

# An Anion-Tuned Solid Electrolyte Interphase with Fast Ion Transfer Kinetics for Stable Lithium Anodes

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The spatial distribution and transport characteristics of lithium ions ( $\text{Li}^+$ ) in the electrochemical interface region of a lithium anode in a lithium ion battery directly determine  $\text{Li}^+$  deposition behavior. The regulation of the  $\text{Li}^+$  solvation sheath on the solid electrolyte interphase (SEI) by electrolyte chemistry is key but challenging. Here, 1 M lithium trifluoroacetate ( $\text{LiTFA}$ ) is induced to the electrolyte to regulate the  $\text{Li}^+$  solvation sheath, which significantly suppresses  $\text{Li}$  dendrite formation and enables a high Coulombic efficiency of 98.8% over 500 cycles. With its strong coordination between the carbonyl groups ( $\text{C}=\text{O}$ ) and  $\text{Li}^+$ ,  $\text{TFA}^-$  modulates the environment of the  $\text{Li}^+$  solvation sheath and facilitates fast desolvation kinetics. In addition, due to relatively smaller lowest unoccupied molecular orbital energy than solvents,  $\text{TFA}^-$  has a preferential reduction to produce a stable SEI with uniform distribution of  $\text{LiF}$  and  $\text{Li}_2\text{O}$ . Such stable SEI effectively reduces the energy barrier for  $\text{Li}^+$  diffusion, contributing to low nucleation overpotential, fast ion transfer kinetics, and uniform  $\text{Li}^+$  deposition with high cycling stability. This work provides an alternative insight into the design of interface chemistry in terms of regulating anions in the  $\text{Li}^+$  solvation sheath. It is anticipated that this anion-tuned strategy will pave the way to construct stable SEIs for other battery systems.

promising anode candidates for high-energy rechargeable batteries.<sup>[1]</sup> Nevertheless, the uncontrolled dendrite formation and poor reversible  $\text{Li}$  plating/stripping efficiency long hinder its practical application. Fundamentally, the reactive nature of  $\text{Li}$  metal can spontaneously trigger side reactions with the electrolyte and form a passivation layer (called solid electrolyte interphase, SEI).<sup>[2]</sup> The chemical heterogeneity and mechanical instability of SEI are generally considered as the reasons for dendrites formation.<sup>[3]</sup> Therefore, manipulating the electrolyte chemistry is considered as the most effective method, for it can directly impact the properties of SEI and alter  $\text{Li}^+$  deposition behavior.<sup>[4]</sup>

In the electrolyte,  $\text{Li}^+$  is solvated by solvents and anions to form the  $\text{Li}^+$  solvation sheath.<sup>[5]</sup> The  $\text{Li}^+$  solvation sheath can diffuse freely in bulk electrolyte, which has a higher probability of touching  $\text{Li}$  surface. Once touching  $\text{Li}$  metal surface, the solvent molecules and anions from

Metallic lithium ( $\text{Li}$ ), with a high specific capacity ( $3860 \text{ mAh g}^{-1}$ ) and the lowest redox potential ( $-3.04 \text{ V}$  vs standard hydrogen electrode), has been considered as the most

the solvation sheath will be reduced by electrons and compose the main components of SEI, thereby modulating  $\text{Li}^+$  transport and deposition behaviors.<sup>[6]</sup> Due to the diverse reactivity and proportion in the  $\text{Li}^+$  solvation sheath, the contributions from solvents and anions to the interface chemistry are distinctly different.<sup>[7]</sup> For the dilute electrolytes (esters and ethers), more solvent molecules dominated the  $\text{Li}^+$  solvation sheath due to high ratio of solvent/anions (e.g., 11.6:1 in 1 M lithium hexafluorophosphate ( $\text{LiPF}_6$ )-ethylene carbonate (EC)/diethyl carbonate (DEC)). The reduction species in the SEI depend on the reactivity and proportion of the components (solvents and anions) in the  $\text{Li}^+$  solvation sheath.<sup>[8]</sup> With a high proportion of solvent molecules in the solvation sheath, the as-obtained SEI was principally composed of solvent-derived organic species ( $\text{ROLi}$ ,  $\text{RCOOLi}$ , and  $\text{ROCO}_2\text{Li}$ ), accompanied with few inorganic species ( $\text{LiF}$ ,  $\text{Li}_2\text{S}$ , and  $\text{Li}_2\text{O}$ ) mainly originating from anions.<sup>[4a,9]</sup> Such solvent-derived SEI with highly resistive nature can bring about sluggish transport and uneven charge distribution of  $\text{Li}^+$ , resulting in notorious dendrite growth with low Coulombic efficiency (CE, 80%).<sup>[10]</sup> Inducing F atoms to the molecular structure of solvent can tune the reactivity of the  $\text{Li}^+$  solvation sheath.<sup>[11]</sup> For instance, fluoroethylene carbonate (FEC) has a relatively smaller lowest unoccupied molecular orbital (LUMO) than EC, which can be preferentially reduced to form a SEI

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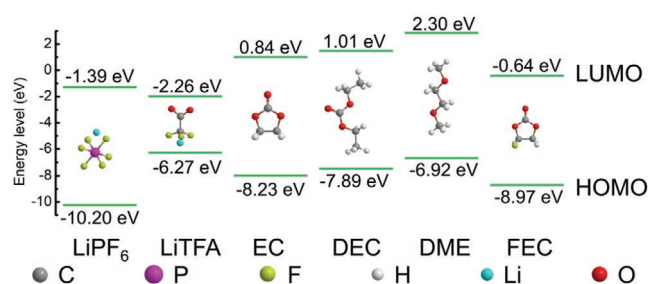
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with high proportion of LiF. The SEI can enhance the interfacial transport of  $\text{Li}^+$  and enable higher CE (90%).<sup>[12]</sup> Employing trifluoromethyl functional groups ( $-\text{CF}_3$ ) to the solvent molecules can adjust the LUMO energy of a SEI layer for stabilizing the Li metal anodes.<sup>[11]</sup> However, the CE performance is still deficient for practical applications of Li metal anodes. In addition, highly concentrated electrolytes have also been demonstrated to modulate  $\text{Li}^+$  solvation sheath for stable Li anode with high CE.<sup>[9,13]</sup> Due to the decreased solvent/salt ratio (almost 1:1 in highly concentrated electrolytes), more anions take in the  $\text{Li}^+$  solvation sheath and produce a SEI layer with a great amount of inorganic components, resulting in uniform  $\text{Li}^+$  transport with fast kinetics. Of course, highly concentrated electrolyte will raise the cost and bring about high electrolyte viscosity, which makes it hard for the practical application of Li metal anodes.<sup>[14]</sup> Recently, the reports have emphasized the importance of regulating the anions for stable Li metal anodes, such as tuning the  $\text{Li}^+$  solvation sheath by inducing  $\text{NO}_3^-$  anions and modulating the inner Helmholtz plane with the introduction of  $\text{NO}_3^-/\text{F}^-$  anions.<sup>[5,15]</sup> Therefore, developing new types of anions is highly desirable for constructing ideal SEI to modulate  $\text{Li}^+$  deposition. A desired Li salt should have a good dissociation in aprotic solvents and produce stable SEI to protect Li metal. Introduction of electron-withdrawing groups to anions, especially electronegative F atoms, can promote easy dissociation because of weak coordination ability between anions and cations.<sup>[16]</sup> Additionally, the electronegative F atom can adjust the frontier molecular orbitals for benefiting the stability of SEI.<sup>[11]</sup> To regulate the environment of  $\text{Li}^+$  solvation sheath, anions with carbonyl group ( $\text{C}=\text{O}$ ) or carboxyl group ( $\text{COO}^-$ ) are better choice for their strong coordination with  $\text{Li}^+$ .<sup>[17]</sup>

Here, an electrolyte based on 1 M lithium trifluoroacetate (LiTFA) in 1, 2-dimethoxyethane (DME)/FEC enables a high CE of 98.8% over 500 cycles. With strong coordination between carbonyl group ( $\text{C}=\text{O}$ ) and  $\text{Li}^+$ , TFA<sup>-</sup> can modulate the environment of  $\text{Li}^+$  solvation sheath and facilitate fast desolvation kinetics. During SEI formation, TFA<sup>-</sup> has a preferential reduction than solvents for its lower LUMO energy, contributing to an abundance of LiF and  $\text{Li}_2\text{O}$ . Such stable SEI renders low nucleation overpotential and fast ion transfer kinetics by reducing the energy barrier when  $\text{Li}^+$  diffuses through SEI. Therefore, uniform  $\text{Li}^+$  deposition with spherical morphologies is achieved. Coupled with lithium iron phosphate (LFP) and aggressive  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  (NCM622) cathodes, the full cells with limited Li as the anode enabled longer cycling stability than the control samples.

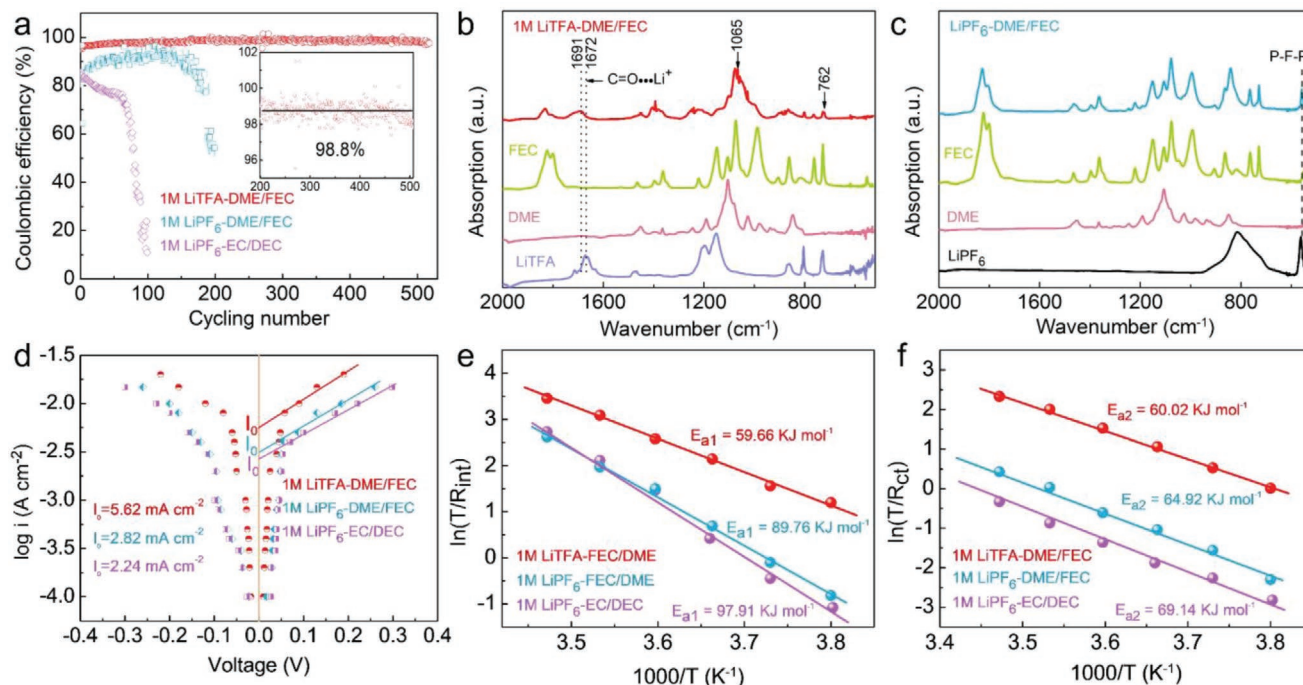
Based on frontier molecular orbital theory, the components of SEI highly depend on the LUMO of the solute or solvent in the electrolyte. Inspired for this, the molecular orbital energy of LiTFA was calculated by density functional theory (DFT) to explore its thermodynamic potential of forming a new interface. **Figure 1** shows the energy levels of LUMO and highest occupied molecular orbital (HOMO) of the solutes and solvents. The reduction potential decreased in the following order: LiTFA > LiPF<sub>6</sub> > FEC > EC > DEC > DME, indicating that LiTFA has a higher tendency to be reduced during SEI formation. Here, 1 M LiTFA was induced to DME/FEC to evaluate its performance. DME was chosen as the solvent for its low reaction activity with Li (LUMO: 2.30 eV). To enhance the oxidation ability of DME



**Figure 1.** Molecular orbital energies of solutes and solvents. The data for the solvents (e.g., EC, DEC, DME, and FEC) are taken from two previous reports.<sup>[19]</sup>

(oxidation potential less than 4.0 V vs  $\text{Li}^+/\text{Li}$ ) for the application in high-voltage cathodes,<sup>[5,18]</sup> FEC (HOMO:  $-8.97$  eV) was used as the corporate solvent.

To investigate  $\text{Li}^+$  plating/stripping behavior, the CE in the different electrolytes was evaluated by Li||Cu cells. In 1 M LiPF<sub>6</sub>-EC/DEC, the initial CE was only 85% and subsequently showed a fast decay at  $0.5 \text{ mA cm}^{-2}$  (**Figure 2a**). In this electrolyte, more solvent molecules dominated the  $\text{Li}^+$  solvation sheath and resulted in a SEI principally composed of solvent-derived organic species ( $\text{ROCO}_2\text{Li}$ ), as well as little LiF produced by decompositions of  $\text{PF}_6^-$ .<sup>[4a]</sup> Such solvent-derived SEI was deficient to construct a stable SEI for protecting Li anode, thereby leading to poor Li plating/stripping efficiency. With a lower LUMO energy than EC (0.84 eV), FEC ( $-0.64$  eV) has a higher potential to preferentially decompose and regulate the SEI with more LiF.<sup>[20]</sup> DME has a lower reactivity with Li metal for its higher LUMO energy (2.30 eV) than carbonates. After replacing EC/DEC to DME/FEC, to some extent, the CE just raised to 90%. Even replacing LiPF<sub>6</sub> to sulfimide-based Li salt (bis(trifluoromethane)sulfonimide lithium, LiTFSI), the CE and cycling stability were still not improved to a significant extent (**Figure S1**, Supporting Information). With lower energy of LUMO ( $-2.26$  eV), LiTFA was introduced to DME/FEC for regulating the reactivity of  $\text{Li}^+$  solvation sheath. As **Figure S2**, Supporting Information shows, although with a moderate ionic conductivity ( $5.4 \text{ mS cm}^{-1}$ ), 1 M LiTFA-DME/FEC achieved a significant higher CE of 95.5% for the initial cycle and gradually ramped up to  $\approx 98.8\%$  after 130 cycles. After increasing to higher current density and higher areal capacity (**Figure S3**, Supporting Information), the average CE in LiTFA-DME/FEC still exhibited higher Li plating/stripping CE than LiPF<sub>6</sub>-EC/DEC and LiPF<sub>6</sub>-DME/FEC electrolytes. To eliminate the effect of DME and FEC on the CE performance, we added the CE testing at  $0.5 \text{ mA cm}^{-2}$  with fixed  $1 \text{ mAh cm}^{-2}$  in other different electrolytes. As shown in **Figure S4**, Supporting Information, the electrolyte of 1 M LiTFA-DME enables higher CE than other electrolytes, indicating that LiTFA plays a critical role on improving the cycling stability of Li metal anode. The interactions among  $\text{Li}^+$ , anions, and solvent molecules were investigated by attenuated total reflection Fourier transform infrared (ATR-FTIR) with  $1 \text{ cm}^{-1}$  resolution. The spectra of LiTFA-DME/FEC electrolyte was depicted in **Figure 2b**, the emerging characteristic bands at 720 and  $1065 \text{ cm}^{-1}$  can be assigned as the aggregates of  $\text{Li}^+$  solvation sheath.<sup>[21]</sup> Notably, the  $\text{C}=\text{O}$  asymmetric stretching frequency of LiTFA exhibited



**Figure 2.** Electrochemical performance in different electrolytes. a) Li plating/stripping efficiency on a Cu working electrode in different electrolytes at a current density of  $0.5 \text{ mA cm}^{-2}$  with a fixed capacity of  $1.0 \text{ mAh cm}^{-2}$ . b) ATR-FTIR spectra of LiTFA, DME, FEC, and  $1 \text{ M LiTFA-DME/FEC}$ . c) ATR-FTIR spectra of LiPF<sub>6</sub>, DME, FEC, and  $1 \text{ M LiPF}_6\text{-DME/FEC}$ . d) Tafel plots for Li plating/stripping in different electrolytes. The Tafel plot was obtained by plotting the overpotential of galvanostatic Li plating/stripping to the natural log of the current density. e) and f) The activation energies of  $R_{\text{int}}$  and  $R_{\text{ct}}$  derived from Nyquist plots.

strong blue shift ( $19 \text{ cm}^{-1}$ ), which indicated strong interaction between  $\text{Li}^+$  and carbonyl oxygen group in the  $\text{Li}^+$  solvation sheath.<sup>[17,21]</sup> In contrast, for LiPF<sub>6</sub>-EC/DEC and LiPF<sub>6</sub>-DME/FEC, the typical characteristic PF<sub>6</sub><sup>−</sup> peak at  $562 \text{ cm}^{-1}$  (P-F-P) was almost the same as the undissolved salt, indicating minimal anions participating in the  $\text{Li}^+$  solvation sheath (Figure S5, Supporting Information and Figure 2c).<sup>[22]</sup> Therefore, the high CE and long cycling stability verify that TFA<sup>−</sup> takes in the  $\text{Li}^+$  solvation sheath and subsequently regulates the properties of SEI to minimize side reactions at Li/electrolyte interface.

In order to understand the process, the electrode kinetics in different electrolytes were investigated. As shown in Figure S6a, Supporting Information, the overpotential of initial  $\text{Li}^+$  plating/stripping in LiPF<sub>6</sub>-EC/DEC was 38 mV, but increased to 58 mV (50th) and 115 mV (100th). The large overpotential was arisen from the highly resistive SEI produced by severe side reactions at Li/electrolyte interface, which increased the ion transport resistance.<sup>[20]</sup> The polarization was slightly reduced in LiPF<sub>6</sub>-DME/FEC (1st: 34 mV, 50th: 47 mV, and 100th: 95 mV) due to low reactivity between Li and DME (Figure S6b, Supporting Information). While after replacing PF<sub>6</sub><sup>−</sup> to TFA<sup>−</sup> (Figure S6c, Supporting Information), the overpotential was greatly reduced (150th: 88 mV). To further evaluate the electrochemical cycling stability of Li metal in different electrolytes, the Li||Li symmetric cells were investigated (Figure S7, Supporting Information). It can be seen that the overpotential of Li||Li cells in LiTFA-DME/FEC electrolyte remains a lower overpotential at  $2 \text{ mA cm}^{-2}$  for more than 320 h, in contrast to the higher overpotential in the LiPF<sub>6</sub>-EC/DEC or LiPF<sub>6</sub>-DME/FEC electrolyte. This result suggested that TFA<sup>−</sup> produced

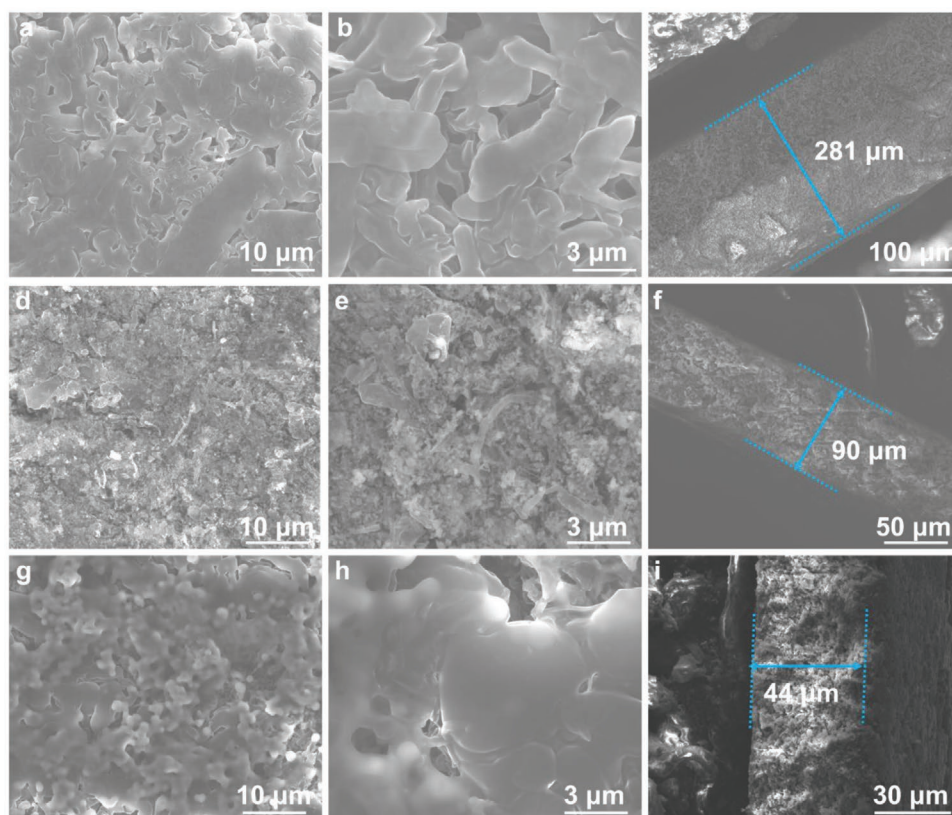
a conductive SEI for lower transporting resistance during  $\text{Li}^+$  plating/stripping. Li||Li symmetric cells were further assembled by galvanostatic cycling at various current densities to explore ion transfer kinetics at the interface (Figure 2d). The fast exchange current density in LiTFA-DME/FEC was almost two times larger than that in LiPF<sub>6</sub>-EC/DEC ( $2.24 \text{ mA cm}^{-2}$ ) and LiPF<sub>6</sub>-DME/FEC ( $2.82 \text{ mA cm}^{-2}$ ), indicating fast ion transfer kinetics during  $\text{Li}^+$  deposition.<sup>[23]</sup> The  $\text{Li}^+$  deposition process could be divided into four parts: diffusion of solvated  $\text{Li}^+$  in bulk electrolyte,  $\text{Li}^+$  desolvation at SEI/electrolyte interface,  $\text{Li}^+$  diffusion through SEI, and  $\text{Li}^+$  plating over Li surface ( $\text{Li}^+ + \text{e}^- = \text{Li}$ ).<sup>[15,24]</sup> The  $\text{Li}^+$  desolvation at SEI/electrolyte interface and  $\text{Li}^+$  diffusion through SEI layer are two rate-determining steps, where large energy barrier needs to be overcome.<sup>[25]</sup>

To measure the activation energy during  $\text{Li}^+$  deposition, the temperature-dependent electrochemical impedance spectroscopy (EIS) was carried out. The as-obtained EIS profiles and the fitted equivalent circuit from 263 to 288 K were shown in Figure S8 and Tables S1–S3, Supporting Information. Based on the Arrhenius equation:

$$k = \frac{T}{R_{\text{res}}} = A \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

where  $k$  represents the rate constant,  $T$  is the absolute temperature,  $R_{\text{res}}$  is the ion transfer resistance,  $A$  is the pre-exponential constant,  $E_a$  is the activation energy, and  $R$  is the standard gas constant. The activation energy ( $E_a$ ) is obtained by fitting the separated semicircles ( $R_{\text{int}}$ ,  $R_{\text{ct}}$ ) in Li||Li symmetric



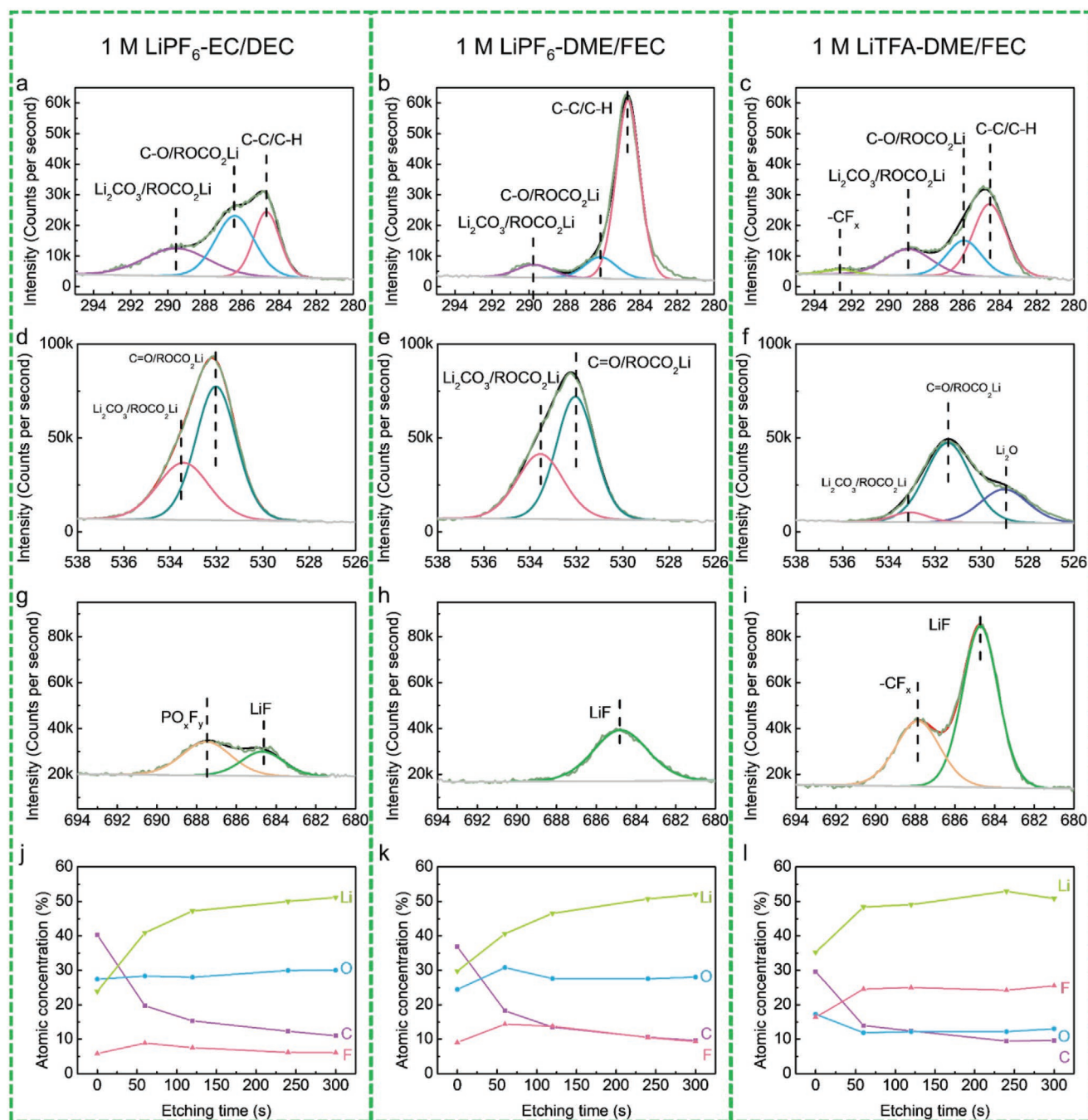


**Figure 3.** Morphologies of the Li surface in different electrolytes after 100 cycles at a current density of  $0.5 \text{ mA cm}^{-2}$ . a)–c) SEM images in  $\text{LiPF}_6\text{-EC/DEC}$ ; d)–f) SEM images in  $\text{LiPF}_6\text{-DME/FEC}$ ; g)–i) SEM images in  $\text{LiTFA-DME/FEC}$ .

cells (Figure 2e,f).  $R_{\text{int}}$  represents the resistance of  $\text{Li}^+$  across the SEI at medium frequencies;  $R_{\text{ct}}$  represents the resistance of  $\text{Li}^+$  desolvation at SEI/electrolyte interface at lower frequencies (also denoted as charge transfer).<sup>[6b,26]</sup> The rate constant  $k$  is determined by  $T$  and the fitted  $R_{\text{int}}$  or  $R_{\text{ct}}$  (Tables S1–S3, Supporting Information). In accordance with the fitted  $R_{\text{int}}$  and  $R_{\text{ct}}$ , the corresponding activation energy  $E_{\text{a1}}$  and  $E_{\text{a2}}$  are obtained by the Arrhenius equation.  $E_{\text{a1}}$ , represents the activation energy of  $\text{Li}^+$  when transporting through SEI, was reduced by more than 40% in  $\text{LiTFA-DME/FEC}$  ( $59.66 \text{ kJ mol}^{-1}$ ), compared with a larger energy barrier in  $\text{LiPF}_6\text{-EC/DEC}$  ( $97.91 \text{ kJ mol}^{-1}$ ) and  $\text{LiPF}_6\text{-DME/FEC}$  ( $89.76 \text{ kJ mol}^{-1}$ ) (Figure 2e). The decreased energy barrier proves that  $\text{TFA}^-$  in the  $\text{Li}^+$  solvation sheath has a significant effect on the  $\text{Li}^+$  transport kinetics of SEI.  $E_{\text{a2}}$  represents the energy barrier of  $\text{Li}^+$  desolvation from  $\text{Li}^+$  solvation sheath. Compared with  $\text{Li}^+$  desolvation energy in  $\text{LiPF}_6\text{-EC/DEC}$  ( $69.14 \text{ kJ mol}^{-1}$ ) and  $\text{LiPF}_6\text{-DME/FEC}$  ( $64.92 \text{ kJ mol}^{-1}$ ),  $\text{LiTFA-DME/FEC}$  ( $60.02 \text{ kJ mol}^{-1}$ ) showed a slightly decrease (Figure 2f). Generally, for aprotic polar solvent containing oxygen atoms, the coordination between  $\text{Li}^+$  and solvent is far stronger than its anion counterpart, giving rise to higher  $\text{Li}^+$  desolvation energy.<sup>[27]</sup> Suppose at  $263 \text{ K}$ , the  $R_{\text{ct}}$  and  $R_{\text{int}}$  for  $\text{LiPF}_6\text{-EC/DEC}$ ,  $\text{LiPF}_6\text{-DME/FEC}$ , and  $\text{LiTFA-DME/FEC}$  are  $4359$ ,  $2636$ ,  $260 \text{ } \Omega$  and  $774$ ,  $598$ ,  $79 \text{ } \Omega$ , respectively. The corresponding  $k_{\text{ct}}$  and  $k_{\text{int}}$  are  $0.060$ ,  $0.100$ ,  $1.012$  and  $0.400$ ,  $0.440$ ,  $3.330$ . Therefore, with strong coordination between  $\text{C=O}$  and  $\text{Li}^+$ ,  $\text{TFA}^-$  can replace part of solvent molecule to regulate the

environment of  $\text{Li}^+$  solvation sheath and facilitate fast ion transfer kinetics.

The impact of different electrolytes on morphology evolutions was characterized by the scanning electron microscopy (SEM). The top and cross-section view of Li metal anodes were obtained from  $\text{Li}||\text{Cu}$  cells at  $0.5 \text{ mA cm}^{-2}$  with fixed  $1.0 \text{ mAh cm}^{-2}$  after 100 cycles. In agreement with the report,<sup>[10]</sup> the plating Li in  $\text{LiPF}_6\text{-EC/DEC}$  showed needle-like dendrites with length of several micrometers (Figure 3a,b). Such notorious dendrite growth induced severe dead Li formation and continuous consumption of electrolyte, leading to a much thick cross-section of cycled Li ( $281 \text{ } \mu\text{m}$ , Figure 3c). For  $\text{LiPF}_6\text{-DME/FEC}$  (Figure 3d,e), the less-dendritic morphology was observed and the corrosive depth of Li decreased to  $90 \text{ } \mu\text{m}$  for a more stable SEI, which reduced the parasitic reactions at the Li/electrolyte interface (Figure 3f). In comparison, when  $\text{LiTFA-DME/FEC}$  was adopted, different morphologies of the cycled Li were observed. Due to the preferential reduction of  $\text{TFA}^-$  in the  $\text{Li}^+$  solvation sheath, a robust SEI reduced the energy barrier for  $\text{Li}^+$  desolvation and diffusion, contributing to a round-shaped Li morphology with a dense and uniform distribution (Figure 3g,h). Moreover, the thickness of the cycled Li metal was only  $44 \text{ } \mu\text{m}$ , indicating less dead Li or side reactions between Li and electrolyte (Figure 3i). Such Li morphology has two advantages: (1) higher CE performance, smaller surface area renders less side reactions between Li and electrolyte; (2) higher safety, spherical Li morphology induces less potential to penetrate through the separator.

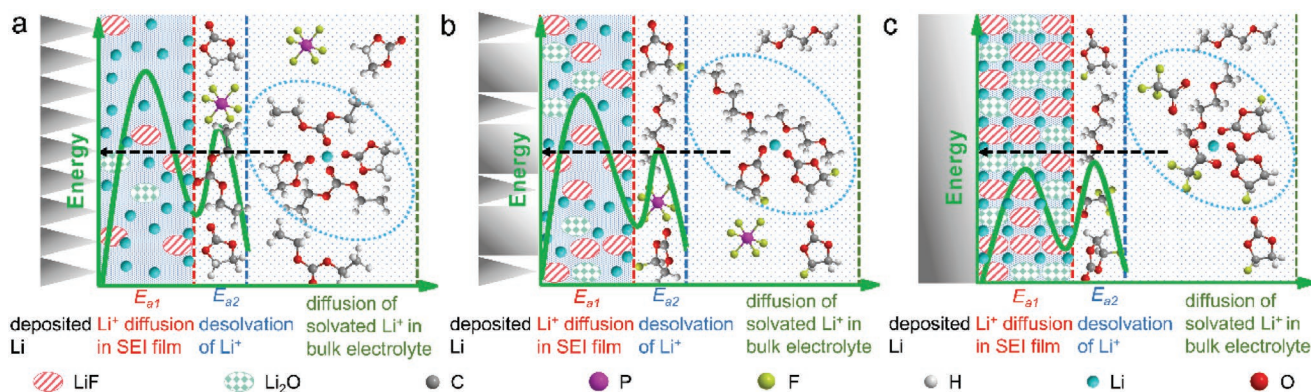


**Figure 4.** XPS characterization of the SEI components on cycled Li anodes in different electrolytes after 100 cycles. a), d), g), and j) are C1s, O1s, F1s spectra and atomic concentrations in the SEI of LiPF<sub>6</sub>-EC/DEC; b), e), h), and k) are C1s, O1s, F1s spectra and atomic concentrations in the SEI of LiPF<sub>6</sub>-DME/FEC; c), f), i), and l) are C1s, O1s, F1s spectra and atomic concentrations in the SEI of LiTFA-DME/FEC.

The chemical compositions of SEI on Li metal were further explored by X-ray photoelectron spectroscopy (XPS) to figure out the underlying mechanism of diverse ion transport kinetics in different electrolytes (Figure 4 and Figures S9–S11, Supporting Information). The signals of C 1s spectra for the three SEI films presented similar peaks corresponding to Li<sub>2</sub>CO<sub>3</sub>/ROCO<sub>2</sub>Li, C-O/ROCO<sub>2</sub>Li, and C–C/C–H centered at 289.5, 286.5, and 284.6 eV<sup>[28]</sup> (Figure 4a–c). The O 1s spectra (Figure 4d–f) were fitted into

Li<sub>2</sub>CO<sub>3</sub>/ROCO<sub>2</sub>Li (533.7 eV) and C=O/ROCO<sub>2</sub>Li (532.0 eV),<sup>[29]</sup> corresponding to the decomposition of solvent molecules. As sputtering time increased, organic ROCO<sub>2</sub>Li always dominated the SEI of LiPF<sub>6</sub>-EC/DEC and LiPF<sub>6</sub>-DME/FEC based on peak areas, as well as small amount of inorganic Li<sub>2</sub>O since 60 s, reflecting an uneven organic-dominated layer (Figure S10, Supporting Information). Interestingly, in SEI of LiTFA-DME/FEC, stable Li<sub>2</sub>O was detected from top to bottom, which can be

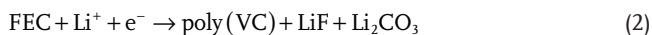




**Figure 5.** Schematics of the  $\text{Li}^+$  deposition process in different electrolytes. a)  $\text{LiPF}_6\text{-EC/DEC}$ , b)  $\text{LiPF}_6\text{-DME/FEC}$ , and c)  $\text{LiTFA-DME/FEC}$ . The aggregates in the light-blue dotted ovals represent the  $\text{Li}^+$  solvation sheath in the bulk electrolyte. The two bold dark-green waves correspond to the activation energies consumed on breakup of the  $\text{Li}^+$  solvation sheath at the SEI/electrolyte interface ( $E_{a2}$ ) and the diffusion of  $\text{Li}^+$  through the SEI film ( $E_{a1}$ ).

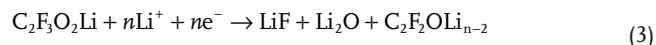
ascribed as the decomposition of  $\text{TFA}^-$ . In addition,  $\text{LiF}$  (arising from  $\text{LiPF}_6$ ,  $\text{FEC}$ , or  $\text{LiTFA}$ ) was detected at  $\approx 684.6 \text{ eV}$ <sup>[30]</sup> in all SEI films (Figure 4g–i). We also compared the atomic contents of elemental composition in different interfaces (Figure 4j–l). Before  $\text{Ar}^+$  sputtering, the SEI of  $\text{LiTFA-DME/FEC}$  showed a lower atomic content of C (30%) and O (17%), in contrast to the SEI of  $\text{LiPF}_6\text{-EC/DEC}$  (C: 41%, O: 27%) and  $\text{LiPF}_6\text{-DME/FEC}$  (C: 38%, O: 25%), implied a less organic content on the outer layer. As the sputtering time increased, the contents of C (organic species) in all SEI films showed a rapid decline within the first 60 s, but O almost kept stable. This was consisted with the report that most organic species ( $\text{ROCO}_2\text{Li}$ ) covered on the outer layer and partial  $\text{ROCO}_2\text{Li}$  were shifted to inorganic products ( $\text{Li}_2\text{CO}_3$  and  $\text{Li}_2\text{O}$ ) in the inner layer.<sup>[31]</sup> In the SEI of  $\text{LiTFA-DME/FEC}$ , inorganic  $\text{Li}_2\text{O}$  dominated the inner SEI rather than organic  $\text{ROCO}_2\text{Li}$  since etching for 120 s (Figure S10, Supporting Information). Notably, the atomic content of F (mainly  $\text{LiF}$ ) in SEI of  $\text{LiTFA-DME/FEC}$  was dramatically increased from 16% to 25% since etching for 60 s, which kept almost three times higher than that in  $\text{LiPF}_6\text{-EC/DEC}$  (9%) and two times higher than in  $\text{LiPF}_6\text{-DME/FEC}$  (14%). The bond strengths of  $\text{TFA}^-$  and  $\text{PF}_6^-$  were further calculated to confirm the difference. As shown in Figure S12, Supporting Information, the bond strength of C–F in  $\text{TFA}^-$  anions ( $203.29 \text{ kJ mol}^{-1}$ ) was remarkably weaker than that of P–F in  $\text{PF}_6^-$  anions ( $346.96 \text{ kJ mol}^{-1}$ ), suggesting the bond-breaking potential of producing a  $\text{LiF}$ -rich layer on Li metal surface. Therefore,  $\text{TFA}^-$  decomposed as the dominant reduction and produced a robust SEI with an abundance of  $\text{LiF}$  and  $\text{Li}_2\text{O}$ , which was responsible for lowering the energy barrier of  $\text{Li}^+$  diffusion and contributing to fast and uniform  $\text{Li}^+$  deposition.

Based on the reports, the components of  $\text{LiF}$  and  $\text{Li}_2\text{CO}_3$  may also be derived from the decompositions of  $\text{FEC}$ . The degradation mechanism is as follows:<sup>[32]</sup>

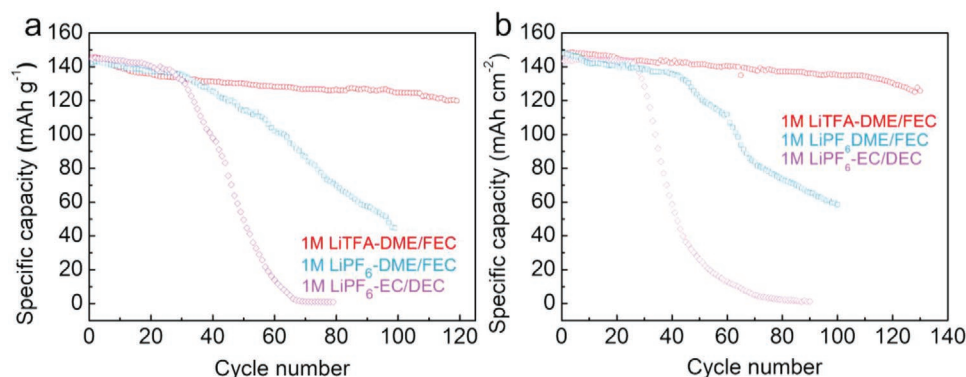


In order to confirm the sources of  $\text{LiF}$  and  $\text{Li}_2\text{CO}_3$ , XPS and surface-enhanced Raman scattering (SERS) were conducted.  $\text{LiF}$  detected at  $684.6 \text{ eV}$  in 1 M  $\text{LiTFA-DME}$  without  $\text{FEC}$  was characterized (Figure S13a, Supporting Information). For O 1s spectrum (Figure S13b, Supporting Information),  $\text{Li}_2\text{CO}_3$

detected at  $533.0 \text{ eV}$  may arise either from  $\text{LiTFA}$  or  $\text{DME}$  solvent. To further explore the source of  $\text{Li}_2\text{CO}_3$ , 0.1 M  $\text{LiTFA}$  was dissolved in  $\text{CH}_2\text{Cl}_2$  solvent (Figure S14, Supporting Information). Obviously, no peak was found at  $1090 \text{ cm}^{-1}$  (corresponding to  $\text{Li}_2\text{CO}_3$ <sup>[33]</sup>). Therefore, the possible degradation process of  $\text{LiTFA}$  is as following:



The reduction potential of  $\text{LiTFA}$  was further explored by cyclic voltammetry (CV) in 1 M  $\text{LiTFA-DME}$  using copper (Cu) electrode at a scanning rate of  $0.1 \text{ mV s}^{-1}$ . A distinct reduction onset potential was found at about  $1.1 \text{ V}$  (vs  $\text{Li}^+/\text{Li}$ ) (Figure S15, Supporting Information). And no similar reduction peak can be observed in the  $\text{DME}$  solvent without  $\text{LiTFA}$ . Therefore, the cathodic current starting from  $1.1 \text{ V}$  (vs  $\text{Li}^+/\text{Li}$ ) can be assigned to the reduction potential of  $\text{LiTFA}$ . The reduction species from  $\text{TFA}^-$ ,  $\text{PF}_6^-$ , or  $\text{FEC}$  in the  $\text{Li}^+$  solvation sheath can become portion of SEI and affect its properties (ion transfer kinetics, surface energy, etc.). In the bulk electrolyte of  $\text{LiPF}_6\text{-EC/DEC}$  (Figure 5a), the  $\text{Li}^+$  solvation sheath was composed of a great amount of  $\text{EC}$ ,  $\text{DEC}$  molecules, and little  $\text{PF}_6^-$ . Once the electrochemical reaction occurs, the  $\text{EC}$ ,  $\text{DEC}$  molecules, and  $\text{PF}_6^-$  in the  $\text{Li}^+$  solvation sheath will be reduced by electrons and compose the main components of SEI. The SEI was principally composed of more organic components ( $\text{ROCO}_2\text{Li}$ ) derived from  $\text{EC}$  or  $\text{DEC}$  solvents distributed in the outer layer, accompanied by few inorganic products ( $\text{Li}_2\text{O}$  and  $\text{LiF}$ ) in the inner layer. Before deposition,  $\text{Li}^+$  had to overcome large energy barrier to break up the  $\text{Li}^+$  solvation sheath. When  $\text{Li}^+$  transported through SEI, the highly resistive organic  $\text{ROCO}_2\text{Li}$  species with large energy barrier blocked  $\text{Li}^+$  diffusion and induced uneven charge distribution, subsequently leading to dendritic Li growth. After replacing  $\text{EC/DEC}$  to  $\text{DME/FEC}$  (Figure 5b), the energy barrier of  $\text{Li}^+$  desolvation had slightly decreased due to weaker solvation of  $\text{FEC}$  compared with  $\text{EC}$ .<sup>[34]</sup> The  $\text{Li}^+$  diffusion barrier across the SEI also be reduced. This can be ascribed to the increased content of  $\text{LiF}$  from  $\text{FEC}$  in addition to  $\text{PF}_6^-$  in the SEI, which enhanced the transport kinetics of  $\text{Li}^+$  and produced less-dendritic morphology. In contrast, for  $\text{LiTFA-DME/FEC}$  electrolyte (Figure 5c),  $\text{TFA}^-$  regulated the environment of



**Figure 6.** Electrochemical performances of Li metal anodes using LFP and NCM622 as cathode materials. a) Cycling stability of LFP||Li cells in different electrolytes when cycled at 0.5 C. b) Cycling stability of NCM622||Li cells in different electrolytes when cycled at 1 C.

Li<sup>+</sup> solvation sheath and facilitated fast desolvation kinetics. Additionally, with lower energy of LUMO than solvents, TFA<sup>-</sup> in the Li<sup>+</sup> solvation sheath was preferentially reduced to form a SEI with an abundance of LiF and Li<sub>2</sub>O from outer to inner layer. Hence, when Li<sup>+</sup> transported through SEI, the components (LiF and Li<sub>2</sub>O) played a significant role. LiF can prevent the electrons exchange, produce uniform diffusion field gradients, and afford uniform Li<sup>+</sup> flux.<sup>[35]</sup> Li<sub>2</sub>O was demonstrated to be beneficial for stabilizing the SEI film.<sup>[36]</sup> As a result, with an abundance of LiF and Li<sub>2</sub>O, more ion channels resulted in smaller energy barrier for Li<sup>+</sup> to get through. Fast and uniform spatial distribution of Li<sup>+</sup> flux finally got uniform deposition morphology.

The oxidation stability of various electrolytes was evaluated via CV. As shown in Figure S16, Supporting Information, the anodic current in LiTFA-DME/FEC remained stable until 4.2 V, which guaranteed it can be used with LFP. LFP with an areal capacity of  $\approx 1.5 \text{ mAh cm}^{-2}$  and Li ( $\approx 2$  times excess) were constructed as the cell. LFP||Li cells in the three different electrolytes all exhibited a flat plateau at 3.4 V vs Li<sup>+</sup>/Li, delivering an initial discharge capacity of  $\approx 142 \text{ mAh g}^{-1}$  (Figure S17, Supporting Information). As Figure 6a showed, the LFP||Li cells with LiTFA-DME/FEC electrolyte presents the best cycling stability, retaining 85% of the original reversible capacity after 100 cycles, with an average CE of 99.5% (Figure S18, Supporting Information), in comparison with <50% capacity retention for LiPF<sub>6</sub>-EC/DEC within 45 cycles. Though DME/FEC mitigates capacity fading, the LFP||Li cells still quickly decays to <50% of the original capacity after 75 cycles. The fast capacity decay is ascribed to the low Li plating/stripping CE in LiPF<sub>6</sub>-EC/DEC and LiPF<sub>6</sub>-DME/FEC electrolyte. In addition, the aggressive LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> (NCM622) cathode was also used to test the full cells. At 1 C ( $160 \text{ mA g}^{-1}$ ), the cell delivered an initial discharge capacity of  $\approx 145 \text{ mAh g}^{-1}$  in three electrolytes (Figure S19, Supporting Information). As shown in Figure S20, Supporting Information, the cells using LiPF<sub>6</sub>-EC/DEC exhibited an average CE of 98.1% in the first 23 cycles. However, beyond 23 cycles, it quickly dropped to <95%, accompanied by a fast capacity decay and terminated cycling after 70 cycles (Figure 6b). Though DME/FEC improved the CE and mitigated capacity fading, LiPF<sub>6</sub>-FEC/DME still experienced abrupt capacity drop after about 40 cycles. In comparison, the cells in LiTFA-DME/FEC retained a stable CE of 98.6% over

130 cycles before failing. The electrochemical performance was mainly ascribed to high Li plating/stripping efficiency.

In this study, stable Li metal with high CE has been achieved by introducing TFA<sup>-</sup> to the Li<sup>+</sup> solvation sheath and regulating the SEI with fast ion transport kinetics. With strong coordination with Li<sup>+</sup>, TFA<sup>-</sup> can replace part of solvent molecule to form the solvation sheath structure, leading to lower energy barrier for Li<sup>+</sup> desolvation. Additionally, due to lower energy of LUMO than solvents in Li<sup>+</sup> solvation sheath, TFA<sup>-</sup> has a preferential reduction to produce a stable SEI with an abundance of LiF and Li<sub>2</sub>O. Such SEI effectively reduces the energy barrier for Li<sup>+</sup> diffusion, contributing to lower nucleation overpotential and faster ion transfer kinetics. As a result, homogeneous Li<sup>+</sup> transport across the interface accounts for a uniform Li<sup>+</sup> deposition and high cycling stability. This work not only provides fresh insight on regulating the reactivity of anions in the Li<sup>+</sup> solvation sheath to manipulate the interface chemistry and alter Li<sup>+</sup> deposition behaviors, but also paves new way on constructing stable SEI for high-energy-density materials.

## Experimental Section

**Materials:** CH<sub>2</sub>Cl<sub>2</sub> and LFP materials were purchased from MACKLIN and used as received. EC, DEC, DME, FEC, LiTFA, LiTFSI, and LiPF<sub>6</sub> were purchased from Sigma-Aldrich.

**Electrochemical Measurements:** The Li||Cu cells were assembled or disassembled in an Ar-filled glove box with oxygen and water contents below 0.1 ppm. Coin cells of 2025 type were used as the Li||Cu, Li||Li symmetric, LFP||Li, and NCM||Li cells. For the Li||Cu cells, Li metal was used as the counter and reference electrodes while a Cu substrate was used as the working electrode. The cells were cycled in the voltage range  $-0.5$  to  $1.0 \text{ V}$  (vs Li<sup>+</sup>/Li) at current densities of  $0.5 \text{ mA cm}^{-2}$  with a fixed capacity of  $1.0 \text{ mAh cm}^{-2}$  by a LAND galvanostatic device. The CE is defined as charging capacity over discharging capacity. For LFP||Li and NCM||Li cells, Li pre-deposited on the Cu substrate at  $\approx 3.0 \text{ mAh cm}^{-2}$  was used as the anode. The LFP ( $\approx 1.5 \text{ mAh cm}^{-2}$ ) and NCM ( $\approx 1.1 \text{ mAh cm}^{-2}$ ) electrodes were prepared by casting a slurry mixture containing 85 wt% active material, 10 wt% Super P, and 5 wt% polyvinylidene fluoride binder (PVDF) in *N*-methyl-2-pyrrolidone onto a carbon-coated aluminum (Al) foil. Celgard 2500 polypropylene membranes were used as the separator for the Li||Cu, LFP||Li, and NCM||Li cells. Liquid electrolyte of 30  $\mu\text{L}$  (1 M LiTFA-DME, 1 M LiTFA-DME/FEC, 1 M LiTFA-EC/DEC, 1 M LiPF<sub>6</sub>-DME/FEC, 1 M LiPF<sub>6</sub>-DME/EC, or 1 M LiPF<sub>6</sub>-EC/DEC) was used for the coin cells.

The ratio of DME:FEC was set at 7:3 and 1:1 for EC:DEC by volume. CV and EIS measurements (10 mV,  $10^5$ – $10^0$  Hz) were performed using a VSP-300 multichannel workstation.

**Characterization:** The Li deposited on the Cu substrate was protected by an Ar atmosphere in a homemade container to avoid contact with air during the transfer process before characterization. The morphologies of the samples were characterized by SEM (FEI Nova Nano-SEM 430, 10 kV). XPS analysis was performed using an ESCALAB 250 instrument with Al K $\alpha$  radiation (15 kV, 150 W) under a pressure of  $4 \times 10^{-8}$  Pa. The ionic conductivity of the different electrolytes was measured by a FE30 at room temperature. All samples were rinsed with DME to remove residual electrolyte, then dried under vacuum. Surface-enhanced Raman scattering was performed using a Jobin Yvon Lab RAM HR800 with a 632.8 nm He–Ne laser. For the surface-enhanced Raman spectroscopy sample, a commercial silver (Ag) foil was immersed in a freshly prepared 12% HNO<sub>3</sub> solution for 5 s. A sponge-type surface with a high degree of roughness was thus created to enhance the signal. ATR-FTIR spectra were recorded on a Nicolet iS5 iD7 ATR spectrometer equipped with a diamond KBr beam splitter. An empty ATR cell blanketed with argon was used to collect the background spectrum.

**Theoretical Calculations:** The chemical structures, bond strengths, and molecular orbital energy levels of the selected solutes and solvents were calculated using the DFT method implemented in the Vienna ab initio simulation package,<sup>[37]</sup> based on the generalized gradient approximation of Perdew–Burke–Ernzerhof with a plane wave energy cutoff of 400 eV.<sup>[38]</sup>

## 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.

## Keywords

anions, energy barriers, lithium metal anodes, solid electrolyte interphase, solvation sheaths

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