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Fluorination promotes lithium salt dissolution in borate esters for lithium metal batteries

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Abstract

Lithium metal batteries promise higher energy densities than current lithium-ion batteries but require novel electrolytes to extend their cycle life. Fluorinated solvents help stabilize the solid electrolyte interphase (SEI) with lithium metal, but are believed to have weaker solvation ability compared to their nonfluorinated counterparts and are deemed ‘poorer electrolytes’. In this work, we synthesize tris(2-fluoroethyl) borate (TFEB) as a new fluorinated borate ester solvent and show that TFEB unexpectedly has higher lithium salt solubility than the nonfluorinated counterpart (triethyl borate). Through experiments and simulations, we show that the partially fluorinated -CH₂F group acts as primary coordination site that promotes lithium salt dissolution. TFEB electrolyte has higher lithium transference number and better rate capability compared to the methoxy polyethyleneglycol borate esters reported in literature. In addition, TFEB supports compact lithium deposition morphology, high lithium metal Coulombic efficiency, and stable cycling of lithium metal/LiFePO₄ cells. This work ushers in a new electrolyte design paradigm where partially fluorinated moieties enable salt dissolution and can serve as primary ion coordination sites for next-generation electrolytes.
Introduction

Lithium metal is viewed as the future of lithium-based batteries because it has an order of magnitude higher specific capacity than the commercially used graphitic anodes (in Li-ion).\textsuperscript{1} Unfortunately, carbonate-based electrolytes currently used in commercial lithium ion batteries suffer from poor reductive stability and uneven lithium deposition, which result in lithium metal cycling Coulombic efficiencies as low as 50%\textsuperscript{2,3}. To promote electrolyte stability against lithium metal and suppress lithium dendrite formation, several electrolyte engineering and electrolyte chemistry approaches have been pursued.\textsuperscript{4} For example, high concentration electrolytes (HCEs) and localized high concentration electrolytes (LHCEs) have changed the electrolyte design paradigm.\textsuperscript{3,5–8} High or locally high salt concentrations promote the formation of ion pairing and salt aggregates, which can increase the Coulombic efficiency of lithium metal cycling to as high as 99.5%.\textsuperscript{9,10} Recently, novel fluoroether solvents have been reported by us and others to support stable lithium metal cycling with Coulombic efficiency as high as 99.9% in single-solvent-single-salt \texttextless{} 1 M electrolytes.\textsuperscript{11–14} Other fluorinated cyclic ethers and fluorinated sulfonamide have also been reported to enable efficient lithium metal cycling.\textsuperscript{15–20}

Among those novel electrolytes, fluorinated solvents or diluents are frequently used because fluorinated moieties are known to passivate lithium metal surface with a robust, lithium fluoride rich solid electrolyte interphase (SEI) as well as increase the oxidative stability.\textsuperscript{21,22} However, fluorination is also generally believed to weaken solvation ability (or ‘solvation strength’) of the solvent. For example, fluorinated ether diluents such as bis(2,2,2-trifluoroethyl) ether (BTFE) and tris(2,2,2-trifluoroethyl)orthoformate (TFEO) are known to improve lithium metal cycling but do not dissolve lithium salts while their nonfluorinated counter parts, diethyl ether and triethyl orthoformate, can dissolve lithium salt to concentrations higher than 1 M.\textsuperscript{17,23} Although some recently reported fluoroether solvents such as fluorinated glymes,\textsuperscript{12,24} fluorinated 1,4-dimethoxybutane (FDMB)\textsuperscript{12} and fluorinated 1,2-diethoxyethane (FDEE)\textsuperscript{13} can dissolve lithium salt to more than 1 M, the corresponding electrolytes show much lower ionic conductivities compared to their nonfluorinated counterparts (glymes, 1,4-dimethoxybutane and 1,2-diethoxyethane). Hence, there has been an inherent compromise between ionic solvation/conductivity and electrochemical properties such as oxidative stability and SEI passivation. On the other hand, some reports hint that fluorine could potentially act as
coordination site to enhance solvation/conductivity. For example, Rustomji et al. reported that monofluorinated alkane gases such as fluoromethane can have ionic conductivity ~ 1 mS/cm with 0.1 M LiTFSI salt when liquefied at low temperatures. Recent studies on fluorinated ethers and carbonates also indicate that partially fluorinated groups such as -CHF_2 and -CH_2F can coordinate to lithium ion more favorably than perfluoro groups (-CF_3 or -CF_2-). Nonetheless, the coordination ability of fluorinated groups is not well understood and there is still no clear evidence that fluorinated groups alone can enable conventional salt concentrations (~1 M).

Borate ester or boroxine type compounds are well known Lewis acids. They have been proposed as “anion acceptors” in polymer electrolytes to promote lithium salt dissociation and increase lithium transference number. However, rarely are borate esters studied as liquid electrolytes, partly because most commercially available borate esters cannot dissolve enough lithium salt alone. For example, tris(2,2,2-trifluoroethyl) borate has been studied as an additive in electrolytes for lithium metal and lithium-ion batteries but it can barely dissolve lithium salts as a single solvent. Fuminari et al. studied a group of tris(methoxy polyethyleneglycol) borate esters as liquid electrolyte solvents. To the best of our knowledge, they are the only group of borate ester solvents that have been reported to dissolve lithium salt up to 1 M. Nonetheless, those nonfluorinated borate esters show very poor cycle life in lithium metal batteries.

Herein, we investigate the influence of fluorination on the ion solvation ability and electrochemical stability of borate esters. We synthesize tris(2-fluoroethyl) borate (TFEB) as a new borate ester solvent. The lithium salt solubility of TFEB is first compared to two commercially available compounds: Triethyl borate (TEB) and tris(2,2,2-trifluoroethyl) borate (TTFEB). Interestingly, moderately fluorinated TFEB has the highest lithium salt solubility (~ 1 M) among these three solvents. This indicates lithium salt dissolution can be promoted by proper fluorination, which challenges the general literature assumption. To explain the unusual salt solubility trend, we investigate ion solvation environment using density functional theory (DFT) and ab-initio molecular dynamics (AIMD) simulations. We show that TFEB prefers to bind to lithium through fluorine of -CH_2F group, which leads to more negative lithium ion binding energy (stronger solvation ability) than TTFEB and TEB. We then study the ion transport and electrochemical properties of 1 M lithium bisfluorosulfonyl amide (LiFSA) in TFEB as an
electrolyte in comparison to the previously reported tris(2-methoxyethyl) borate (TMEB) electrolyte. Despite slightly lower ionic conductivity compared to TMEB, TFEB electrolyte has higher lithium transference number and can sustain much higher current densities. TFEB electrolyte also produces a denser lithium deposition morphology and higher Coulombic efficiency (97.1% vs 51.7%) than TMEB, which enables stable cycling in lithium metal/LiFePO₄ (Li/LFP) full cells.

**Results and discussion**

**Molecular design and synthesis**

**Figure 1 | Molecular design.** Most commercially available borate ester solvents such as nonfluorinated triethyl borate (TEB) and heavily fluorinated tris(2,2,2-trifluoroethyl) borate (TTFEB) have limited lithium salt solubility. In this work, we synthesize a new compound, tris(2-fluoroethyl) borate (TFEB), with tuned fluorination degree. TFEB has higher lithium salt solubility than TEB or TTFEB, making it a relevant electrolyte solvent. Compared to previously reported...
tris(2-methoxyethyl) borate (TMEB).\textsuperscript{32} TFEB electrolyte enables higher lithium transference number and better stability against lithium metal.

Borate esters have been widely studied as additives in electrolytes as “anion acceptors”, but most borate ester solvents have limited lithium salt solubility.\textsuperscript{27–29} As shown in Figure 1, TEB has three oxygen atoms that could potentially coordinate to lithium ion but still barely dissolves lithium salt. TTFEB can be viewed as a perfluorinated-methyl-group version of TEB that has been studied as an electrolyte additive to promote lithium metal cycling stability.\textsuperscript{30,31} However, TTFEB also has no lithium salt solubility. Tris(methoxy polyethyleneglycol) borate esters such as TMEB, where additional ether units are added as coordination sites, are the only known example that can dissolve lithium salt to concentrations higher than 1 M. Recently, Yu et al. illustrated that partially fluorinated -CHF\textsubscript{2} group led to faster ion transport compared to perfluorinated groups.\textsuperscript{26} Here, we designed a “partially fluorinated TEB”: tris(2-fluoroethyl) borate (TFEB). The structure of TFEB can be viewed as a compromise between TEB and TTFEB. It can also be viewed as analogous to TMEB where the methoxy group is replaced with fluorine. We expect TFEB to maintain the interfacial passivation ability of fluorinated compounds while having a stronger solvating ability compared to TTFEB. TFEB is synthesized through the condensation reaction between boric oxide and 2-fluoroethanol (Figure S1). Synthesis and purification procedure were modified from literature and details can be found in the Supporting Information.\textsuperscript{33} The structure and product purity was verified by \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F, and \textsuperscript{11}B nuclear magnetic resonance (NMR) spectroscopy (Figure S11).

### Ion solvation structure

The effect of fluorination degree on lithium salt solubility was investigated. Figure 2a shows digital images of 1 M LiFSA salt (1 mol of salt per 1 liter of solvent) mixed with different borate esters, where TFEB and TMEB can fully dissolve 1 M LiFSA to form a clear solution whereas undissolved salt remains in TEB and TTFEB. To verify salt solubility and study ion solvation structure, \textsuperscript{7}Li and \textsuperscript{19}F NMR was performed on 1 M LiFSA solutions (TFEB and TMEB) or LiFSA saturated solutions (TEB and TTFEB). Figure 2b shows that no lithium-ion signal is
observed in TEB and TTFEB while 1 M LiFSA solutions in TFEB and TMEB have lithium ion signals at −2.36 ppm and −1.97 ppm, respectively. Compared to TMEB, the more upfield $^7$Li chemical shift in TFEB indicates either more ion pairing or stronger solvent coordination. $^{19}$F NMR spectra in Figure S2 also confirms the poor salt solubilities in TEB and TTFEB as no FSA anion signal is observed. The surprisingly high lithium salt solubility in TFEB compared to TEB and TTFEB indicates the -CH$_2$F group likely promotes lithium salt dissolution.

To explain this unexpected lithium salt solubility trend, the interaction energy between lithium ion and borate esters was calculated using density functional theory (DFT). Figure 2c shows the lithium binding energy with a single solvent molecule, which is defined as $G$(solvent + Li$^+$) − $G$(solvent) − $G$(Li$^+$). The lithium binding energy trend explains the lithium salt solubility trend as Li$^+$ binding energy goes less negative from TMEB to TFEB to TEB to TTFEB, which indicates TFEB has higher salt solubility than TEB and TTFEB because of stronger binding to lithium ion. To probe the differences in ion binding modes, lithium-solvent pair structure optimized in DFT calculations are shown in Figure S3. TEB prefers to bind to lithium ion with the borate ester oxygen since it is the only available binding site. Interestingly, the most favorable lithium binding mode of TFEB is only through the three fluorine atoms and the second most favorable mode binds through two fluorine atoms and one oxygen atom. TTFEB also prefers to bind to lithium ion with two fluorine atoms and one oxygen atom, but the more positive binding energy indicates fluorine atoms in -CF$_3$ groups are less available than in the -CH$_2$F groups of TFEB. In TMEB, the ether oxygen is preferred for lithium ion coordination than the borate ester oxygen. It is well known that the B-O bond in borate esters group has partial sp$^2$ nature and oxygen lone pairs conjugate to boron atom, which likely weakens the coordination ability of borate ester oxygens. The binding mode in TFEB suggests that -CH$_2$F group can act as coordination site that is similar to the methoxy group in TMEB.
Figure 2 | Lithium salt solubility and ion solvation structure. a) Digital photos of 1 M LiFSA salt in TEB, TFEB, TTFEB and TMEB. b) $^7$Li NMR spectra of LiFSA saturated TEB, 1 M LiFSA in TFEB, LiFSA saturated TTFEB and 1 M LiFSA in TMEB. c) Binding energy between Li$^+$ and borate ester solvents simulated by density functional theory (DFT) calculations. d-f) ab-initio molecular dynamics (AIMD) simulations of 1 M LiFSA in TFEB: (d) Radial distribution function (RDF) between lithium ion and possible coordination sites; (e) Coordination number of lithium ion as a function of radius; (f) Snapshot of a representative lithium solvation environment extracted from production run. g) Raman spectra of 1 M LiFSA in TMEB and 1 M LiFSA in TFEB with
pure solvent spectra background. (SSIP: solvent separated ion pair; CIP: contact ion pair; AGG: salt aggregation). h) Fitting of FSA Raman peak after subtracting solvent background. i) Cyclic voltammetry of borate ester electrolytes containing 1 mM ferrocene (Fc) with platinum as working electrode and lithium metal as counter and reference electrode. The dash line indicates halfway potential between Fc oxidation and reduction peaks.

To further understand the unexpected strong solvation ability of TFEB, *ab-initio* molecular dynamics (AIMD) simulation was used to simulate the solvation structure of 1 M LiFSA in TFEB. Figure 2d shows the radial distribution function (RDF) of different binding sites with respect to lithium ion. Consistent with the DFT calculations, the first solvation shell of lithium ion is dominated by oxygen of FSA anion and fluorine of TFEB molecule with little contribution from the oxygen of TFEB. The coordination number \( N_c \) is quantified from cumulative integration curve as shown in Figure 2e using 2.5 Å as cutoff, which also confirms that lithium ion is mainly coordinated by TFEB fluorine \( (N_c = 2.19) \) and FSA oxygen \( (N_c = 1.77) \) instead of TFEB oxygen \( (N_c = 0.38) \). As an example, Figure 2f shows a representative solvation environment of lithium ion in TFEB, where the lithium ion is coordinated by two fluorine atoms from TFEB solvent and two oxygen atoms from FSA anion.

The solvation structure of 1 M LiFSA in TMEB and TFEB electrolytes was also characterized using spectroscopic and electrochemical techniques. Figure 2g shows Raman spectra corresponding to the FSA stretching and B-O stretching modes. FSA peak in TFEB has a blue shift compared to TMEB, which indicates TFEB favors more contact ion pair (CIP) and salt aggregates (AGG).\(^{35}\) Assuming a constant solvent background to be subtracted from FSA peak, the remaining ‘true FSA peak’ can be fit and fraction of ion pairing can be roughly quantified. As shown in Figure 2h, TFEB leads to a much higher fraction of ion pairing (93% AGG and 7% CIP) than TMEB (12% AGG and 36% CIP). Following the protocol recently reported by Ko et al., the lithium redox potential \( (E_{Li}) \) in borate ester electrolytes is calibrated to a ferrocene (Fc) internal standard.\(^{36}\) Figure 2i shows the cyclic voltammetry curve of borate ester electrolytes containing 1 mM Fc with platinum as working electrode and lithium metal as counter and reference electrode. Assuming a constant potential of Fc/Fc\(^+\) as reference, Li/Li\(^+\) potentials in different electrolytes can be calculated and serve as an indicator of ion solvation structure. TFEB
electrolyte has an $E_{\text{Li}}$ of $-2.95$ V, which is 0.35 V higher than TMEB electrolyte ($-3.30$ V). This indicates lithium ion has a weaker binding environment in TFEB and verifies that TFEB leads to an ion solvation structure rich in ion pairing between cation and anion. As discussed later, the high $E_{\text{Li}}$ in TFEB electrolyte leads to more reversible lithium metal cycling as compared to TMEB electrolyte.

**Does anion coordinate to borate esters?**

In prior reports, it is generally believed that the anion can coordinate to the Lewis acidic boron atom in borate esters, which may promote salt dissociation and ion transport.\textsuperscript{27–29} Therefore, we also investigated potential anion-solvent interactions using DFT and AIMD. As discussed in supporting information (Figure S4), simulation results do not show FSA coordination to the borate esters, which also agrees with the lithium transference number below 0.5 (Figure 3b). While our preliminary study does not support anion-solvent coordination, future work will investigate other borate esters as well as probe anions with stronger coordination ability beyond FSA$^-$.

**Ion transport**

Ion transport in borate esters was probed by electrochemical impedance spectroscopy (EIS) and pulsed-field gradient nuclear magnetic resonance (PFG NMR) spectroscopy. Figure 3a shows the ionic conductivity of 1 M LiFSA in borate ester solvents as a function of temperature. TFEB electrolyte shows slightly lower ionic conductivities than TMEB at all temperature investigated, which is likely due to lack of free ion as revealed previously by Raman spectra and cyclic voltammetry. Nonetheless, the ion pairing nature of TFEB electrolyte has positive effects in promoting lithium transference number. Figure 3b shows the ion diffusivity measured by PFG NMR and corresponding lithium transference number calculated as $t_{\text{Li}} = D_{\text{Li}}/(D_{\text{Li}}+D_{\text{FSA}})$. Since most of Li$^+$ and FSA$^-$ in TFEB are closely bound in ion pairs, they have almost identical diffusivity, which leads to a transference number close to 0.5. In contrast, TMEB electrolyte has a lower transference number similar to diglyme. In addition, 1 M LiFSA in TFEB electrolyte also has lower viscosity (7.85 mPa·s) compared to 1M LiFSA in TMEB electrolyte (11.19
mPa·s) even though TFEB solvent has higher viscosity (5.12 mPa·s) than TMEB solvent (2.84 mPa·s) as shown in Table S1. This indicates TMEB has stronger interaction with LiFSA salt, which agrees with the solvation structure study.\textsuperscript{37}

Figure 3 | Ion transport. a) Ionic conductivity as a function of temperature of 1 M LiFSA in TMEB and 1 M LiFSA in TFEB. The lines are Arrhenius fitting of conductivity. b) Ion diffusivities and lithium transference number of 1 M LiFSA in diglyme, 1 M LiFSA in TMEB and 1 M LiFSA in TFEB. c) Critical current density test of 1 M LiFSA in TMEB and 1 M LiFSA in TFEB in lithium metal symmetrical cells (Li/Li). Voltage indicates overpotential versus Li/Li$^+$. To study the effects of ion transport properties on battery cycling performance, critical current density tests were performed in lithium metal half cells (Li/Li cells). Figure 3c shows that TFEB electrolyte maintains stable overpotentials at current densities of 0.02, 0.1 and 0.5 mA/cm$^2$ and can still be cycled at current density as high as 1 mA/cm$^2$. However, the overpotential of TMEB cell increases rapidly at 0.5 mA/cm$^2$ and the cell cannot be cycled at higher current densities. At
0.02 mA/cm$^2$ and 0.1 mA/cm$^2$ current densities where both electrolytes can be cycled, TFEB has lower overpotential compared to TMEB (9 mV vs 18 mV at 0.1 mA/cm$^2$). As discussed later, less resistive solid electrolyte interphase (SEI) formed in TFEB electrolyte as a result of ion pairing and solvent passivation outweigh the small difference in ionic conductivity and leads to the better rate capability of TFEB over TMEB.

**Lithium metal compatibility**

The influence of fluorination on lithium metal compatibility was investigated. Figure 4a shows the Coulombic efficiency of lithium metal cycling measured by a modified Aurbach protocol at 0.1 mA/cm$^2$. The fluorinated TFEB achieves a Coulombic efficiency of 97.1% that is much higher than the nonfluorinated TMEB (51.7%). As shown in Figure S5, TFEB electrolyte maintains high Coulombic efficiency (97.1%) at 0.5 mA/cm$^2$ current density while TMEB electrolyte can hardly cycle at higher current density. The good lithium metal compatibility of TFEB can also be probed by examining the lithium metal morphology using scanning electron microscopy (SEM). Figure 4b shows that lithium metal deposited in TFEB electrolyte (0.5 mA/cm$^2$ to 1.5 mAh/cm$^2$ in Li/Cu cell) has a desired chunky morphology with granular size in microns. In contrast, TMEB electrolyte produces a more dendritic lithium morphology composed of lithium whiskers (Figure 4c). To exclude the effect of rate capability, Figure S6 shows the lithium metal morphology in TMEB electrolyte deposited at lower current density (0.1 mA/cm$^2$ to 1.5 mAh/cm$^2$ in Li/Cu cell), where no significant improvement is observed compared to the morphology at 0.5 mA/cm$^2$. The stark contrast between TFEB and TMEB in lithium metal Coulombic efficiency and lithium morphology indicates fluorination of borate esters significantly improves their performance with lithium metal.
Figure 4 | Lithium metal compatibility. a) Coulombic efficiency test in lithium metal/copper (Li/Cu) cells using a modified Aurbach protocol at 0.1 mA/cm². Voltage indicates overpotential versus Li/Li⁺. b, c) SEM images of lithium metal deposited in (b) 1 M LiFSA in TFEB and (c) 1 M LiFSA in TMEB. d-f) XPS spectra of lithium metal deposited in 1 M LiFSA in TFEB, 1 M LiFSA in TMEB and LiClO₄ saturated TFEB (TFEB LiClO₄). Lithium metal was deposited at 0.5 mA/cm² to 1.5 mAh/cm² in Li/Cu cells for SEM and XPS.

To explain the superior lithium metal compatibility of TFEB, interfacial resistance in Li/Li cell was probed by EIS. As shown in Figure S7, TFEB leads to a much lower solid electrolyte interphase (SEI) resistance (14.44 Ω cm²) than TMEB (110.14 Ω cm²). The lower SEI resistance enables faster lithium ion diffusion through SEI, which likely promotes continuous growth of lithium particles into larger size and improves lithium deposition/stripping reversibility. X-ray photoelectron spectroscopy (XPS) was used to study the chemical composition of the lithium metal SEI. Three electrolytes: 1 M LiFSA in TFEB, 1 M LiFSA in TMEB and LiClO₄ saturated TFEB (< 0.2 M) were studied to decouple the contribution of solvent and salt in the SEI. Figures 4d and 4e show the C1s and O1s spectra of the lithium metal SEI, where common SEI components such as C=O, C−O, C−C/C−H and Li₂O are observed for all three electrolytes. Interestingly, Figure
4f shows that regardless of anion selection, TFEB electrolytes produce more LiF (LiF peak integration = 4554 and 5416 for LiFSA and LiClO₄) compared to the TMEB electrolyte (LiF peak integration = 3665). As is widely acknowledged in literature, high LiF concentration may improve SEI robustness, which may lead to the improved lithium compatibility of TFEB electrolyte. Additionally, the fact that TFEB LiClO₄ electrolyte also produces a high concentration of LiF proves that a significant fraction of LiF originates from TFEB solvent molecules. As shown in Figure 4g, B1s spectra also support that borate ester solvents contribute to SEI since BₓOᵧ and B−OR components are observed in all three electrolytes. To speculate regarding the borate ester degradation pathway, DFT calculations were performed on the reduction of borate esters. As shown in Figure S8, TMEB molecule prefers a reduction pathway via breaking the B-O-C bond while TFEB has a more favored (higher reduction potential) reduction pathway by breaking C-F bond and eliminating a fluoride. DFT calculations support XPS observations that TFEB solvent degradation likely makes significant contribution to SEI.

**Full cell cycling**

**Figure 5 | Lithium metal cell cycling.** a) Galvanostatic cycling of 20 μm lithium metal/LiFePO₄ (ThinLi/LFP) cells. Two replicates of each electrolyte are shown. b) Enlarged view of Coulombic efficiency of TFEB and EC/DMC cells at later stage of cycling.

To illustrate that fluorinated borate ester electrolytes can be viable candidates for lithium metal batteries, cycling of lithium metal (20 μm thickness)/LiFePO₄ (ThinLi/LFP, n/p ≈ 3.2, 1C ≈ 1.81
mA/cm², E/C ≈ 26 g/Ah) full cells with limited lithium content was performed. Figure 5a shows that TFEB electrolyte can enable stable cycling of ThinLi/LFP cells while the TMEB electrolyte leads to rapid capacity decay from the third cycle. In addition, TFEB electrolyte outperforms EC/DMC 1 M LiPF₆ electrolyte with better capacity retention at 40th cycle (82% vs. 68%) and overall higher Coulombic efficiency (Figure 5b). Figure S9 shows the voltage profile of ThinLi/LFP cells at selected cycles, where TFEB electrolyte maintains stable voltage profile despite slow capacity decay and little polarization. To verify that the poor cycling performance of TMEB is not due to rate capability, lithium metal (375 μm thickness)/LiFePO₄(Li/LFP) cells were cycled at varying current rates with five cycles at each rate. As Figure S10 shows, TMEB cell cannot be cycled even at C/10. By contrast, TFEB electrolyte can support cycling up to C/2 and full capacity can be recovered after cycling at 1C. The lithium metal full cell cycling results verify that the fluorination of borate ester greatly improves its ion solvation ability while also enables stability against lithium metal.

Conclusions

This work studies the effect of fluorination degree on solvation ability of borate esters and proves that partially fluorinated groups can enable salt dissolution up to 1 M with fluorine as the main binding site. We synthesized a novel partially fluorinated borate ester TFEB and found that TFEB has surprisingly higher lithium salt solubility compared to the nonfluorinated TEB and heavily fluorinated TTFEB counterparts. Through DFT and AIMD simulations, we discovered that the -CH₂F group in TFEB acts as primary coordination site that leads to the high lithium salt solubility. Owing to the ion solvation structure rich in ion pairing, TFEB electrolyte shows high lithium transference number and facile lithium-ion transport despite moderate ionic conductivity. The high lithium metal Coulombic efficiency and stable Li/LFP full cell cycling supports TFEB as a promising electrolyte solvent candidate for lithium metal batteries. While TFEB is only one example that still requires further optimization, we believe the coordination ability of partially fluorinated groups highlighted in this work would broaden the scope of molecular design and enable novel fluorinated electrolytes for next generation batteries.
Supporting Information

Additional data and figures including physical data, synthetic scheme, NMR spectra, DFT calculation data, AIMD simulation results, SEM images, EIS data, battery cycling data and DSC data.

Author Contributions

C.V.A. and Peiyuan Ma conceived the idea and designed the experiments. Peiyuan Ma performed most of experiments and DFT calculations. R.K. performed AIMD simulation. M.C.V. collected XPS data. K.H.W. collected part of cycling data. Priyadarshini Mirmira contributed to data analysis. All authors contributed to the discussion. Peiyuan Ma and C.V.A. wrote the manuscript, and all the authors contributed to editing the manuscript.

Notes

A provisional patent containing molecular structures shown in this work has been filed.

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authors thank Edward F. Barry at Argonne National Laboratory for providing the 20 μm Li electrode.
Experimental section

Materials

Boric anhydride (98%), 1,2-dimethoxyethane (anhydrous), diethylene glycol dimethyl ether (anhydrous), tris(2,2,2-trifluoroethyl) borate (97%), α,α,α-trifluorotoluene (anhydrous), p-toluenesulfonic acid monohydrate (99%) and 4 Å molecular sieves were purchased from Sigma-Aldrich. Toluene (certified ACS grade), 2-methoxyethanol (anhydrous) and 2-fluoroethanol (95%) were purchased from Fisher. Triethyl borate (97%) was purchased from TCI America. Lithium perchlorate (99%) was purchased from Oakwood Chemical. Deuterated acetonitrile (≥99.8 atom % D) and deuterated dimethyl sulfoxide (≥99.8 atom % D) were purchased from Cambridge Isotope Laboratories. Lithium bis(fluorosulfonyl) amide (99%) was provided by Arkema Inc. All solvents used for preparing electrolytes were dried by 4 Å molecular sieves overnight inside an Argon-filled glovebox (VigorTech, O₂ and H₂O < 1 ppm). Lithium salts were vacuum dried at 120°C overnight in a heated glovebox antechamber before use and was not exposed to air at any time. Other chemicals were used as received.

Celgard 2325 separator was purchased from Celgard LLC. Separator was cut into 18 mm diameter disks, washed multiple times using acetone and vacuum dried at 70°C overnight before they were transferred into the argon glovebox without air exposure (using a BUCHI B-585 glass oven). All stainless steel coin cell parts were obtained from Xiamen TOB New Energy Technology. Lithium foil (375 µm thick) was purchased from Sigma-Aldrich. Lithium foil was polished with a brush to remove oxide layer and cut into 12 mm diameter disks before use. LiFePO₄ (LFP) electrode was kindly provided by Cell Analysis, Modeling, and Prototyping (CAMP) facility of Argonne National Laboratory. LFP electrode has a total mass loading of 13.40 mg/cm² with 90 wt% of Johnson Matthey LFP, 5 wt% of Timcal C-45 and 5 wt% of Solvay 5130 PVDF binder. LFP electrode was cut into 12 mm diameter disks and vacuum dried at 120°C overnight in a heated glovebox antechamber before use.

Synthesis

In the example of TFEB, 4.18 g B₂O₃ (1 eq.), 200 mL toluene, 24.6 g 2-fluoroethanol (6.4 eq.) and 0.2 g p-toluenesulfonic acid monohydrate (0.018 eq.) were added into a round-bottom flask
under nitrogen protection. The mixture was heated to reflux and water is removed by a Dean-Stark apparatus. The reaction was kept refluxing for 4 hours until no more water is generated. Toluene was removed under vacuum and the remaining was purified by fractional distillation under reduced pressure (boiling point of 60°C at ~ 5 mbar). To minimize hydrolysis of product in air, the receiving flask was refilled with nitrogen at the end of distillation and sealed before transferring into glovebox. 10.0 g (42% yield) of TFEB product was collected as a colorless liquid.

TMEB was synthesized by reacting B$_2$O$_3$ with 2-methoxyethanol following similar procedure. TMEB product was collected as a colorless liquid in 51% yield with a boiling point of 82°C at ~5 mbar. NMR spectra of TFEB and TMEB can be found in Figure S11.

Physical characterization

Nuclear magnetic resonance (NMR) spectroscopy: NMR spectroscopy was performed on either a Bruker Ascend 9.4 T / 400 MHz (1D spectra) or a Bruker Ultrashield Plus 11.7 T / 500 MHz (Pulsed-field gradient NMR) instrument. All NMR samples were prepared and sealed inside an argon filled glovebox. NMR sample for synthesis products was prepared by dissolving several milligrams of product into 0.5 mL molecular-sieve-dried deuterated dimethyl sulfoxide. For the characterization of electrolyte solutions, a capillary tube setup was used as described in ref.$^{11,42}$ The LiFSA saturated solutions (TEB and TTFEB) were first passed through a PTFE filter (0.45 µm) while the electrolyte solutions (TMEB and TFEB) were directly filled into a capillary tube (New Era Enterprises) and sealed by a PTFE cap. For 1D $^7$Li and $^{19}$F NMR, a reference solution having 0.1 M LiClO$_4$ and 0.1% volumetric fraction of α,α,α-trifluorotoluene in deuterated acetonitrile was used. The reference solution peak of $^7$Li NMR spectra was calibrated to ~2.80 ppm$^{43}$ and the reference peak of $^{19}$F NMR spectra was calibrated to ~62.5 ppm.$^{44}$ For PFG NMR, around 0.5 mL of deuterated acetonitrile was added to an NMR tube (Wilmad) and the capillary tube with sealed electrolyte was added subsequently. The NMR tube was capped and sealed by parafilm before tested by a Bruker Ultrashield Plus 11.7 T / 500 MHz instrument following programs described in our previous work.$^{12}$
Viscosity measurement: Viscosity of borate ester solvents and electrolytes were measured using a microVISC viscometer (RheoSense). Inside an argon-filled glovebox, the sample was inserted into a pipette. Then, measurements were performed directly after taking out of the glovebox.

Raman spectroscopy: A HORIBA LabRAM HR Evolution Confocal Raman Microscope was used for Raman spectroscopy. A 532 nm ULF laser was used as light source. Sample was prepared by sealing electrolytes in glass chambers inside an argon filled glovebox. The glass chamber was assembled using glass slides (Chemglass life science) and silicone isolators purchased from Grace Bio-Labs.

Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) of lithium metal: Lithium sample was prepared in Li/Cu cells. Five precycles were first performed prior to lithium deposition to clean copper surface (at a current density of 0.02 mA/cm² between 0 V and 1 V). Lithium was then deposited on copper electrode in current of 0.5 mA/cm² or 0.1 mA/cm² to a capacity of 1.5 mAh/cm². Li/Cu cells were opened in an argon filled glovebox. Copper foil with lithium deposited was rinsed with 1,2-dimethoxyethane twice to remove lithium salt and dried under vacuum before testing. A Carl Zeiss Merlin Field Emission Scanning Electron Microscope was used for SEM characterization. XPS analysis was performed by the PHI 5000 VersaProbe II System (Physical Electronics). The spectra were obtained using an Al Ka radiation (hv = 1486.6 eV) beam (100 µm, 25 W), Ar⁺ and electron beam sample neutralization, in Fixed Analyzer Transmission mode. XPS spectra were aligned to the C−C component in the C1s spectra at 284.6 eV.

Electrochemical characterizations

Lithium potential test in Li/Pt cells: 200 µL electrolyte containing 1 mM ferrocene was added into a micro beaker cell with a platinum wire as working electrode and a lithium wire as counter and reference electrode. Cyclic voltammetry was performed at a scan rate of 5 mV/s for three scans (oxidation first) and the second scan was used for plotting and calculating lithium potential.

Coin cell preparation: All the electrochemical characterizations except for lithium potential test were performed in CR2032 type coin cells with the following configuration: negative
case||spring||spacer||anode (counter electrode)||25 μL electrolyte||1 separator||25 μL
electrolyte||cathode (working electrode)||spacer||positive case.

**Electrochemical impedance spectroscopy (EIS):** Stainless steel/stainless steel (SS/SS) coin
cells were tested inside an ESPEC environmental chamber (BTZ-133). Temperature was first set
to 80°C and cooled in 10 degree intervals to 20°C while holding at each temperature for 1 hour
before EIS measurement. A Biologic VSP-300 Potentiostat was used to measure impedance
spectra between 7 MHz and 100 Hz. To calculate realistic conductivity, raw conductivity was
multiplied by a cell constant of 12.6, which is calibrated using 1 M LiFSA in TFEB electrolyte
by a Platinum-Cell Conductivity Probe (Vernier).\(^{12}\)

**Coin cell cycling:** A Neware BTS4000 battery tester was used to cycle Li/Li, Li/Cu and Li/LFP
coin cells at 20°C (±0.1°C) or uncontrolled room temperature (~26°C). All cells were rested for
10 hours before testing. Li/Li cells were first cycled 0.02 mA/cm\(^2\) to 0.1 mAh/cm\(^2\) for five
formation cycles and then cycled at current densities increasing from 0.1 mA/cm\(^2\) to 1 mAh/cm\(^2\)
with 1 hour duration of charge and discharge. For Coulombic efficiency (CE) measurement in
Li/Cu cells, a formation cycle was first performed by depositing lithium on copper electrode for
10 hours and then stripping to 1 V. Afterward, a ten-hour deposition was done and followed by
10 cycles of two-hour deposition and two-hour stripping (yielding 0.2 mAh/cm\(^2\) for 0.1
mA/cm\(^2\)). Finally, lithium was stripped from copper electrode until cell voltage reaches 1 V. CE
was calculated as the ratio of total stripping capacity over total depositing capacity (excluding
the formation cycle). LFP cells were cycled in a voltage window of 2.9-3.8 V with current rates
calculated based on the exact mass of cathode material, using 150 mAh/g as the full capacity of
LFP. For an average mass loading of 12.1 mg LFP/cm\(^2\), 1C ≈ 1.81 mA/cm\(^2\). For cycling of
ThinLi/LFP cells, two formation cycles at C/10 were first performed and then the cell was cycled
at C/5 charging rate and C/3 discharging rate. For rate capability test of Li/LFP cells, five cycles
were performed at each current rate.

**Simulations**

**Ab-initio molecular dynamics (AIMD) simulations:** The AIMD calculations were performed
using CP2K (version 9.1).\(^{45}\) The simulation box for pristine TFEB of size 20×20×20 Å\(^3\)
containing 29 TFEB molecules was first created by using Packmol. This simulation box underwent constant pressure NPT ensemble calculations (at 300 K) for 5 ps to obtain the correct box size. Five molecules of LiFSA were then added to this box using Packmol. The initial 1 M LiFSA in TFEB simulation box was annealed at 500 K for 5 ps (NVT ensemble) and then the final production run (NVT ensemble) was performed at 300 K for 15 ps. The RDF was calculated for trajectories from the final 13 ps production run using the MDAnalysis python library. All AIMD calculations employed a double \( \zeta \) basis set, GTH pseudopotentials using a 400 Ry cutoff for the auxiliary plane wave basis, PBE functional along with Grimme’s D3 dispersion correction, and periodic boundary conditions. The Nosé-Hoover thermostat was used for equilibration.

**Density functional theory (DFT) calculations:** DFT calculations were performed using the Gaussian 16 computational package. All geometries were optimized at B3LYP/6-31G(d,p) level of theory. After stationary points were verified by the absence of imaginary frequencies, single point energies of the optimized geometries were calculated using B3LYP/6-311++G(d,p). Solvent effects were accounted by employing the SMD model. THF was selected because of its moderate dielectric constant. Grimme’s DFT-D3 method with BJ-damping (GD3BJ) was used for dispersion correction. To calculate the binding energy, Gibbs free energies of solvents and solvent-ion clusters were calculated. Ion (lithium ion or anion) binding energy is defined as \( G(\text{solvent} + \text{ion}) - G(\text{solvent}) - G(\text{ion}) \). The reduction energy was calculated from \( G(\text{solvent}) - G(\text{solvent}^-) \), where the geometry of solvent\(^-\) is optimized. The reduction energy value was divided by Faraday’s constant and then 1.4 V was subtracted from it to convert to reduction potentials versus Li/Li\(^+\) electrode.
References


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