Fluoroalkyl ether electrolyte with redefined in-cell ion affinity upgrades rate performances of lithium ion batteries

Liwei Dong  
Harbin Institute of Technology

Yuanpeng Liu  
Harbin Institute of Technology

Kechun Wen  
Harbin Institute of Technology

Dongjiang Chen  
University of Electronic Science and Technology of China

Jipeng Liu  
Harbin Institute of Technology

Botao Yuan  
Harbin Institute of Technology

Yunfa Dong  
Harbin Institute of Technology

Ze Wu  
Harbin Institute of Technology

Yifang Liang  
Harbin Institute of Technology

Mengqiu Yang  
Harbin Institute of Technology

Jianyi Ma  
Sichuan University

Chunhui Yang  
Harbin Institute of Technology

Weidong He (weidong.he@hit.edu.cn)  
Harbin Institute of Technology

Article

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Abstract

Lithium ion batteries have profound impact on every corner of human life. However, strong solvation of Li+ and rough interfacial ion transfer associated with conventional electrolytes limit the long cycle, high-rate battery operation of lithium ion batteries. Herein we design an electrolyte system based on fluoroalkyl ether 2,2,2-trifluoroethyl-1,1,2,3,3,3-hexafluoropropyl ether (THE) and ether electrolytes to effectively upgrade the long-cycle rate performances of electrodes in general. With THE rich in fluoroalkyl groups adjacent to oxygen atoms, the electrolyte owns an ultra-high polarity, enabling solvation-free Li+ transfer with an energy barrier of 0.11 eV, only 1/7 of that for conventional ether electrolytes, and 10-times enhancement in Li+ transference at electrolyte/anode interface. In addition, the uniform adsorption of fluorine-rich THE on anode and subsequent LiF formation suppress dendrite formation and stabilize the solid electrolyte interphase layer. With the electrolyte, LiFePO4 cathodes deliver unprecedented cyclic performances with only 0.0012% capacity loss cycle-1 over 5000 cycles at 10 C, along with upgraded rate performances as observed for other mainstream electrodes including LiCoO2, LiNi0.5Mn0.3Co0.2O2 and Li4Ti5O12.

Introduction

Humans have entered an era featured with information technology, instant communication and convenient transportation, together calling up the extensive applications of rechargeable lithium ion batteries (LIBs). Towards high-capacity LIBs, cathode materials have gone through generation transitions from LiCoO2 (LCO) to LiFePO4 (LFP) and then to LiNi\(_x\)Mn\(_y\)Co\(_{1-x-y}\)O\(_2\) (NCM), and in the meanwhile anodes beyond graphite such as Li\(_4\)Ti\(_5\)O\(_12\) (LTO) have also been commercialized. In addition to the aforementioned commercial electrodes, many other materials have been actively investigated and some have been regarded as promising energy storage materials to meet the requirements of high-capacity, long cycle and high rate LIBs, such as Li air batteries and Li-S batteries among other novel batteries with Li metal anode. Despite the widespread adoption and countless research efforts, there still exist unsatisfactory and even disastrous drawbacks associated with current LIBs, including degrading capacity over cycles, slow charge/discharge rate and safety-related fatalities. These battery properties are all closely correlated with the composition of the electrolyte which transfers Li+ between electrodes and forms electrolyte/electrode interfaces. For instance, the electrolyte with excellent wettability increases the contact area with the separator and expedites ion migration to enhance rate capacity. The compatibility between electrolyte and electrode ensures uniform and reversible Li+ transmission. Further, the electrolyte directly determines the composition and electrochemical property of solid electrolyte interface (SEI), laying a profound impact on the cycle life and safety of LIBs. Electrolyte solvents used in LIBs are mainly ethers and carbonates, owing to their wide electrochemical windows and the capability to form stable cathode interface. However, multiple challenges, including dendrite electrodeposition and parasitic reactions, arise from reactive anodes as well as rough and sluggish electrolyte/electrode interface ion transference of conventional electrolytes. In addition, these commercial ether-based and carbonate-based electrolytes are highly flammable, posting potential safety
hazards. Extensive efforts have been focused on developing powerful new electrolyte systems to address these challenges including: (1) solid-state electrolytes with safety and high-energy-density, such as inorganic solid electrolyte\textsuperscript{15} and solid-state polymer electrolyte\textsuperscript{16} (2) novel electrolyte solvents with excellent physicochemical properties, such as ionic liquid with excellent ion conductivity,\textsuperscript{17} non-toxic and non-flammable aqueous solvent,\textsuperscript{18} and nitrile with high oxidation potential;\textsuperscript{19} (3) electrolyte additives with SEI formation or flame retardancy, such as lithium difluorobis (oxalato) phosphate (LiDFBOP),\textsuperscript{20} fumed silica,\textsuperscript{21} and trimethyl phosphate;\textsuperscript{22} (4) high concentrated electrolytes with advanced solvation structure.\textsuperscript{23,24} However, solid-state electrolytes with rough electrolyte/electrode interfaces cause excessive interface impedance and result in low ionic conductivity, and novel solvents, additives and highly-concentrated electrolytes often come with increased viscosity, resulting in poor wettability of separators and the electrodes.

In this report, we develop an electrolyte system based on fluoroalkyl ether 2,2,2-trifuoroethyl-1,1,2,3,3,3-hexafluoropropyl ether (THE) and ether electrolytes. The THE electrolyte significantly enhances the interface ion transference to ultimately enhance the in-cell ionic conduction of batteries with prototype conventional electrodes, and effectively suppresses the Li dendrite growth by forming an inorganic LiF-rich SEI. With the electrolyte, the LiFePO\textsubscript{4} cathode exhibits unprecedented cyclic performances with 0.0012% capacity loss cycle\textsuperscript{−1} over 5000 cycles at 10 C, in addition to the upgraded performances of other typical commercial electrodes including LCO, NCM523 and LTO.

**Results And Discussion**

**Physicochemical properties of THE electrolyte:**

The compositions of the electrolytes investigated in this work are shown in Table S1 (Supporting Information). THE has outstanding anti-oxidation stability owing to robust electron-withdrawing groups (CF\textsubscript{3} and CF\textsubscript{2}). As shown in Figs. 1(a) and 1(e), it exhibits a much lower highest occupied molecular orbital (HOMO) energy value (-8.48 eV) and a much lower lowest unoccupied molecular orbitals (LUMO) level (-0.75 eV) as compared with commercial 1, 3-dioxolane (DOL) and dimethoxyether (DME) solvents, indicating its high-voltage stability and ready reduction on the anode with SEI formation. As shown in Fig. 1(b), conventional DOL + DME electrolyte causes uneven deposition of Li\textsuperscript{+} since rough and sluggish interfacial ion transference between anode and electrolyte produces dead Li on the anode surface, leading to irreversible Li\textsuperscript{+} transmission. After 100 cycles in the DOL + DME electrolyte, a loose layer is observed on the surface of Li anode (Fig. S1a, Supporting Information). This porous layer (Fig. 1c) further aggravates the rough deposition, resulting in continuous corrosion of the Li metal, as evidenced with the low Coulombic efficiency (CE) and poor cycling stability (Figs. 3d-g). The porous dead Li layer with a thickness of 124 µm is clearly observed from the cross-sectional scanning electron microscopy (SEM) image (Fig. 1d). This means that the Li metal is severely corroded with the DOL + DME electrolyte, causing the rapid decay of the capacity.\textsuperscript{25} In contrast, for 60%THE electrolyte, abundant LiF is formed at the electrolyte/electrode interface (Fig. 1f). LiF owns excellent ion transmission ability and stability (6.4 V
vs Li/Li+), and enables compact packing in the SEI to isolate the Li metal from the electrolyte. Furthermore, LiF owns high interfacial energy with Li metal, which accelerates Li+ migration along the interface and promotes the parallel growth of Li dendrites along Li metal plane instead of vertical growth. The protective effect of LiF-rich SEI on the Li anode is clearly observed in the SEM images. The anode surface layer in the 60% THE electrolyte (Figs. 1g and S1b, Supporting Information) is much more compactly integrated than that in the DOL + DME electrolyte. Especially, the corrosion of the Li metal is greatly reduced in the 60% THE electrolyte, and only the top layer (20 µm) is corroded after 100 cycles (Fig. 1h). The dense surface layer owns three advantages: (1) reliable security because the ball-like Li morphology is less likely to pierce separator; (2) high CE because the dense layer prevents continuous reaction to reduce the consumption of Li anode and electrolyte; (3) additional volumetric capacity because dense Li packing reduces the volume. In the elemental mappings of Li anodes in DOL + DME (Figs. S2a and S2b, Supporting Information) and 60% THE (Figs. S2c and S2d, Supporting Information) electrolytes after cycling, C elemental mapping is mainly derived from electrolyte solvents and, thus, is selected as the representative of organic species. The Li metal in the 60% THE electrolyte contains less C element as compared with that in the DOL + DME electrolyte, implying reduced solvent decomposition in the 60% THE electrolyte. F elemental mapping is taken as the representative of the SEI layer. The Li metal in the 60% THE electrolyte contains more F element as compared with that in the DOL + DME electrolyte, indicating that the addition of THE is favorable for the formation of the SEI layer. Figures 1(i-k) show X-ray photoelectron spectroscopy (XPS) of the SEI layer in the 60% THE electrolyte. The organic species formed with the ether electrolyte solvent, including C = O, C-O, and C-H/C-C, are studied with C 1 s spectrum (Fig. 1i). Obvious signals of CF3 and C-F are observed, as attributed to the cleavage of the fluorinated groups of THE. As shown in Fig. 1(j), a main peak at ~ 685.7 eV is observed, implying that the F element in the SEI layer exists mainly in the form of F-Li bond. The signal of F-Li bond is also observed in Li 1 s XPS spectra, as shown in Fig. 1(k). In-situ Raman spectroscopy is used to study the internal change of THE-based electrolyte during charging and discharging. The test battery configuration is shown in Fig. S3 (Supporting Information). As displayed in Figs. 1(l) and 1(m), extensive LiF (≈ 409 cm−1) is formed in the 60% THE electrolyte, considerably above that in the DOL + DME electrolyte, which is attributed to the cleavage of numerous C-F in THE. This is also demonstrated through Fourier-transform infrared (FTIR) spectra of the Li anodes after cycling (Fig. S4, Supporting Information). For the 60% THE electrolyte, the peak of fluorine-containing species (C-F stretching vibration) at ~ 1000 cm−1 increases apparently after the first charge, indicating the cleavage of the fluorinated segment of THE molecules. In contrast, there is no obvious fluorine-containing signal in the DOL + DME electrolyte.

Flammable commercial electrolytes exists a safety risk in high-rate operations of lithium ion batteries. The thermal stability of ethylene carbonate (EC) + dimethyl carbonate (DMC), DOL + DME, and 60% THE electrolytes is evaluated, as shown in Figs. 2a-c and Videos S1-S3 (Supporting Information). In Videos S1-S3, commercial EC + DMC and DOL + DME electrolytes are readily ignited and burned quickly, whereas the 60% THE electrolyte is non-flammable even with repeated igniting. As the objective leaves the heat source, there are raging flames in EC + DMC and DOL + DME electrolytes, but no flame is observed in the 60% THE...
electrolyte (Fig. 2c). The ultra-low flammability of THE is attributed to the fluorine substitution at the alkyl moiety of THE, inhibiting the propagation of free oxygen radicals during combustion. The affinity of electrolyte solvents with the polypropylene (PP) separator is studied with density functional theories (DFT). As shown in Fig. 2d, the adsorption energy of THE-CH$_2$CHCH$_3$ (-0.12 eV) is much below those of DOL-CH$_2$CHCH$_3$ (-0.076 eV) and DME-CH$_2$CHCH$_3$ (-0.044 eV), indicating the outstanding affinity between PP and THE. The 60%THE electrolyte owns a high wettability with the separator, leading to an increased electrolyte uptake (Figs. 2e and 2f). The viscosity of the 60%THE electrolyte is only 1.8 mPa s, considerably lower than those of EC + DMC (3.1 mPa s) and DOL + DME (3.5 mPa s) electrolytes. In particular, the 60%THE electrolyte maintains the hardly unchanged viscosity at low temperatures (Fig. 2g). The conductivities and Li$^+$ transference numbers (t$_{Li^+}$) of the electrolytes are displayed in Fig. 2h. The conductivity of the 60%THE electrolyte is slightly lower, but reasonably comparable to those of EC + DMC and DOL + DME electrolytes (that is, 6.2 mS cm$^{-1}$ versus 10.3 mS cm$^{-1}$ and 9.2 mS cm$^{-1}$). Different from conductivity, t$_{Li^+}$ increases with increasing THE in the electrolytes from 0.240 for 20%THE, 0.262 for 40%THE, and 0.301 for 60%THE to 0.310 for 80%THE, which are all above those of for EC+DMC (0.211) and DOL+DME (0.225). In particular, as shown in Fig. 2i, compared with commercial electrolytes the 60%THE electrolyte exhibits a wider electrochemical window and is thus capable of supporting higher voltage battery systems.

**Electrochemical behaviors of commercial electrodes with THE electrolyte**

As shown in Fig. S5, the Li/LFP battery with the 60%THE electrolyte owns the largest capacity and the electrochemical performances of the 60%THE electrolyte are investigated. Due to the high ion transmission capability of LiF-rich SEI and excellent separator wettability, the 60%THE electrolyte greatly increases the rate performance (Figs. 3a-c) and cycling performance (Figs. 3d-g) of the battery. As shown in Figs. 3(a) and S6 (Supporting Information), the LFP cathode with the 60%THE electrolyte delivers discharge capacities of 153.2 mAh g$^{-1}$, 124.1 mAh g$^{-1}$, 109.8 mAh g$^{-1}$, 95.2 mAh g$^{-1}$, 82.0 mAh g$^{-1}$, 72.8 mAh g$^{-1}$, 49.8 mAh g$^{-1}$ and 38.1 mAh g$^{-1}$ from 1 C to 100 C. The capacity recovers to 97.8% of the initial capacity as the current density is decreased from 100 C back to 1 C, indicating the excellent reversibility of the 60%THE electrolyte. In contrast, the discharge capacities are considerably lower at all C rates for the EC + DMC electrolyte. For further verification, a high-loading LFP electrode of 13.46 mg cm$^{-2}$ is utilized. As shown in Fig. 3(d), the battery with the 60%THE electrolyte maintains a stable cycle at 0.61 mA cm$^{-2}$, while the battery with original electrolyte undergoes decrease in both capacity and CE. The Li/LTO battery using 60%THE electrolyte also exhibits obvious advantages in electrochemical performances over the commercial electrolyte (Fig. S7, Supporting Information). In addition, the LFP cathode is assembled into full cells with LTO and graphite anodes. Significantly improved cycling and rate performances are achieved in full batteries (Figs. 3b, 3e, and S8, Supporting Information). For other major commercial cathode materials including LCO and NCM532, the batteries with the 60%THE electrolyte also achieve improved rate and cycling performances as compared with these with the commercial electrolyte (Figs. 3c, 3f, and S9, Supporting Information), indicating that the 60%THE electrolyte owns a wide-range applicability. It is noted that less improvement in performances is observed
for NCM811 full cells using 60%THE electrolyte (Fig. S10, Supporting Information), as attributed to the similarity in the radii of Ni$^{2+}$ and Li$^+$. In the delithiation state, the rapid transfer of Li$^+$ in THE-based electrolyte generates a large number of vacant sites as occupied by Ni$^{2+}$, resulting in an irreversible phase transition of the cathode structure.

The long-cycle, high-rate performances of the Li/LFP cells with EC + DMC and 60%THE electrolytes are shown in Figs. 3g and S11. The cells with the 60%THE electrolyte give rise to higher capacity and better capacity retention as compared with the EC + DMC electrolyte at all rates (Table S2, Supporting Information). In particular, the battery shows an unprecedented cycle retention with only 0.0012% capacity loss cycle$^{-1}$ over 5000 cycles at 10 C (Table S3, Supporting Information). The low-temperature performances of the Li/LFP batteries with EC + DMC and 60%THE electrolytes are studied (Fig. S12, Supporting Information). The battery with the 60%THE electrolyte also exhibits more pronounced rate capacities as compared with the commercial electrolyte at low temperatures. As displayed in Table S4 (Supporting Information), with the 60%THE electrolyte, the battery capacities have no significant change at various rates (< 5 mAh g$^{-1}$) at 25 °C and 0 °C. The outstanding low-temperature performances of the 60%THE electrolyte are due to the hardly unchanged viscosity with changing temperature (Fig. 2g) and excellent compatibility between electrolyte and separator (Figs. 2d-f), ensuring efficient in-cell ionic conduction. In contrast, the high viscosity of the EC + DMC electrolyte at low temperatures causes slow ion transport and the battery is severely polarized, leading to the low capacity.

**Mechanism of rate-performance improvement with THE-based electrolyte**

*Ab initio* molecular dynamics (AIMD) simulations are employed to investigate the solvation structure and rate performances of electrolytes. Fig. S13 shows the simulation snapshots of EC + DMC, DOL + DME and 60%THE electrolytes, respectively. The representative configurations of coordinated molecules in the first Li$^+$ shell in the three different electrolyte systems are depicted with a ball-and-stick model (Figs. 4a-c). Li$^+$ prefers to coordinate with oxygen from EC, DMC, DOL and DME solvent molecules, facilitating the dissociation of the lithium salts, while THE is a free solvent molecule and does not coordinate with either Li$^+$ or anions. Therefore, the dissociation of lithium salts and the number of charge carriers in the THE-based electrolyte decrease with increasing volume ratio of THE, resulting in reduced Li$^+$ cations () and TFSI$^-$ anions (). In the 60%THE electrolyte, the Li$^+$ cations are weakly solvated with solvent molecules, and meanwhile the anions are seriously dragged by the Li$^+$ cations in return, resulting in a low the mobility of TFSI$^-$ anions (). As shown in Eqs. 1 and 2, the ion conductivity and Li$^+$ transference number own opposite trends with increasing volume ratio of THE (Fig. 2h). Electrostatic potential (ESP) is calculated to study the impact of electron-withdrawing fluoroalkyl groups on the properties of solvent molecules (Figs. 4d-f). For the DME molecule, the negative potential mainly is concentrated on O atoms (Fig. 4d), while the THE molecule owns a uniform negative potential distribution in the presence of electron-withdrawing fluoroalkyl groups, demonstrating that THE is unable to coordinate with positively-charged Li$^+$ (Fig. 4e). As the two F atoms on the carbon adjacent to the O atom are replaced with H atoms, the isopotential surfaces of 2,2,2-trifluoroethyl-2,3,3,3-tetrafluoropropyl ether (TTEE) show similar
trends with that of DME (Fig. 4f), indicating that the two electron-withdrawing fluoroalkyl groups adjacent to the oxygen atom result in the low solvating capability of lithium ions.

As shown in Tables S5 and S6, the ion conductivity of each component in the battery with DOL + DME and 60%THE electrolytes is studied. The slowest ion conduction inside the battery occurs at the electrolyte/anode interface and is on the order of $10^{-7}$ S/cm, which is far below that of the electrolytes. The ion transport at electrolyte/electrode interface and in the electrodes is contributed by Li$^+$ transfer. Therefore, the Li$^+$ conduction at the electrolyte/electrode interfaces, instead of the Li$^+$ conduction in the electrolyte, is the limiting factor for the rate performances of the battery system. With a smaller ionic conductivity, the THE-based electrolyte owns a larger Li$^+$ transference number and enables much enhanced rate performances of the batteries, indicating the THE-based electrolyte greatly enhances the Li$^+$ conduction at the electrolyte/electrode interfaces. Due to the extremely low HOMO energy value (<8.4 eV) and the high oxidation potential (>5.6 V), THE is free of oxidation on the surface of the cathode (Figs. 1e and S14, Supporting Information). Therefore, the composition of cathode electrolyte interphase (CEI) in the 60%THE electrolyte is the same as that in commercial electrolyte. As shown in XPS (Figs. 1j and 1k) and AIMD (Fig. 4h) results, compared with DOL and DME molecules, abundant LiF forms at the surface of Li metal due to the C-F bond cleavage in THE, resulting in an increased F element ratio in the SEI layer. As shown in Figs. 1j and 4h, the added F element ratio in the SEI layer exists almost entirely in the form of LiF after the introduction of THE. After introducing THE, the increased ratio of F element is ~0.29 for the 60%THE electrolyte. Based on Eq. 3, $\sigma_2$ is calculated to be ~1.9 $\times$ $10^{-7}$ S/cm, which is on the same order of that for LiF ($\sigma_{\text{LiF}}$, 6.4 $\times$ $10^{-7}$ S/cm$^2$) and far beyond that of conventional electrolyte/anode interface ($\sigma_1$, 1 $\times$ $10^{-9}$ S/cm$^2$). Such an enhancement on the ionic conductivity at electrolyte/anode interface gives rise to the improved rate performances with the 60%THE electrolyte. It is noted that regardless of the anode material the SEI film is mainly formed through the reaction of the deposited Li with the electrolyte. Therefore, the THE electrolyte improves the ionic conductivity of SEI and rate performances of lithium ion batteries in general.

The mechanism of C-F bond cleavage is further studied. Owing to a low LUMO energy value (Fig. 1e), THE on the anode surface is prone to defluorination through reduction reaction. AIMD simulations (Fig. S15, Supporting Information) show the C-F bond breaks on the C atom between the CF$_2$ and the CF$_3$ groups of THE. As shown in Fig. 4g, the energy barriers for the C-F bond cleavage of TTEE and 2,2,2-trifluoroethyl-1,1,2-trifluoropropyl ether (TTRE) are 0.69 eV and 0.14 eV, considerably above that of THE (0.04 eV), indicating that the efficient formation of LiF through C-F bond cleavage with the THE electrolyte.

The energy barrier for Li$^+$ mobility at the deposited Li (0 0 1)/electrolyte interface is calculated through AIMD simulations (Figs. 4i and S16, Supporting Information). For the THE-based electrolyte, the energy barrier is ~1/7 and 1/6 those of the conventional DME and DOL electrolytes, since THE is a free solvent molecule and Li$^+$ does not completely strip off the solvent molecules before intercalation into the anode, verifying that the addition of THE is beneficial for improving the ion transmission at electrolyte/anode interface.
interface. AIMD calculations (Fig. 4h) show that F transfers from the THE solvent to the deposited Li surface, resulting in LiF-rich inorganic species near the anode surface, as observed with in-situ Raman (Figs. 11 and 1 m). The LiF-rich interphase layers on the electrodes improve the reaction kinetics and cycle stability of the batteries.

**Conclusion**

In summary, THE-based electrolyte is first developed by employing fluoroalkyl ether THE as the cosolvent in LiTFSI/DOL + DME. Both experiments and computational simulations demonstrate that the THE-based electrolyte with interface ion affinity owns excellent wettability to the commercial separator, rapid and uniform Li$^+$ transmission, and promotes the formation of LiF-rich SEI with mitigated Li dendrites. Using the 60%THE electrolyte, the LiFePO$_4$ cathode exhibits sustainably enhanced cycling stability and unparalleled low capacity fading in high-rate long cycle. This study offers a promising strategy to enable THE-based electrolytes with rapid interface ion transference for high-performance energy-storage devices.

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