease in exchange current density,



$j_0$ , as the SEI develops in all of the cells, indicating that the transport of  $\text{Li}^+$  ions through the SEI decreases with SEI growth (Fig. S28, Table S14). We find that across all time points, the 1:1 PN cell displays the largest value of  $j_0$  with the 1:1 PB cell showing the next highest values of  $j_0$  after the first measurement point. As 1:1 PN and 1:1 PB cells display opposite performance values, we do not see a clear trend between either the rate of SEI growth nor  $j_0$  in the presence of a native SEI at any of the time points and CE (Figs. S28).

Next, we measure PEIS following electrochemical deposition of Li (denoted ePEIS) to understand how transport of  $\text{Li}^+$  through the SEI generated after formation impacts  $j_0$ . We take ePEIS measurements every 10 minutes during the first  $1 \text{ mA/cm}^2$  charging period with a 1-minute rest inserted between the 10-minute  $1 \text{ mA/cm}^2$  bias and the stationary PEIS measurement. For each ePEIS experiment, we take a total of six PEIS scans, resulting in an overall charging capacity of  $1 \text{ mAh/cm}^2$  at the conclusion of the experiment (see Fig. S29 for experimental schematics and Fig. S30 for example Nyquist plots). All cell types display a decrease in measured resistance and thus an increase in  $j_0$  as a function of charge capacity (Fig. S31, Table S14). This decrease in resistance is most pronounced for poorly performing cells (e.g., the cell containing  $\text{NO}_3^-$  that short circuited, and the pure-component cells) and least pronounced for cells cycled with 1:1 PB and 1:1 PN electrolytes that exhibit CE values  $>95\%$ , possibly indicating that the electrochemically SEI stabilizes quickly in high performing cells (Fig. S31b). Increasing values of  $j_0$  across the measurements may suggest that the transport of  $\text{Li}^+$  ions through the electrochemically-derived SEI becomes easier with continued cycling. Alternatively, as we take ePEIS measurements after plating steps, the active surface area of the lithium at each measurement point may be changing according to the nonuniform deposition morphologies identified in Fig. 3. As such, the slight increase in  $j_0$  values may be due to increasing active surface area. Still, we note that the  $j_0$  values derived from ePEIS do not show substantial deviation between individual electrolyte formulations. For example, cells with opposing performance such as 1:1 PB and 1:1 BN show similar values of  $j_0 = 0.7 \pm 0.04 \text{ mA/cm}^2$  and  $0.6 \pm 0.07 \text{ mA/cm}^2$ , respectively at the 30 min measurement point, but have CE values of 69.9% and 97.8%. In other words, transport through the electrochemically formed SEI does not seem to be a largely variable factor in this electrolyte series.

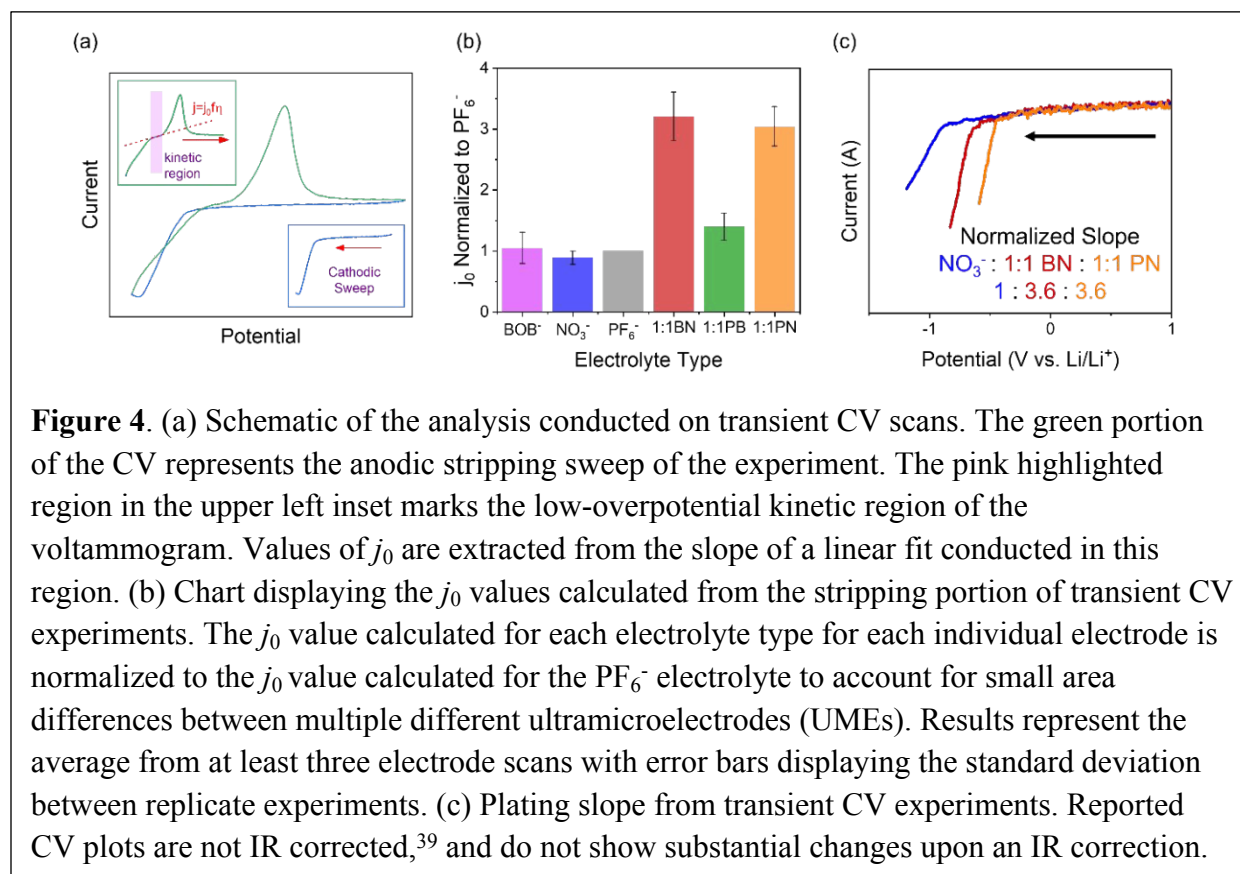
### *Measuring exchange current density in the absence of an SEI*

Next, we perform cyclic voltammetry (CV) measurements on tungsten ultramicroelectrodes (UMEs) at transient scan rates of  $10 \text{ V/s}$  (Fig. S33) to eliminate the presence of  $\text{Li}^+$  transport through the SEI and isolate charge transfer kinetics dominated by solvation/desolvation events. When we use rapid scan rates, the interface does not have time to form an SEI during an individual voltammetry sweep (unlike our EIS measurements). These measurements allow us to extract the  $j_0$  that corresponds to electron transfer by analyzing the low overpotential region of the stripping portion of the voltammogram (Fig. 4a).<sup>39,43</sup>



During analysis, we normalize  $j_0$  for each electrolyte type from individual electrodes to the results obtained from  $\text{PF}_6^-$  to account for uncontrollable differences in electrochemically active surface area between different electrodes. In Fig. 4b, we see that the addition of  $\text{NO}_3^-$  to  $\text{BOB}^-$ - and  $\text{PF}_6^-$ -based electrolytes to make 1:1 BN and 1:1 PN formulations results in a roughly 3-fold increase in  $j_0$  while the 1:1 PB cell displays a normalized  $j_0$  value similar to that of  $\text{BOB}^-$  and  $\text{PF}_6^-$  (Fig. 4b, Table S14). This substantial increase in  $j_0$  for 1:1 BN and 1:1 PN cells signifies that the addition of  $\text{NO}_3^-$  to the electrolyte greatly increases the rate of charge transfer in our mixed electrolyte formulations. Recall that these two formulations also exhibit high Li metal CE (95.7% and 97.8% for 1:1 BN and 1:1 PN, respectively).

While beneficial to the rate in mixed salt systems, the  $\text{NO}_3^-$  electrolyte on its own does not display a high value of normalized  $j_0$  as derived from the stripping portion of the voltammogram. However, it is important to consider stripping results in the larger context of plating as the stripping reaction is ultimately limited by the amount of lithium that is successfully plated onto the working electrode. Upon analyzing the plating region of the voltammogram, we see that the  $\text{NO}_3^-$  cell has a significantly smaller normalized plating slope than other  $\text{NO}_3^-$  containing formulations (Fig. 4c). This small slope indicates that plating from an entirely  $\text{NO}_3^-$ -based electrolyte is challenging. Therefore, in the case of the  $\text{NO}_3^-$  voltammogram, we have less Li metal plated on the UME that can be stripped during the return wave of the CV experiment, resulting in a correspondingly low value of calculated  $j_0$ . This small plating slope is unique to  $\text{NO}_3^-$ , and thus the availability of plated lithium to strip is not a major limitation for the other

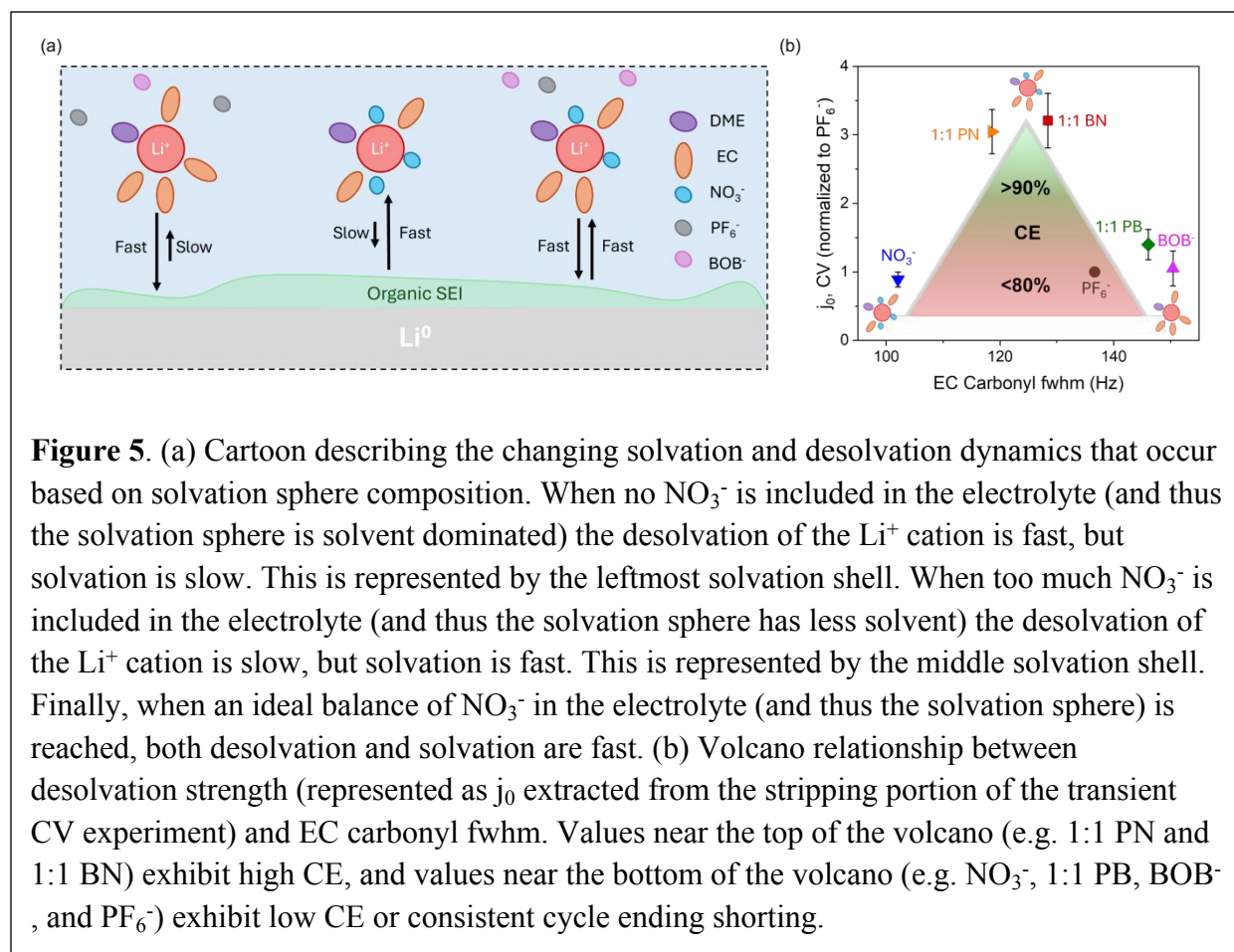


electrolyte formulations (Fig. S33). The larger plating slopes of 1:1 PN and 1:1 BN systems imply that adding an additional anion to a  $\text{NO}_3^-$ -containing system results in more facile plating.

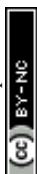
The  $\text{NO}_3^-$  anion is a strongly coordinating high donor-number salt and, as shown in our NMR results, dominates the solvation shell of  $\text{Li}^+$  over solvent coordination, meaning that  $\text{Li}^+$  solvation is stronger in  $\text{NO}_3^-$  containing electrolytes. This conclusion is consistent with previous literature, which suggests that when solvation of a  $\text{Li}^+$  cation is exceptionally strong, dendritic growth dominates, increasing the risk of short circuiting as is seen in the pure  $\text{LiNO}_3^-$  cell (Fig. S15).<sup>43</sup>

## Discussion

Our data indicates that solvation shell dynamics, specifically the ability for the  $\text{Li}^+$  cation to solvate and desolvate in a facile fashion, is a significant factor in CE performance for moderately concentrated, fluorine-free LMB electrolytes. We find that coordination strength of the solvation shell, and thus rate of the stripping/plating reaction, can be tuned with  $\text{NO}_3^-$  concentration (Fig. 5a). When ion-ion interactions are too strong, even in relatively diluted electrolytes, as is the case with the 100%  $\text{NO}_3^-$  system as indicated by the small CV plating slope,  $\text{Li}^+$  desolvation has a large barrier and plating is unfavorable. Analysis of  $^7\text{Li}$  and  $^{17}\text{O}$  chemical shifts and linewidths support that such a solvation sphere is composed of fewer solvent molecules compared to anion



**Figure 5.** (a) Cartoon describing the changing solvation and desolvation dynamics that occur based on solvation sphere composition. When no  $\text{NO}_3^-$  is included in the electrolyte (and thus the solvation sphere is solvent dominated) the desolvation of the  $\text{Li}^+$  cation is fast, but solvation is slow. This is represented by the leftmost solvation shell. When too much  $\text{NO}_3^-$  is included in the electrolyte (and thus the solvation sphere has less solvent) the desolvation of the  $\text{Li}^+$  cation is slow, but solvation is fast. This is represented by the middle solvation shell. Finally, when an ideal balance of  $\text{NO}_3^-$  in the electrolyte (and thus the solvation sphere) is reached, both desolvation and solvation are fast. (b) Volcano relationship between desolvation strength (represented as  $j_0$  extracted from the stripping portion of the transient CV experiment) and EC carbonyl fwhm. Values near the top of the volcano (e.g. 1:1 PN and 1:1 BN) exhibit high CE, and values near the bottom of the volcano (e.g.  $\text{NO}_3^-$ , 1:1 PB, BOB<sup>-</sup>, and  $\text{PF}_6^-$ ) exhibit low CE or consistent cycle ending shorting.



pairs that are weaker Lewis bases (like  $\text{BOB}^-$  or  $\text{PF}_6^-$ ). When solvation is too weak, as is the case for electrolytes with no  $\text{NO}_3^-$  anions, such as 1:1 PB,  $\text{BOB}^-$ , and  $\text{PF}_6^-$  as indicated by the low  $j_0$  value calculated from CV experiments, solvation of  $\text{Li}^+$  upon stripping is not a strong driving force and Li metal CE suffers.  $^7\text{Li}$  and  $^{17}\text{O}$  NMR indicate that the  $\text{Li}^+$  cations are increasingly coordinated by solvent molecules in these formulations. Thus, we use these datasets to construct a volcano-shaped plot to illustrate the balance between strength of solvation/desolvation and its relationship to  $\text{Li}^+$ -solvent interactions from  $^{17}\text{O}$  NMR that these electrolytes must meet to achieve high CE for Li, as is the case for our 1:1 BN and 1:1 PN formulations (Fig. 5b).

The correlation between CE and  $\text{Li}^+$  solvation dynamics rather than ionic transport through the SEI is likely impacted by the fact that all formulations evaluated in this work lead to solvent-derived passivation layers. No cell type displays a composition made of uniquely conductive SEI constituents. Instead, XPS shows that all SEIs exhibit high concentrations of phases like C=O (likely from EC reduction), an environment not expected to show any uniquely facile ionic conductivity. As such, the transport of the  $\text{Li}^+$  cation as probed by EIS techniques is similarly hindered in all cell types, and the solvation dynamics measured via transient voltammetry emerges as the unique determinant between cells.

From these above results, we can rationalize a few directives for the formulation of fluorine-free electrolytes for LMBs, particularly in the moderate salt concentration regime. Specifically, the influence of fluorine-derived phases in the SEI does not appear to dominate or play a significant role in determining Li metal CE. Therefore, adding fluorinated salts solely for the purpose of tailoring the SEI is ineffective at moderate concentrations and does not improve the CE of cells. Instead, adding a salt with a strongly coordinating anion such as  $\text{LiNO}_3$  should be utilized to tune the  $\text{Li}^+$  solvation sphere and improve the solvation and subsequent stripping kinetics of the reaction.

## Conclusion

Beyond the formulation of fluorine-free electrolytes for LMBs, this work highlights the importance of optimizing electrochemical methodology for a specific battery chemistry. While stationary PEIS is a prevalent electrochemical technique in literature, it very specifically probes ionic transport through the SEI, and can readily become subject to overfitting and over analysis if attempts are made to separate out specific components. Furthermore, ionic transport through the SEI is not necessarily the performance determinant process in every battery chemistry and thus PEIS is not always the ideal electrochemical technique for all investigations. Rather, for chemistries displaying similar SEIs across an electrolyte series, as is the case in this work, transient voltammetry coupled with solvation-probing spectroscopy to investigate solvation dynamics may be more appropriate, whereas ePEIS describes the rate of passivation. Following this logic, a similar stepwise investigation of different electrochemical techniques for higher concentration fluorine-free LMB electrolytes may reveal a different ideal electrolyte formulation



than that proposed here and would help to further our understanding of the role of specific electrolyte components on performance.

### Author Contributions

A.S.M and L.E.M conceptualized the study. A.S.M. carried out all experimental investigation and formal analysis. S.P. aided in data acquisition and formal analysis of XPS results. S.C.B. aided in the data acquisition of voltammetry results. A.S.M. and L.E.M. wrote the manuscript, which was reviewed and edited by all authors.

### Conflicts of interest

There are no conflicts to declare.

### Data availability

Data for this article, including NMR, XPS, and cycling data are available at The Open Science Framework at <https://doi.org/10.17605/OSF.IO/BKQAW>.

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# Decoupling interfacial processes in the formulation of fluorine-free lithium metal batteries

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## Data availability

Data for this article, including NMR, XPS, and cycling data are available at The Open Science Framework at <https://doi.org/10.17605/OSF.IO/BKQAW>. Additional data supporting this article have been included as part of the Supplementary Information. Supplementary information: Materials and further experimental details, Figures S1-S32, Tables S1-S14, Supplementary Note 1, depicting experimental setups, additional NMR data, electrochemistry, SEM, XPS, cosine similarity analysis.

