# 50C Fast-Charge Li-Ion Batteries using a Graphite Anode

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Li-ion batteries have made inroads into the electric vehicle market with high energy densities, yet they still suffer from slow kinetics limited by the graphite anode. Here, electrolytes enabling extreme fast charging (XFC) of a microsized graphite anode without Li plating are designed. Comprehensive characterization and simulations on the diffusion of Li<sup>+</sup> in the bulk electrolyte, charge-transfer process, and the solid electrolyte interphase (SEI) demonstrate that high ionic conductivity, low desolvation energy of Li<sup>+</sup>, and protective SEI are essential for XFC. Based on the criterion, two fast-charging electrolytes are designed: low-voltage 1.8 M LiFSI in 1,3-dioxolane (for LiFePO₄ ||graphite cells) and high-voltage 1.0 м LiPF<sub>6</sub> in a mixture of 4-fluoroethylene carbonate and acetonitrile (7:3 by vol) (for LiNi0.8Co0.1Mn0.1O2 graphite cells). The former electrolyte enables the graphite electrode to achieve 180 mAh  $g^{-1}$  at 50C (1C = 370 mAh  $g^{-1}$ ), which is 10 times higher than that of a conventional electrolyte. The latter electrolyte enables LiNi0.8Co0.1Mn0.1O2||graphite cells (2 mAh cm<sup>-2</sup>, N/P ratio = 1) to provide a record-breaking reversible capacity of 170 mAh g<sup>-1</sup> at 4C charge and 0.3C discharge. This work unveils the key mechanisms for XFC and provides instructive electrolyte design principles for practical fast-charging LIBs with graphite anodes.

# 1. Introduction

As the most advanced and portable energy storage devices, lithium-ion batteries (LIBs) have promoted the rapid development of electric vehicles (EVs) over the past few years.<sup>[1]</sup> Compared to

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gasoline cars (GCs), EVs are more environmentally friendly, energy-efficient, and economical. However, one prominent drawback for current EVs is the long wait time for battery charging from the empty to fully charged state, while it only takes a few minutes to fill up the GCs. In this context, "extreme fast charging" (XFC)<sup>[2]</sup> is proposed by the US Department of Energy with the specific requirement of 15 min recharging time (at the rate of 4C) to ensure mass adoption of EVs.

So far, commercial LIBs using graphite anodes and ethylene carbonate (EC)-based electrolytes are impossible to achieve XFC without Li plating because the operating potential of graphite is easily lower to 0 V versus Li/Li<sup>+</sup> at high rates.<sup>[3]</sup> A myriad of attempts is dedicated to the structural modification of the graphite to improve the rate performance, such as reducing tortuosity<sup>[4]</sup> and increasing the porosity.<sup>[5]</sup> However, these attempts to trade high power for low energy density are not suit-

able for practical applications due to the inevitable reduction in the energy density of batteries. On the other hand, accelerating the Li<sup>+</sup> transport process in bulk electrolytes seems to be an efficient way to realize high kinetics<sup>[6]</sup> without sacrificing of energy density. Aliphatic esters<sup>[7]</sup> with low viscosity are employed as

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co-solvents to improve the ionic conductivity (IC), which effectively reduces Li<sup>+</sup> transport resistance due to the weak interactions of solvation structures. Ketones, amides,<sup>[8]</sup> and other liquids<sup>[9]</sup> or salts<sup>[10]</sup> have been used as the electrolyte additive to increase the ICs or facilitate the kinetics for Li<sup>+</sup> across the interphase.<sup>[11]</sup>

In addition to the above, the recent innovation in battery electrolytes has provided new ideas for fast charging. For instance, high-concentration electrolytes (HCE)<sup>[12]</sup> and localized high concentration electrolytes (LHCEs)<sup>[13]</sup> are able to achieve higher specific capacities of graphite anodes than commercial electrolytes  $(ICs > 10 \text{ mS cm}^{-1})$  at high rates, despite the relatively low ICs (usually  $< 5 \text{ mS cm}^{-1}$ ). Unlike in low-concentration electrolytes (<2 м), Li<sup>+</sup> are transported via repeated "solvation/desolvation" processes in HCEs or LHCEs. The Li-ion desolvation process near the interphase is believed to dominate the kinetics. Thus, reducing the desolvation activation energies ( $\Delta E_{dsv}$ ) of Li<sup>+</sup> tends to facilitate the transport of Li ions<sup>[14]</sup> in these electrolyte systems. With the robust solid electrolyte interphase (SEI) derived from anions,<sup>[15]</sup> these electrolytes enable a stable cycling performance of graphite anode-based LIBs. Although the currently state-of-the-art study has shown that graphite can achieve a capability of 280 mAh g<sup>-1</sup> at 5C,<sup>[12b]</sup> there is still a long way to go for XFC. Other endeavor has been made in low-concentration electrolytes with low  $\Delta E_{dsv}^{[16]}$ regrettably, only introducing mediocre improvements.

Herein, we challenge the traditional consideration of unilaterally improving the rate performance and propose an electrolyte design criterion for high-rate graphite anode based LIBs. We demonstrate that low desolvation energy of Li<sup>+</sup> in electrolyte endows a fast interfacial kinetics, and ultrahigh rate graphite anode with a decent cycling stability can be achieved by simultaneously improving the IC of electrolyte and forming thin but robust SEI. According to the theoretical calculations and experimental results, we formulate 1.8 м LiFSI in 1,3-dioxolane electrolytes which enable micro-sized natural graphite (NG) electrodes to achieve a long-cycling capacity of 315 mAh g<sup>-1</sup> at 20C  $(1C = 370 \text{ mAh g}^{-1})$  without capacity decay. Even in 50C, a highly reversible capacity of 180 mAh g<sup>-1</sup> is retained. The NG electrodes achieve a reversible capacity of 310 mAh g<sup>-1</sup> after reducing the temperature to -30 °C at 0.3C. The 1.8 м LiFSI 1,3-dioxolane (DOL) electrolyte enables LiFePO<sub>4</sub>(LFP)||graphite cells to achieve a capacity of 60 mAh g<sup>-1</sup> (of LFP) without decay during longtime cycling along with a stable Coulombic efficiency of 99.99%. To couple with high voltage LiNi<sub>0.8</sub>Mn<sub>0.1</sub>Co<sub>0.1</sub>O<sub>2</sub> (NCM811) cathode, a high-voltage fast-charging electrolyte consisting of 1.0 м LiPF<sub>6</sub> in 4-fluoroethylene carbonate (FEC) and acetonitrile (AN) (7:3 by vol) is also designed. Our results demonstrate that 1.0 м LiPF<sub>6</sub> in FEC/AN electrolyte enables NCM811||NG cells (cathode loading: 2 mAh cm<sup>-2</sup>) to deliver a reversible capacity of 170 mAh g<sup>-1</sup> at 4C charge and 0.3C discharge. The design principle makes XFC promising for practical applications in graphite-anode-based LIBs.

#### 2. Results and Discussions

# 2.1. Electrolyte Design for High-Rate Graphite Anodes

The energy storage rate relies on how fast the  $\rm Li^+$  can migrate between the cathode and the anode. In principle,  $\rm Li^+$  undergoes

three steps during charging processes (Figure 1a): a) diffusion of solvated Li<sup>+</sup> in the bulk electrolyte, b) desolvation of the solvated Li<sup>+</sup> before crossing the SEI, and c) naked Li<sup>+</sup> crossing the SEI.<sup>[6]</sup> These three steps are highly intertwined. The physicochemical properties of the solvents and concentration determine the diffusivity of the Li<sup>+</sup>, while the components of the Li<sup>+</sup> inner solvation shell affect the SEI compositions and thereby play a decisive role in the Li<sup>+</sup> crossing kinetics in SEI. Accelerating the Li<sup>+</sup> transport in all three steps will dramatically enhance the electrochemical kinetics, which calls for the electrolyte with high IC, low desolvation energy ( $\Delta E_{dsv}$ ), and low Li<sup>+</sup> crossing energybarrier SEI ( $\Delta E_{SEI}$ ) with a low area-specific resistance (ASR). To design an electrolyte with these properties, the IC (Figure 1b),  $\Delta E_{dsv}$  (Figure 1c), and reduction potential ( $G_{red}$ , Figure 1d) for the commonly used salts and solvents were first measured via experiments and DFT calculations (Figure 1c,d). According to the results, FSI<sup>-</sup> anion exhibits the lowest  $\Delta E_{dsv}$  (Figure 1c) and highest reduction potential among the anions (Figure 1d), which indicates that FSI- anion can endow low desolvation kinetics and inorganic-rich SEI. For the solvents, AN-based electrolytes show superior IC to enhance the Li<sup>+</sup> migration and transport inside the electrolyte (Figure 1b), while DOL solvent which demonstrates the weakest interaction with Li+ (Figure 1c) should be a good choice to improve the desolvation kinetics. FEC solvent is favorable for the LiF-rich SEI as it can promote the formation of LiF at around 1.0 V. LiF-rich SEI is very thin and has a low ASR because LiF has a high ratio of IC to electronic conductivity. The corresponding Quantum Chemistry calculations of reduction potentials for Li-solvent/anion with different dielectric constants are shown in Figure S1, Supporting Information.

We selected LiFSI as the salt because it has the best dissociation and highest potential to form LiF (Figure 1d) among the studied common salts, and DOL as the solvent for the lowest  $\Delta E_{dsv}$  of Li<sup>+</sup> (Figure 1c). To maximize the rate performance, 1.8 м LiFSI DOL was blended since the conductivity maxima locates at this concentration (Figure S2b, Supporting Information). The correlating solvation structures were examined by Raman spectroscopy (Figure S2c, Supporting Information). The C-O-C bending peak ascribed to DOL is slightly perturbed (721 to 730 cm<sup>-1</sup>) by the dissolution of LiFSI, while the other three C–O stretching peaks of DOL (940, 958, and 1088 cm<sup>-1</sup>) keep intact,<sup>[17]</sup> implying weak coordination of DOL molecules bound by Li+, id est, a low  $\Delta E_{dsv}$  of Li<sup>+</sup> in 1.8 м LiFSI DOL electrolyte. The viscosity and contact angle tests prove the benefit of 1.8 м LiFSI DOL by showing a lower viscosity of  $0.43 \pm 0.12$  cP and a lower contact angle of  $29.1 \pm 3.2^{\circ}$  compared with those of carbonate electrolytes  $(2.98 \pm 0.27 \text{ cP} \text{ and } 59.8 \pm 4.5^{\circ})$  (Figure S3a, Supporting Information). The wetting images (Figure S3b, Supporting Information) demonstrate both two electrolytes can infiltrate the separator and 1.8 M LiFSI DOL can spread out more. These results indicate that the Li-ion transport in bulk electrolytes is faster for 1.8 м LiFSI DOL than the carbonate electrolyte, in line with the conductivity tests (Figure 1b and Figure S2b, Supporting Information).

Molecular dynamics (MD) simulation was performed to analyze the detailed solvation structures of the electrolytes (Figure S4, Supporting Information). Unlike the strong coordination of Li<sup>+</sup> with solvent in 1.0  $\times$  LiPF<sub>6</sub> EC/DMC electrolyte, Li<sup>+</sup> prefers to bond with FSI<sup>-</sup> in 1.8  $\times$  LiFSI DOL electrolyte as evidenced by a much higher peak of Li–O<sub>FSI</sub> than that of Li–O<sub>DOL</sub>. The







**Figure 1.** Design principles and solvation structures of the electrolytes. a) Schematic of fast-charging for the graphite anode considering all steps that the electrolyte affects  $Li^+$  transport from cathode to anode during charging. b) Measured ionic conductivities of 1.0 M LiFSI in different solvents. EC/DMC\* means the conventional electrolyte. c) Quantum chemistry calculated binding energies and measured desolvation energies. d) Calculated reduction potentials for anions and solvents using M05-2X/6-31++G(d, p).

corresponding pie chart (Figure S4d, Supporting Information) indicates a low solvent number of 1.26, which means an easier Li<sup>+</sup> desolvation process. Besides the electrolytes, the properties of graphites (morphologies and particle sizes) will also affect the rate performance.<sup>[18]</sup> In the current work, the intercalation/ deintercalation behaviors of Li+ in different graphites were evaluated via electrochemical impedance spectroscopy (EIS) tests under 100% state-of-charge (SOC) to screen a suitable graphite anode (Figure S5, Supporting Information). The total resistances  $(R_{cell})$  are in the descending order of mesocarbon microbeads (MCMB) > artificial graphite (AG) > NG in both two electrolytes (Figure S5a,b, Supporting Information). Three NGs with different average diameters of 2.5, 10, and 15 µm are named as 2.5NG, 10NG, and 15NG. With the smallest average diameter, 2.5NG holds the lowest  $R_{cell}$  (15  $\Omega$ ) in 1.8 M LiFSI DOL electrolyte (Figure S5c, Supporting Information), which is beneficial for fast kinetics, and thus is served as the anode material. The morphologies of different graphites were characterized by scanning electron microscopy (SEM), and no defects or cracks that contribute to a capacitive process are observed (Figure S6, Supporting Information).

#### 2.2. Fast Kinetics for Graphite Anodes

The rate performance of microsized NG (2.5NG) was evaluated in different electrolytes between 1.0 and 0.0 V using an NG||Li half-cell configuration. The referred rate of nC meant a full charge or discharge in 1/n h. Compared to the rapid capacity decline starting from 1C in the carbonate electrolyte. NG anode in 1.8 м LiFSI DOL electrolyte yield a revolutionary breakthrough by providing capacities of 315 and 180 mAh g<sup>-1</sup> even at 20 and 50C (Figure 2a), respectively. The recoverable capacity of 370 mAh  $g^{-1}$  is obtained when the rate returned to 0.2C, indicating no damage to the graphite anode. The corresponding charge/discharge curves from 1 to 50C reveal the intercalation process of Li<sup>+</sup> into graphite (Figure 2b) with three voltage plateaus emerging below ≈0.2 V at 1C for 1.8 м LiFSI DOL due to the formation of multistage structures of LiC<sub>r</sub>.<sup>[12b]</sup> However, no potential plateau can be observed for charging/discharging of graphite in commercial carbonate electrolytes (1.0 м LiPF<sub>6</sub> EC/DMC) at a high rate (Figure S7a, Supporting Information). At a low rate (< 1C), the Li insertion kinetics is quasi-independent of the electrolytes, showing similar voltage profiles in 1.8 M LiFSI DOL and commercial carbonate electrolytes. As the rate increased to 5C and above, significant differences appear between cells with two electrolytes, particularly in voltage profiles. At such high rates, the battery with 1.8 м LiFSI DOL electrolyte shows a more defined potential plateau and a much lower overpotential in comparison with the commercial carbonate electrolyte. Even when the rate increased up to 20C, the potential plateaus are still defined for the cell with 1.8 M LiFSI DOL electrolyte (Figure 2b, magenta line). Since the rate performance was measured in a two-electrode cell, the total



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**Figure 2.** Electrochemical performance of graphite anodes in half cells. a) Rate performance of NG||Li cells with 1.8 M LiFSI DOL and 1.0 M LiPF<sub>6</sub> EC/ DMC (1:1 by vol). b) The corresponding charge/discharge curves of NG||Li cells with 1.8 M LiFSI DOL. c) Evolution of the overpotential at different rates of graphite electrode in two electrolytes. d) Discharge-voltage profiles of NG||Li cells via GITT measurements at 10C. The inset shows a voltage relaxation process during the rest taken from the black ellipses. e) Impedance spectra and f) long-cycling performance at 20C of NG||Li cells with two electrolytes. The rates of charge and discharge are the same for each cycle. g) Top-viewed SEM image of the Li metal electrode after 1100 cycles. The insets show photographs of the Li-metal electrode and separator after 1100 cycles. The SEM image was taken from the dotted boxes.

overpotentials are comprised of two parts: overpotentials for graphite anodes and Li metal electrodes. The real overpotentials for graphite anodes (Figure 2c) were obtained by subtracting Li metal overpotentials in the galvanostatic Li plating/stripping tests from the total overpotentials of the above charge/discharge curves (Figure S7c, Supporting Information). When C-rate increases from 1 to 50C, the overpotential of graphite electrode in 1.8  $\mbox{M}$  LiFSI DOL electrolyte is from 0.032 to 0.153 V, which is much lower than that in the carbonate electrolytes (from 0.037 to 0.335 V) (Figure 2c). Considering the narrow voltage gap ( $\approx 0.1$  V) between the Li<sup>+</sup> intercalation/de-intercalation potential of graphite with Li metal potential, this variation poses a vital impact on the rate performance of graphite anode.

Galvanostatic intermittent titration technique  $(GITT)^{[19]}$ using a high rate (10C) lithiation current was performed to gain insights into the overpotentials in lithiation/delithiation processes of graphite electrodes/LiC<sub>x</sub>. During the lithiation process, a capacity of > 360 mAh g<sup>-1</sup> is achieved in the 1.8 M FSI DOL electrolyte in contrast to that of 80 mAh g<sup>-1</sup> in the commercial carbonate electrolyte (Figure 2d). The representative potential changes in lithiation and relaxation processes at open-circuit in the middle profiles during GITT experiments are shown in the inset. The whole potential rise in the commercial carbonate electrolyte (142 mV) is 4.6 times higher than that in 1.8 M LiFSI DOL electrolyte (31 mV). Similar phenomena were also observed in the delithiation process with overpotentials of 152



DVANCED IENCE NEWS www.advancedsciencenews.com and 31 mV in the commercial carbonate electrolyte and 1.8 м LiFSI DOL electrolyte (Figure S8, Supporting Information), respectively. The extremely large overpotential of commercial carbonate electrolyte should be attributed to the high resistance of the interphases and Li<sup>+</sup> desolvation,<sup>[20]</sup> which leads to sluggish kinetics. At the same lithiation/delithiation state of graphite, the similar values of equilibrated potentials (61 vs 67 mV, 9.3 vs 12 mV, 3.4 vs 10 mV) in two electrolytes (Figure S8c,d, Supporting Information) indicate that the thermodynamic equilibrium state is independent of the electrolyte. Based on the fitting of Nyquist plot, the cell resistance mainly comprises of bulk resistance  $(R_{\rm b})$ , surface layer resistance  $(R_{\rm sei})$ , and chargetransfer resistance ( $R_{ct}$ ) (Figure 2e).<sup>[3a,21]</sup> The much lower values of  $R_{\rm sei}$  and  $R_{\rm ct}$  (9.1 and 4.7  $\Omega$ ) in 1.8 M LiFSI DOL electrolyte than those in the carbonate electrolyte (33.2 and 15.1  $\Omega$ ), quantitatively verified a faster interfacial reaction kinetics in 1.8 M LiFSI DOL electrolyte. The rate performances of graphite electrodes in both electrolytes were further investigated via cyclic voltammetry (CV) using NG||Li cells (Figure S9, Supporting Information). Basically, the graphite electrode in 1.8 M LiFSI DOL electrolyte experiences significantly deintercalation peaks with lower voltages but intercalation peaks with higher voltages than those in carbonate electrolyte from 0.01 to 1 mVs<sup>-1</sup>, due to faster Li-ion kinetics. The b-values of each peak, from which we can infer the nature of the redox reaction (limited by semi-infinite diffusion or a capacitive process), were obtained via mathematic fitting,<sup>[22]</sup> denoted as C1-C3 (charge) and D1-D3 (discharge), respectively (Figure S9b,d, Supporting Information). Based on the fitting, the *b*-values obtained from cells in 1.8 м LiFSI DOL electrolyte are higher than those in

carbonate electrolyte. Due to the fast kinetics in 1.8 M LiFSI DOL electrolyte, Li<sup>+</sup> can easily reach a ready state to diffuse within the graphite, which endows a strong driving force for the Li<sup>+</sup> diffusion in the graphite indicated by the large b-values of each redox peak.

The cycling reversibility of 2.5NG in 1.8 м LiFSI DOL and commercial carbonate electrolytes was evaluated at 20C using NG||Li half cells (Figure 2f). In stark contrast to only 40 mAh g<sup>-1</sup> for the cell with the carbonate electrolyte, the cell with 1.8 м LiFSI DOL electrolyte presents a highly reversible capacity of 315 mAh g<sup>-1</sup>. At high current densities, the Li metal electrode has to be replaced every ≈1000 cycles to eliminate the pernicious impact (high resistance, dendrites, and electrolyte consumption).<sup>[23]</sup> Due to the surface corrosion of Li electrode, the cell capacity decreases to 180 mAh g<sup>-1</sup> after 4000 cycles without replacing the Li metal (Figure S10b,c, Supporting Information), which can be recovered by replacing Li count electrodes. Different sized NGs in LiFSI-DOL at various concentrations were also evaluated (Figures S11 and S12, Supporting Information). As can be seen, the cell comprised of 2.5NG and 1.8 м LiFSI DOL electrolyte displays the best rate performance. To reach a commercial level, NG electrodes with high loadings of 2 mAh cm<sup>-2</sup> and 3.5 mAh cm<sup>-2</sup> (Figure S13a, Supporting Information) were tested with 1.8 M LiFSI DOL and showed a high reversible capacity of 340 mAh  $g^{-1}$  and 325 mAh  $g^{-1}$ at 4C respectively. Compared with the state-of-the-art value of 150 mAh g<sup>-1</sup> (Figure S13b, Supporting Information), the high capacity of NG in our work brought a breakthrough for fast-charging battery chemistry.

X-ray photoelectron spectroscopy (XPS) was performed to identify the chemical composition of the SEI on cycled graphite electrode with various time of Ar<sup>+</sup> sputtering. For the SEI formed in carbonate electrolyte (**Figure 3**a), both the organic (RCH<sub>2</sub>OLi, 290.7 eV) and inorganic (Li<sub>2</sub>CO<sub>3</sub>, 291.2 eV) species are detected in the C 1s spectra on the top surface. The composition of SEI layer is dominated ( $\approx$  80%) by carbon species according to the XPS elemental analysis after 120 s sputtering with Ar<sup>+</sup> (Figure 3b), indicating most of the SEI components are derived from the EC decomposition. Meanwhile, the relatively weak signals for Li<sub>2</sub>CO<sub>3</sub> and other inorganic species (O, C, P) (Figure S14a, Supporting Information) during the sputtering process demonstrate the SEI formed in carbonate electrolyte is organic-rich.

Unlike SEI derived from carbonate electrolyte, the SEI of NG in 1.8 M LiFSI DOL electrolyte contains more inorganic (LiO, LiF) species (Figure 3c,d and Figure S14b, Supporting Information). LiF-rich feature can be confirmed by the intensive LiF signals in F 1s spectra (685.9 eV) and the high ratio of F content (≈ 18% vs 5% for SEI in carbonate electrolyte) in XPS elemental analysis. It is well known that LiF-rich SEI stabilizes the Li metal<sup>[24]</sup> and alloy anodes,<sup>[25]</sup> but few have focused on LiFrich SEI for graphite anode since the organic-rich SEI derived from the carbonate electrolyte sufficiently enables decent cycling stability. Compared to the organic-rich SEI, the LiFrich SEI is more promising for fast kinetics since two or three atomic layers of LiF could block the side reactions thanks to the wide band gap and high chemical/electrochemical stability.<sup>[26]</sup> Some other inorganic species containing N and S were also discovered in the SEI due to the decomposition of FSI- anions (Figure S15, Supporting Information). The ab initio molecular dynamic (AIMD) simulated atomic SEI structures on the graphite was provided in Figure 3e and Figure S16. Supporting Information. For the carbonate electrolyte, the open-ringed EC, Li<sub>x</sub>PF<sub>6</sub>, and Li<sub>2</sub>CO<sub>3</sub> clusters can be found, validating that the SEI mainly resulted from the decomposition of EC solvents. For 1.8 м LiFSI DOL electrolyte, LiF and LiN<sub>v</sub>S<sub>v</sub>O<sub>z</sub> clusters are formed at the interface without the capture of DOL decomposition, revealing that LiFSI is much easier to decompose at the interface, consistent with the XPS results. The formed LiF on graphite with low ionic electronic and high interface energy<sup>[26]</sup> effectively blocks the continuous reaction of electrolytes, thus increasing the Coulombic efficiency.

Cryogenic transmission electron microscopy (cryo-TEM) technique, which can retain the morphology of in situ SEI,<sup>[27]</sup> was carried out to analyze the specific structures of the SEI films. The morphologies and elemental components of the SEI are explicated by high-resolution cryo-TEM with the corresponding fast Fourier transform (FFT) pattern (Figure 3f,j). For the carbonate electrolyte, the generated SEI presents a classic mosaic-type structure with nanoscale Li<sub>2</sub>CO<sub>3</sub> (orange and magenta circles) and Li<sub>2</sub>O particles (red circles) (Figure 3g) dispersed into amorphous organic components.<sup>[28]</sup> However, the main inorganic components of the generated SEI in the 1.8  $\mbox{ LiFSI DOL electrolyte are LiF (yellow circle) and Li<sub>2</sub>O (red circles) with a size of 5–10 nm (Figure 3j,k), which is also confirmed by the results of other SEI regions (Figure S17,$ 



a

295 290

b

C1s

Li2CO3

80

60

40

20

0.

(%)

Atomic ratio

f

J

<u>10' nm</u>



Figure 3. Characterization of the SEI on cycled graphite anodes. a,b) XPS spectra of the SEI formed on graphite electrodes with carbonate electrolyte (a) and 1.8 M LiFSI DOL (b). The C 1s, O 1s, and F 1s spectra are displayed after Ar<sup>+</sup>-sputtering for 0 and 120 s. c,d) Elemental contents of the SEI on graphite anodes cycled in carbonate electrolyte (c) and 1.8 M LiFSI DOL (d). e) AIMD simulated atomic SEI structure between graphite and electrolytes. (Color code: Li, pink, P, purple, F, cany, C, brown, O, red, N, blue, S, yellow, graphite, brown wireframe). f,j) High-resolution cryo-TEM images of SEI films formed in carbonate electrolyte (f) and 1.8 M LiFSI DOL electrolyte (j). The insets show the corresponding FFT pattern. g,k) Corresponding schematics of the two high-resolution cryo-TEM images. h,l) Different elemental mass content of the SEI films formed in carbonate electrolyte (h) and 1.8 M LiFSI DOL electrolyte (I). i,m) High-resolution ADF STEM and EELS results of the graphite surface in carbonate electrolyte (i) and 1.8 M LiFSI DOL electrolyte (m).

50

0

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8.13

Ó F Elements

2.61

4.08

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Supporting Information). Unlike the SEI with a thickness of >40 nm formed in the carbonate electrolyte (Figure 3g), the SEI derived in 1.8 м LiFSI DOL electrolyte is only 15 nm (Figure 3k), which is favorable for the fast transport of Li<sup>+</sup> crossing the SEI. On the other hand, the interphase generated in the 1.8 м LiFSI DOL electrolyte exhibits a homogeneous laminar structure (Figure S18b, Supporting Information) compared to the irregular morphology formed in the carbonate electrolyte (Figure S18a,

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Supporting Information). Since the detective depth of energydispersive X-ray spectroscopy (EDX) is micrometer-scale, the detected signal reflects the overlap of both SEI and graphite, which leads to a less apparent content for all elements except C. However, we can still infer that the interphase formed in 1.8 M LiFSI DOL electrolyte is more than ten times richer in inorganic species (2.61 wt% F and 4.08 wt% S) (Figure 3l) than that formed in the carbonate electrolyte (0.15 wt% F and 0.01 wt% P)

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**Figure 4.** Electrochemical performances of cells under practical conditions. a) Rate, b) low-temperature performances, and c) their corresponding charge/discharge curves of NG||Li cells with two electrolytes. The loadings of graphite anodes are 2 mAh cm<sup>-2</sup>. Same rates of charge/discharge for each cycle. d) Long cycling performance of LFP||NG pouch cells with two electrolytes. The inset shows a photograph of the LFP||NG pouch cell.

(Figure 3h) from the relative contents. The interphase formed in 1.8 M LiFSI DOL electrolyte was also identified by ADF STEM and EELS, showing edge enriched distribution of the detected elements (Figure 3m), which differs from the broad distribution of elements in the carbonate electrolyte (Figure 3i).

# 2.4. LiFePO<sub>4</sub>||Graphite Full Cells Capable of Fast Charging and Low-Temperature Operation

Ultrafast-charging capability of 1.8 м LiFSI DOL for Li-ion batteries (LIBs) was evaluated using microsized NG anodes and LiFePO<sub>4</sub> cathodes with high loading, although the high loading would challenge the rate performance.<sup>[29]</sup> We first evaluated the cycle stability of 2 mAh cm<sup>-2</sup> graphite electrodes at different charging C-rate. Notably, the 1.8  $\mbox{ M}$  LiFSI DOL electrolyte enables the graphite electrodes to achieve a capacity of 320 mAh g<sup>-1</sup> at 4C and 150 mAh g<sup>-1</sup> at 10 C (Figure 4a) under such high loading conditions, in sharp contrast to a capacity of 20 mAh g<sup>-1</sup> for the carbonate electrolyte at 4C (Figure 4a). Meanwhile, a significantly improved cycling performance with high-capacity retention of 250 mAh g<sup>-1</sup> over 400 cycles is also achieved for 1.8  $\mbox{ M}$  LiFSI DOL electrolyte (Figure S19, Supporting Information). In this harsh condition, the Li metal electrode has to be replaced by a fresh one at the 180th cycle to ensure that the degradation of the Li metal under a current

density of 8 mA cm<sup>-2</sup> does not affect the cycling performance (Figure S19c, Supporting Information). When the rate increased to 8C (16 mA cm<sup>-2</sup>), the degradation of the Li metal would be more severe, leading to a more noticeable capacity decay (Figure S20, Supporting Information). Another tough condition with the lithiation rate of 4C and delithiation rate of 0.3C (Figure S21, Supporting Information) was also employed to verify the practical feasibility and a high capacity of 320 mAh g<sup>-1</sup> was retained over 200 cycles in 1.8 M LiFSI DOL electrolyte.

LIBs deployed at ultralow temperatures (≤−30 °C) have limited success due to the dramatic capacity drop, which largely limits their practical application in extreme environments.<sup>[30]</sup> Although some progress has been reported, the utilized cycling protocol was to charge at room temperature and discharge at low temperatures. Worse kinetics of graphite lithiation at low temperatures remains one of the most challenges for LIBs. Therefore, the low-temperature performances of the cells with the designed electrolytes were also evaluated. Compared to the rapid drop for the ICs of 1.0  $\mbox{m}$  LiPF<sub>6</sub> EC/DMC (11.59 to 1.11 mS cm<sup>-1</sup> from 25 to -30 °C), the IC of 1.8 м LiFSI DOL strictly follows the Vogel-Tamman-Fulcher (VTF) empirical equation<sup>[30a]</sup> and decreases slowly (15.14 to 7.49 mS cm<sup>-1</sup> from 25 to -30 °C) (Figure S22, Supporting Information), showing a great advantage for Li<sup>+</sup> transport in bulk electrolyte at low temperatures. Further low-temperature test (Figure 4b,c), id est, cycling at C/3 under gradually decreasing temperatures from 25 to -30 °C, proves the superiority of the electrolyte by showing a capacity of 300 mAh  $g^{-1}$  at -30 °C compared with the carbonate electrolyte (no capacity at -30 °C).

LiFePO<sub>4</sub> (LFP) cathode was selected to construct a full cell due to its high safety, low cost, and stability.<sup>[31]</sup> The instability of DOL at higher voltages was another reason that LFP was used with 1.8 M LiFSI DOL electrolyte. Preliminary evaluation of the LFP||Li cells shows the advantages of 1.8 м LiFSI DOL electrolyte by presenting a capacity of 90 mAh g<sup>-1</sup> at 20C, four times higher than that in the carbonate electrolyte (20 mAh  $g^{-1}$ ) (Figures S23 and S24, Supporting Information). Coin and pouch full LFP||NG cell tests were also conducted to examine the long cycling stability at 20C. As can be seen, the cell with 1.8 м LiFSI DOL electrolyte delivers an initial capacity of 90 mAh g<sup>-1</sup> and has no capacity decay after 1000 cycles (Figure S25c, Supporting Information). The possible Li plating at a high charging rate is the key issue restricting the LIB rate performance.<sup>[32]</sup> Both the digital and SEM images demonstrate that no Li plating occurs at any state of charge (SOC) during the fast-charging process (Figure S26, Supporting Information), which guarantees the stable long cycling performance of full cells. At 60C (1 min to full charge and discharge respectively), the pouch cell with 1.8 м LiFSI DOL electrolyte exhibits a capacity of 60 mAh g<sup>-1</sup> without decay during long-time cycling along with a stable Coulombic efficiency of 99.99% (Figure 4d and Figure S27, Supporting Information), which far exceeds the cell performance with the carbonate electrolyte.

# 2.5. Electrolyte Design for Fast-Charging Graphite Pairing with NCM811

High-voltage NCM811||graphite cells have received much attention because of their high energy density.<sup>[33]</sup> Following the criterion above, an electrolyte with 1.0  $\mbox{M}$  LiPF<sub>6</sub> in FEC/AN (7:3 by vol) was designed for NCM811||graphite cells. Compared to the carbonate electrolyte, 1.0  $\mbox{M}$  LiPF<sub>6</sub> FEC/AN exhibits a lower  $\Delta E_{dsv}$  (31.43 kJ mol<sup>-1</sup>) and superior ionic conductivities at room temperature (13.22 mS cm<sup>-1</sup>) (Figure S28a, Supporting Information) and low temperature (2.50 mS cm<sup>-1</sup> at -30 °C) (Figure S28b, Supporting Information). The typical Li<sup>+</sup> solvation structures with and without anions were presented in Figure 5a,b. The RDF results demonstrate an average first shell solvation structure of Li(PF<sub>6</sub>)(FEC)<sub>3</sub>AN. The FEC solvent and PF<sub>6</sub> anions in the solvation shell tend to be reduced to form LiF at the interface while the AN solvent accelerates the Li-ion transport within the electrolyte, thus meeting the requirements of our proposed mechanisms. Detailed solvation structures of 1.0  $\mbox{M}$  LiPF<sub>6</sub> FEC/AN are shown in Figure S29, Supporting Information.

The 1.0  $\[mmm]$  LiPF<sub>6</sub> FEC/AN electrolyte enables the graphite electrode to achieve a higher capacity of 230 mAh g<sup>-1</sup> at 20C, which is superior to that of the carbonate electrolyte (40 mAh g<sup>-1</sup>) (Figure 5c and Figure S30a,b, Supporting Information). Moreover, the NCM811||NG cell in 1.0  $\[mmm]$  LiPF<sub>6</sub>/FEC:AN with the cathode loading of 2 mAh cm<sup>-2</sup> maintains a highly reversible capacity of 170 mAh g<sup>-1</sup> under a harsh cycling condition (4C charge 0.3C discharge).

# 3. Conclusions

Extremely fast-charging LIBs have been developed by rational design of electrolytes with a criterion, which includes low  $\Delta E_{dsv}$ of Li<sup>+</sup>, high ICs as well as the ability to form thin and robust SEI on graphite surfaces. Based on the criterion, two fast-charging electrolytes 1.8 м LiFSI DOL and 1.0 м LiPF<sub>6</sub> FEC/AN (7:3 by vol) were developed. The former electrolyte enabled the graphite electrode to achieve an extremely high capacity of 315 mAh g<sup>-1</sup> and 180 mAh g<sup>-1</sup> at 20 and 50C, respectively. XPS and cryo-TEM characterizations suggested a uniform and LiF-rich SEI at the surface of the graphite electrode. The NG||Li cells with a ≈2 mAh cm<sup>-2</sup> loading exhibited a high capacity of 320 mAh g<sup>-1</sup> at 4C and 300 mAh g<sup>-1</sup> at C/3 under -30 °C. LFP||NG cells showed a capacity of 80 mAh g<sup>-1</sup> at 20C and the pouch cells demonstrated a highly reversible capacity of 60 mAh g<sup>-1</sup> at a rate of 60C (1 min to full charge and discharge respectively). The latter electrolyte enabled NCM811||NG cells with the cathode loadings of 2 mAh cm<sup>-2</sup> to retain a capacity of 170 mAh g<sup>-1</sup> at a tough cycling condition (4C charge 0.3C discharge). Our study established a simple and achievable principle for designing electrolytes for fast-charging graphite anode-based LIBs, which was instructive for practical application.

# 4. Experimental Section

*Materials*: Three sets of NG powders (NG, average diameters: 2.5, 10, and 15  $\mu$ m) were provided by Beijing Xinjincheng Science and Trade Co., Ltd. Artificial graphite powders (AG, average particle size: 15  $\mu$ m) were purchased from BTR Co., Ltd. Mesocarbon microbeads powders (MCMB, average particle size: 15  $\mu$ m), LiFePO<sub>4</sub> powders (LFP, average particle size: 15  $\mu$ m), and carbon black (Super P C45) were received from Hefei Kejing Co., Ltd. Lithium chips with a thickness of 450  $\mu$ m ( $\Phi$  = 15.8 mm) were obtained from Tianjin China Energy Lithium Co., Ltd. Poly(acrylic

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**Figure 5.** Solvation structures of the high-voltage electrolyte and the battery performance. a,b) Representative Li<sup>+</sup> solvation structures for the 1.0 M LiPF<sub>6</sub> FEC/AN electrolyte with anions (a) and without anions (b). c) Rate performance of NG||Li cells, d) long-cycling performance at a tough condition (4C charge 0.3C discharge), and e) the corresponding charge/discharge curves of NCM811||NG cells with 1.0 M LiPF<sub>6</sub> FEC/AN. The loading of active material is 2 mAh cm<sup>-2</sup> in NCM811||NG cells. The N/P ratio was fixed at 1.

acid) (PAA,  $\overline{M}_{\nu}$  = 450 000) and lithium hydroxide (LiOH, 99.5%) were purchased from Shanghai Aladdin Co., Ltd. Polyvinylidene fluoride (PVDF, HSV900) and *N*-methyl pyrrolidone (NMP, 99.5%) were purchased from Duoduo Co., Ltd. 1,3-Dioxolane (DOL, 99.8%), FEC (99.8%), AN (99.5%), LiFSI (99%), and LiPF<sub>6</sub> (99%) were purchased from Changde Dadu New Material Co., Ltd. All the solvents were dried with molecular sieves at least 48 h to ensure the moisture content was below 20 ppm (titrated by the Karl–Fischer method).

Preparation of Electrolyte and Electrode: The electrolyte was prepared and stored inside a glovebox filled with high-purity argon (water and oxygen both <0.01 ppm). 0.748 g LiFSI was dissolved in 2 mL DOL to obtain 1.8 м LiFSI DOL. 0.167 g LiPF<sub>6</sub> was dissolved in 1 mL FEC:AN (7:3 by vol) mixture to obtain 1.0 м LiPF<sub>6</sub> FEC/AN. The carbonate electrolyte was used as the control. The anodes were prepared by casting the mixture containing 80 wt% graphite, 10 wt% carbon black, and 10 wt% PAALi in deionized water onto a Cu foil current collector using a doctor blade. For the cathode, the mixture of 80 wt% LiFePO<sub>4</sub>, 10 wt% carbon black, and 10 wt% PAALi in deionized water was cast onto an Al foil current collector. As for NCM811 cathode, the mixture of 80 wt% NCM811, 10 wt% carbon black, and 10 wt% PVDF in NMP was cast onto an Al foil current collector. The prepared electrodes were dried at 80  $^\circ\text{C}$ for 2 h and further dried under vacuum at 100 °C for at least 12 h before use. The loading of the prepared electrodes was about 0.3 mAh cm<sup>-2</sup>. For the LFP||NG pouch cells, the N/P ratio was fixed at 1 and the loading of LFP cathode was 1 mAh cm<sup>-2</sup>. To prepare the electrode with a higher loading of about 2 mAh cm<sup>-2</sup>, the mixture containing 85 wt% active material, 10 wt% carbon black, and 5 wt% PVDF in NMP was used.

Electrochemical Measurements: The ionic conductivities of different electrolytes were investigated by the EIS test using two fixed Pt electrodes. The NG||Li, LFP||Li, LFP||NG, and NCM811||NG cells were assembled in 2025-type coin cells using a polyethylene separator (ND16, SK Innovation Co.). The adding electrolyte in each coin cell was about 120  $\mu$ L to make sure the separator and electrodes were fully wetted. Pouch cells were also assembled with different electrolytes for further testing. The CV tests were

conducted from 0.01 to 1 V (vs Li/Li<sup>+</sup>) at different scanning rates of 0.01, 0.05, 0.10, 0.50, and 1.00 mV s<sup>-1</sup>. The EIS measurements were performed at the fully discharged state of NG||Li cells with the amplitude of 10 mV over the frequency from 0.01 to 10<sup>6</sup> Hz. All the measurements above were conducted on a multichannel electrochemical analyzer (ivium-n-stat, Ivium Technologies BV Co.). Galvanostatic charge–discharge cycling and rate performances were conducted on a battery test station (Wuhan LAND Electronics Co., Ltd.) at 25 °C.

Characterization: The contact angle measurements were carried out on JC2000, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd. The Viscosity measurements were performed using Anton Paar MCR102e Rheometer, SEM measurements were performed on the pristine graphite particles with a Hitachi SU-70 microscope at 3 kV. For postmortem analyses, NG||Li cells after 5 charge-discharge cycles at 0.2C were disassembled in the glovebox to collect the graphite electrodes. XPS measurements were conducted on a Thermo Scientific ESCALAB 250Xi scanning X-ray microprobe with a monochromatic Al K $\alpha$  X-ray (1486.6 eV) source. The samples were etched by Ar<sup>+</sup> ions (2 kV, 2  $\mu$ A, 45° incident angle) with increasing the sputtering time (0, 120, 300, 600, 900, and 1500 s) before the measurements. Cryo-TEM measurements were conducted on a JEOL JEM-ARM200 aberration-corrected microscope at 200 kV. The specimens were first collected on the Cu grids by dispersing the graphite particles in the corresponding solvent, which was operated in a glovebox. Then the specimens were immediately transferred into the TEM column in vacuum under the flow of Ar. Liquid nitrogen was poured into the cryo-TEM holder to cool the specimens below -170 °C, at which temperatures of the specimens were observed.

Quantum Chemistry Calculations: All quantum chemistry calculations were performed using the Gaussian 09 package. The calculated species included AN, DME, EC/DMC, DOL, TMP, FEC, DEC, TMS, FSI<sup>-</sup>, TFSI<sup>-</sup>, and PF6<sup>-</sup>. The geometries of Li-solvent (anion) complexes were first optimized using the B3LYP functional in combination with 6-31+G(d, p) basis sets. All the optimized structures were confirmed as potential minima, with no frequency modes with imaginary eigenvalues,

through frequency analyses following geometry optimizations. The different dielectric constants (epsl) represent the different electrolyte with acetone (epsl = 20.49) for carbonate-based electrolyte, THF (epsl = 7.19) for ether-based electrolyte, and diethyl ether (epsl = 4.24) for the lower dielectric constant at the interface. The de-solvation energies for complexes ( $E_{dsv}$ ) were evaluated as the energy difference as follows:

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$$G_{\rm dsv} = G_{\rm Li-Solvent} - G_{\rm Li} - G_{\rm Solvent} \tag{1}$$

where  $G_{\text{Li-Solvent}}$ ,  $G_{\text{Li}}$ , and  $G_{\text{Solvent}}$  are the Gibbs free energies of the free Li<sup>+</sup> ions, free solvent, and complex, respectively. All free energies were evaluated using M05-2X functional with 6–31+++G(d,p) basis sets.

The reduction potentials versus Li<sup>+</sup>/Li for various solvents and anions (TFSI<sup>-</sup>, FSI<sup>-</sup>, and PF<sub>6</sub><sup>-</sup>) were predicted using quantum chemistry calculations by subtracting 1.4V from the absolute reduction potentials, as given in Equation (2):<sup>[34]</sup>

$$E_{\rm red}(M) = -\left[\Delta G_{\rm e} + \Delta G_{\rm S}(M^{-}) - \Delta G_{\rm S}(M)\right] / F$$
<sup>(2)</sup>

In the equations,  $\Delta G_{\rm e}$  is the or electron affinity in the gas phase at room temperature (298.15 K),  $\Delta G_{\rm S}({\rm M})$  and  $\Delta G_{\rm S}({\rm M}^-)$  are the Gibbs free energies of solvation for the M and M<sup>-</sup> complexes, respectively, and F is the Faraday constant. M05-2X density functional was adopted because it precisely predicts electron affinity and ionization potential.

Solvation Structure Simulations: MD simulations were performed in LAMMPS using the all-atom optimized potentials for liquid simulations (OPLS-AA) force-field with the  $Li^+$ ,  $PF_6^-$ , and  $FSI^-$  anions description from previous publications.<sup>[35]</sup> The electrolyte systems were setup initially with the salt and solvent molecules distributed in the simulation boxes using Moltemplate (http://www.moltemplate.org/). For each system, an initial energy minimization at 0 K (energy and force tolerances of  $10^{-5}$ ) was performed to obtain the ground-state structure. After this, the system was slowly heated from 0 K to room temperature (298 K) at a constant volume over 0.2 ns using a Langevin thermostat, with a damping parameter of 100 ps. The system was equilibrated in the constant temperature (298 K) and constant pressure (1 bar) (NpT ensemble) for 5 ns before finally being subjected to 5 ns of constant volume and constant temperature dynamics. Radial distribution functions were obtained using the Visual Molecular Dynamics (VMD) software. Snapshots of the most probable solvation shells were also sampled from the simulation trajectory using VESTA.

AIMD Calculations: The AIMD calculations were employed using Vienna ab initio simulation package (VASP) code. Exchange-correlation potentials were parameterized using the generalized gradient approximation (GGA) employing the functional of Perdew-Burke-Ernzerhof (PBE). The projector augmented wave (PAW) approach was used to represent the core electrons and a kinetic energy cutoff of 450 eV was chosen to expand the mono-electronic states in plane waves. The long-range dispersion was accounted for using the DFT-D3 corrections. Because of the large size of the cells, only the Gamma point in the reciprocal space was used in the calculations. Tritium masses were applied for all protons to allow Born–Oppenheimer dynamics time steps of 1 fs, and a  $1 \times 10^{-6}$  eV energy convergence criterion. The anode was comprised of two layers of fully discharged graphite (LiC<sub>6</sub>) with an arm-chair edge. Carbon armchair edges were functionalized with either all oxygens. Two electrolyte systems, 1.8 м LiFSI DOL (2 LiFSI and 14 DOL molecules) and 1.0 м LiPF<sub>6</sub> EC/DMC (2 LiPF<sub>6</sub>, 14 EC, and 10 DMC molecules) were tested in this work. Initial geometries of the electrolyte were created with PACKMOL and then quenched using density functional forces. AIMD simulations were then performed at an elevated temperature of 350 K using a Nose thermostat to allow fast equilibration. At least 10 ps of dynamic simulations were performed for each system studied.

# **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.

#### **Data Availability Statement**

Research data are not shared.

#### Keywords

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