Fluorine-donating electrolytes enable highly reversible 5-V-class Li metal batteries

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.
Fluorine-donating electrolytes enable highly reversible 5-V-class Li metal batteries

Liumin Suoa,b,*, Weijiang Xueb,c, Mallory Gobeta, Steve G. Greenbaumd, Chao Wanga,b,c, Yuming Chenb,c, Wanlu Yangd, Yangxing Li³, and Ju Li³,b,c,†

*Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, 100190 Beijing, China. †Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139; ‡Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139; §Department of Physics and Astronomy, Hunter College of City University of New York, New York, NY 10065; and †Watt Laboratory, Central Research Institute, Huawei Technologies Co., Ltd., 518129 Shenzhen, China

Lithium metal has gravimetric capacity ~10× that of graphite which incentivizes rechargeable Li metal batteries (RLMB) development. A key factor that limits practical use of RLMB is morphological instability of Li metal anode upon electrodeposition, reflected by the uncontrolled area growth of solid–electrolyte interphase that traps cyclable Li, quantified by the Coulombic incompressibility (CI). Here we show that CI decreases approximately exponentially with increasing donatable fluorine concentration of the electrolyte. By using up to 7 m of Li bis(fluorosulfonyl)imide in fluoroethylene carbonate, where both the solvent and the salt donate F, we can significantly suppress anode porosity and improve the Coulombic efficiency to 99.64%. The electrolyte demonstrates excellent compatibility with 5-V LiNi0.5Mn1.5O4 cathode and Al current collector beyond 5 V. As a result, an RLMB full cell with only 1.4× excess lithium as the anode was demonstrated to cycle above 130 times, at industrially significant loading of 1.83 mAh/cm² and 0.36 C. This is attributed to the formation of a protective LiF nanolayer, which has a wide bandgap, high surface energy, and small Burgers vector, making it ductile at room temperature and less likely to rupture in electrodeposition.

Nonrechargeable batteries like Li/NaClO₂ can achieve 650 Wh/kg and 1,280 Wh/L at full-cell level, demonstrating the enormous advantage of Li metal anode (LMA). However, to make rechargeable batteries that can charge hundreds of times, the Coulombic efficiency (CE) and growth of porosity of LMA must get under control. In terms of anode gravimetric and volumetric capacity, while fully dense Li metal enjoys a huge advantage at the beginning (gravimetric capacity: 3,861 mAh/g; volumetric capacity: 3,861 mAh/g × 0.534 g/cm³ = 2,062 mAh/cm³, where 0.534 g/cm³ is the theoretical density of Li metal), it would quickly form a large amount of dead lithium and gain porosity (1) upon redeposition in typical organic electrolytes. When the non-Li metal volume fraction ϕ grows beyond 70%, the LMA volumetric capacity would drop below that of graphite (372 mAh/g × 1.6 g/cm³ = 600 mAh/cm³), at which point it is no longer commercially viable. The gain in porosity and interfacial area of LMA can be attributed to an effectively negative interfacial energy \( y_{LMA} < 0 \), since thermodynamically all liquid electrolytes are unstable at 0 V vs. Li/Li⁺, and will reductively decompose to form solid–electrolyte interphase (SEI) that covers every electron-conductive surface of LMA, incentivizing growth of the interfacial area. This explosive area growth will cause electrolyte dry-out, as well as exhaustion of cyclable lithium (2, 3). The latter is semiquantitatively reflected by the CE and Coulombic inefficiency (CI ≡ 1 − CE), which characterizes the ratio of Li⁺ that can be pulled out of the anode within a fixed cell voltage window, after a known amount of Li⁺ is deposited into it in the same voltage window, assuming only Li⁺ can be transferred in the electrolyte in a nonblocking manner (4) and the anode is initially free of cyclable lithium. There is an industry lore that in order for a Li-matched full cell to cycle 200 times, CE needs to exceed 99.9% (CI < 10⁻³). Even though this is not exact (4), there is no question that an excellent CE is key for highly reversible LMA.

The most effective way to enhance the full-cell energy density is to introduce high-voltage and -capacity electrodes. Take the electrochemical couple of 5-V-class spinel LiNi₀.₅Mn₁.₅O₄ (LNMO)/LMA for example: This combination is likely to bring totally about 80% increase in full-cell energy density compared with commercial lithium-ion battery (LIB) with 4-V-class cathodes and graphite anode. However, 5-V rechargeable lithium metal battery (RLMB) is currently limited by the unavailability of electrolytes which must simultaneously satisfy wide enough electrochemical stability window, good compatibility with LNMO electrode, Al current collector corrosion resistance, and superior reversibility of LMA. Traditionally, carbonate-based electrolytes were exclusively used in commercial LIB thanks to its wide electrochemical stability window (0–4.5 V) and robust SEI on the graphite anode, enabling the high voltage of LIB (5). But, they cannot work well in RLMB due to low CE for LMA [propylene carbonate (PC): CE < 80%, ethylene carbonate (EC): <95%, dimethyl carbonate (DMC): <30%, EC-DMC: <91%, and EC-diethyl carbonate (DEC): <95%] (6–11). Highly concentrated electrolytes have attracted much attention recently (12–24). On the cathode side, highly concentrated fluoro-organic Li salt electrolyte has been used to prevent the corrosion of Al current collector (18, 19, 25), as well as improving oxidative stability of cathode (17, 20, 22). With highly concentrated Li bis(fluorosulfonyl)imide (LiFSI) in DMC (1:1 by molar ratio), Li ion full cell (LNMO/graphite) present very good cycling stability.

Author contributions: L.S. and J.L. designed research; L.S. performed research; L.S., W.X., Y.C., W.Y., Y.L., and J.L. analyzed data; and L.S. and J.L. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

Published under the PNAS license.

1To whom correspondence may be addressed. Email: liju@mit.edu or li.yangxing@huawei.com.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1712895115/-/DCSupplemental.

Significance

Rechargeable lithium metal battery (RLMB) is the holy grail of high-energy-density batteries. If lithium metal anode (LMA) could be combined with 5-V LiNi0.5Mn1.5O4 cathode, energy density could exceed 600 Wh/kg based on the cathode and anode electrode mass. Despite such promises, 5-V RLMB is still a vacant research space so far due to the unavailability of electrolytes which simultaneously satisfy a wide enough electrochemical stability window, good compatibility with LiNi0.5Mn1.5O4 and superior reversibility of LMA. In this work, a class of full-fluoride (FF) electrolyte is invented for 5-V RLMB which not only has good compatibility with cathode and a wide stability window but also possesses the capability to make LMA more stable and reversible.
The positive effect of fluoride donation on LMA is empirically known, through ex situ surface treatment by fluoride-containing gases (CF$_4$ and CF$_3$$_2$), and in-situ LiF-rich SEI formation by introducing F-containing additives such as HF (27), LiF (28, 29), fluoroethylene carbonate (FEC) (30), and LiPF$_6$ (31). Li is one of the most electropositive elements on the periodic table, while F is the most electronegative, and also has the smallest ionic radius among all anions. Therefore, LiF possesses many extreme properties among solids, such as the largest bandgap (13.6 eV) and the widest electrochemical stability window (32). This makes LiF an excellent SEI passivation component since a very thin LiF nanolayer can stop electron tunneling. Ozharbes et al. (33) showed by ab initio calculations that LiF has very high surface energy and low Li adatom surface diffusion barrier; they attributed the large $\gamma > 0.45$ to the electronegativity difference, but also to the small lattice constant (LiCl, the second smallest lithium halide, has a surface area 1.6x that of LiF). Therefore, adding nanoscale LiF to the SEI should increase the formation energy of the SEI, thereby reducing the magnitude of the negative $\gamma_{LMA}$ which promotes interfacial area growth. Finally, from a mechanical stability viewpoint, according to the Griffith fracture criterion, a ceramic with large surface energy is more resistant to fracture. Indeed, LiF is known to be able to deform plastically by dislocation glide due to its small Burgers vector (34, 35), rare among ceramics at room temperature. This mechanical and electrochemical stability compared with, say, Li$_2$CO$_3$ or Li$_2$O could be essential in explaining the relative morphological stability of LMA with LiF protection during Li redeposition and volume expansion, as we will discuss below.

For all these reasons, we believe the degree of fluoride donation, which controls LiF formation, is a key parameter in predicting good electrolytes for RLMB. Meanwhile, because of the extreme bandgap and electrochemical stability, LiF is also electropositive and protects the cathode. In the work below, we correlate the donatable fluoride concentration (DFC) of many liquid electrolytes with CI of the LMA, and show that CI decays nearly exponentially with increasing DFC. Guided by this rule, a class of high-concentration full-fluoride (HFF) electrolytes with a large DFC is designed for 5-V RLMBs. Our preferred organic solvents are carbonic esters due to their thermodynamic stability and good compatibility with LNMO. To drive up DFC, a fluorinated cyclic carbonic ester (FEC) was used as the sole solvent. Previously, FEC was only used as an additive ($< 10\text{ wt \%}$) (36, 37). FEC is expected to have dual purposes of stabilizing LMA imparted by LiF-rich SEI formation and enhancing oxidation stability of electrolyte (25). At the same time, a fluorine-organic Li salt (LiFSI) is utilized, considering its high yield of LiF upon decomposition (38).

The systematic role of donatable fluoride on the reversibility of LMA is evaluated by the average (CE) via “clean-slate” Li deposition-stripping on Cu foil (Fig. 1). To identify the trend, the logarithm of the average Li-cycling CI ($\log_{10}(CE)$) is shown in the vertical axis (39), with the corresponding cycling details shown in SI Appendix, Figs. S1 and S2. Obviously (CI) is highly dependent on DFC. Taking 1 m concentration electrolyte, for example, (CI) is above 50% in fluoride-free electrolyte (1 m LiClO$_4$ in PC), but falls dramatically to 31.6% and even less than 20% when LiClO$_4$ is replaced by fluoride-organic salts, LiTFSI and LiFSI, respectively. Impressively, in the case of full-fluoride-based (FF) system constituted by 1 m LiFSI in fluorinated carbonate (FEC), LMA exhibits extreme high reversibility with a very low (CI) < 4% when averaged over 100 cycles. (CI) also depends on the salt concentration in FF. With increasing ratio of LiFSI to FEC, (CI) monotonously drops (Fig. 14) from 4% in 1 m FF to 2.3% in HFF (7 m). Based on the data above, it is clear that (CI) has a strong negative correlation with donatable fluoride of the liquid electrolyte. Note that donatable fluoride is not the absolute F amount in the electrolyte but the active F atomic content in salt/solvent whose reduction effectively generates LiF in SEI. As shown by molecular simulations of Li salt and solvent reductions (40, 41), the number of LiF generated per LiClO$_4$, LiTFSI, LiFSI, and FEC molecule is 0, 1, 2, and 1, respectively. DFC is thus defined straightforwardly as the molar sum of donatable F of salt and solvent molecules in 1 L electrolyte solution (detailed calculations can be found in SI Appendix, Table S5). As shown in Fig. 1B, (CI) decays nearly exponentially with DFC across many electrolytes.

LMA exhibits excellent cycling stability in HFF electrolyte. As shown in Fig. 24, the voltage polarization of Li deposition-dissolution at 0.25 mA/cm$^2$ is very symmetrical with nearly no increase in 200 cycles (polarization: 60 mV at the 100th and 200th cycles) and, subsequently, with a slight increase to 70 mV at the 300th cycle and 90 mV at the 400th cycle. As the cycle number increases, (CE) continuously increases from 97.7% at the first 100 cycles to 99.64% during the 300th~400th cycles, indicating a self-healing mechanism (Fig. 2B) (39). The typical charge–discharge polarizations at different rates (0.25, 0.50, and 1.00 mA/cm$^2$) are 60, 140, and 160 mV, respectively, with (CE) of 98.37% and
At 25 °C are determined were detected without Li⁺ + poly(VC) occurs at an earlier stage after 2-min sputtering, but the (lower LiF (1). For these reasons, the and E and \( E_2 \) \( 2 \) \( \rightarrow \) \( \mu \) and Li⁺ + poly(VC) occurrence, and anion \( (\text{FSI}^-) \) transference numbers \( (\text{FSI}^-) \) transference numbers \( t_a \) at 25 °C are determined by NMR spectroscopy (SI Appendix, Fig. S5 and Table S6). \( t_a \) increases from 0.43 to 0.53 when the concentration increases from 0.43 to 0.53 when the concentration increases from 1 to 7 m. From Sand’s equation (42, 43), higher \( t_a \) (lower \( t_a \)) decreases anion depletion, which is beneficial for suppressing mode III morphological instabilities of LMA (1).

X-ray photoelectron spectroscopy (XPS) in Fig. 3 A–C reveals that the surface chemical components of cycled Li anode are mainly LiF, organic C–O group, Li₂CO₃, and Li₂O, derived from two possible ways: by the surface passivation film on the lithium anode (Li₂O, Li₂CO₃) due to sample transfer, and by the decomposition of electrolyte (LiF, organic C–O group, Li₂CO₃, and Li₂O). Before Ar ion sputtering, LiF, organic C–O group, residual LiFSI, and Li₂CO₃ were detected without Li₂O signal. Sputtering depth profiling of the absolute intensity of SEI components (LiF, Li₂O, and Li₂CO₃) (Fig. 3 B and C) shows that from outer layer to inner layer, the components are LiF/ Li₂CO₃, Li₂CO₃, and Li₂O. The strongest intensity of LiF and Li₂CO₃ occurs at an earlier stage after 2-min sputtering, but the intensity of Li₂O continues to increase with the sputtering time. We thus conclude that all of LiF and a small part of Li₂CO₃ and Li₂O are likely to originate from SEI formation by the decomposition of electrolyte, while most of Li₂O and Li₂CO₃ probably belong to the inherent passivation film on Li metal. Surface chemistry analysis of cycled LMA further confirmed that the SEI layer contained a large amount of LiF. HF formation and attack of electrodes is a common concern in LIBs. FEC is known to be a HF generator with certain electrode materials like Si. However, in our case, considering that only LiF shows up without C–F signal, and also the fact that Ni or Mn dissolution and transfer are not detected at all from the LNMO cathode to the anode (SI Appendix, Fig. S6), we believe HF is completely absent in our system due to the HF scavenging effect of Li metal. Based on our results and others’ experiments (44, 45), the following FEC reduction reaction, FEC + Li⁺ + e⁻ → poly(VC) + LiF + Li₂CO₃, is proposed.

While LiF layer can shut down electron tunneling and stop SEI growth, it will take some time for it to form a completely covering layer on the surface. Electrochemical impedance spectra of LMA in HFF are shown in SI Appendix, Fig. S7. Fig. 3 D and E and SI Appendix, Fig. S8 show the deposited LMA morphologies in different electrolytes for identical current density (0.25 mA/cm²) and deposition time. PC-based electrolytes clearly give more porous LMA, and the porosity decreases with increasing DFC. If we compare Fig. 3 D and E with Fig. 3 F and G, we see the long slender whiskers (diameter ~1 μm and aspect ratio >10) in PC are conspicuously missing in the high-DFC samples. These whiskers are determined to be mode II rather than mode III (1) because the Sand’s time are very long for such low current density. Also, true dendrites which are long-range transport-limited tend to have branches. Different from PC, the growth of Li in LiFSI-FEC exhibits no long-aspect-ratio whiskers but much bigger and uniform grain size. Especially in HFF electrolyte (7 m LiFSI in FEC), the particle size exceeds 20 μm. As indicated by previous in situ transmission electron microscopy (TEM) observations (1), the growth of mode II Li whiskers usually starts by tensile stress-driven mechanical failure of SEI, followed by compressive stress-driven extrusion of lithium like toothpaste or volcanic eruption from a fumarole. At the potential of concern, SEI forms everywhere a conductive surface and electrolyte meet. In order for lithium deposition to continue, Li⁺ in the electrolyte must diffuse through the SEI to meet with electron beneath the SEI, which causes compressive stress to build up in the lithium metal, and tensile stress to build up in the SEI layer on top. If the SEI layer is brittle and cannot plastically stretch, then inevitably it will fracture mechanically at some point (Fig. 3H) (1, 46), after which the lithium whisker can be squeezed out from the fracturing SEI layer due to the stress relaxation via creep deformation. The same stress-relaxation causes Sn whisker formation in microelectronic solders. This will greatly increase the surface area. Also, the slender whisker geometry, as shown in the in situ TEM observations (1), is highly irreversible, since upon Li stripping it tends to narrow and neck first at the root due to younger/thinner SEI and lower impedance at root, causing loss of electrical connection to the rest of the whisker (“dead lithium”), and/or simply mechanically break off at the stem to become “lithium flotsam” (1). For these reasons, the suppression of whisker formation due to ductility of SEI formed in HFF electrolyte could be key for the high reversibility of LMA. It is already known that alkali halides including LiF are ductile in tension at room temperature and nonaqueous condition (34). Compared with Li₂CO₃, LiF has higher surface energy, which makes brittle fracture more difficult according to the Griffith fracture criterion. Meanwhile, LiF has a very small lattice constant among halides, and therefore Burgers vector, which allows easy plastic deformation. Thus, LiF generated by the decomposition of HFF electrolyte is good at suppressing morphological instabilities. Equiaxed Li particles without a preferential growth direction (Fig. 3G) are a positive trait against porosity growth (47, 48).

Cathode-side issues include compatibility with LNMO, oxidative stability of electrolyte, as well as corrosion of Al current collector. Highly concentrated electrolytes are typically beneficial with respect to the oxidation of solvent and Al corrosion

Fig. 2. Reversibility of LMA in HFF electrolytes (7 m LiFSI in FEC). The current density is 0.25 mA cm⁻² with the capacity of 0.5 mAh. (A) Li deposition–stripping profiles on Cu foil. (B) CE at cycle 1–400.

98.02% at the higher current densities (1 and 2 mA) (SI Appendix, Fig. S3). Symmetric Li/Li cell in SI Appendix, Fig. S4 also shows very stable and nearly constant polarization even after 300 h of charge–discharge without any short-circuiting. The cation (Li⁺) and anion (FSI⁻) transference numbers \( t_a \) at 25 °C are determined by NMR spectroscopy (SI Appendix, Fig. S5 and Table S6). \( t_a \) increases from 0.43 to 0.53 when the concentration increases from 1 to 7 m. From Sand’s equation (42, 43), higher \( t_a \) (lower \( t_a \)) decreases anion depletion, which is beneficial for suppressing mode III morphological instabilities of LMA (1).
Fig. 3. Surface chemical analysis of cycled LMA (10 cycles at 0.5 mA, 1 h) in FF electrolyte (A–C). (A) XPS spectra of C, F, and O before and after Ar ion sputtering. Depth profiles with atomic concentration ratio (B) and with the intensity of SEI components (LiF, Li2O, and Li2CO3) (C). Morphologies of Li deposition on Cu foil in different electrolytes (1 m LiTFSI in PC (D), 1 m LiFSI in PC (E), 1 m LiFSI in FEC (F), and 7 m LiFSI in FEC (G)). The Li deposition current density is 0.5 mA/cm² and the deposited capacity is 1 mAh/cm². (H) Schematic diagram of corresponding Li growth mechanism in different electrolytes.

(17, 18, 22). Linear sweep voltammetry (LSV) with Al mesh as the working electrode (Fig. 4.4) shows that high salt concentration is very effective in expanding the electrochemical stability window and suppressing Al corrosion. The onset of oxidation in HFF electrolyte was pushed to well above 5 V and no peak corresponding to Al corrosion occurs in the range of 3.5–5.5 V. The oxidation of electrolyte prefers to take place on oxygen with electron lone pairs, like the O=S bond in anion FSI and C=O bond in FEC. High concentration creates extensive Li cation coordination, resulting in enhanced stability of the electron lone pair of anion and solvent (18). In HFF, the minimal distance between solvent molecules and Al current collector should be increased due to high salt concentration and solvent surrounded by salt rather than the traditional solvation shell structure, resulting in lower electron tunneling current to the solvent. In addition, LiF formation on the cathode electrode confirmed by F1s and Li1s XPS spectra (SI Appendix, Fig. S9), which has a large bandgap (13.6 eV) and therefore a fast tunneling decay rate, is also favorable for Al anti-corrosion and electrolyte stabilization (Fig. 4B) (19). Fig. 4A (Inset) displays their first charge–discharge profiles on active LiNiMoO4 electrode. For 1 m FF electrolyte, abnormal charge–discharge plateau, excessive charge capacity, and huge irreversible capacity loss signify oxidative decomposition of electrolyte before the delithiation of LiNi0.5Mn1.5O4. But, in HFF (7 m), the batteries presented the high first discharge capacity of 123.8 mAh/g (LiNiMoO4 with CE of 92.78% and the superior cycle stability with the capacity retention of 94.26% after 150 cycles. Such capacities are compatible with the commercial carbonate-based electrolyte (SE: 1.0 M LiPF6 in EC/DEC/DMC = 1:1:1 by weight, purchased from BASF) (Fig. 4C and SI Appendix, Fig. S10) with superabundant lithium. The charge–discharge polarization of the former does not obviously enlarge compared with the latter thanks to the higher t0 in HFF, offsetting the relatively lower ionic conductivity of HFF electrolyte (1.25 mS/cm at 25 °C (SI Appendix, Fig. S11) than commercial carbonate-based electrolyte (8–9 mS/cm at 25 °C). For comparison, identically concentrated carbonate electrolyte (7 m LiFSI in 1 L DMC) is also evaluated (SI Appendix, Fig. S12B), but is found to lead to serious Al corrosion once the potential is above 4.7 V, consistent with previous report (17). If the concentration is increased

Fig. 4. Oxidation of HFF liquid electrolyte and its compatibility with the LiNi0.5Mn1.5O4 cathode. (A) Concentration-dependent oxidation potential by LSV in three-electrode device (work electrode: Al mesh, counter- and reference electrodes: Li foil, scanning rate: 10 mV/s). (Inset) First charge-discharge profile of LiNi0.5Mn1.5O4 in 1 m FF and 7 m HFF. (B) Al corrosion in 1 m FF and 7 m HFF at the constant current (0.5 mA) charge to 5 V. Optical microscopy images (OMIs) of (B, 1) fresh Al foil, (B, 2) OMIs of Al foil in 1 m FF electrolyte after charging 1 h at 0.5 mA, and (B, 3) OMIs of Al foil in 7 m HFF after charging into 5 V at 0.2 mA. (C) Cycle life and CE of LiNi0.5Mn1.5O4/HFF full cell with only 1.4x excess lithium. For reference, half-cell results using standard “SE” electrolyte (SE: 1.0 M LiPF6 in EC/DEC/DMC = 1:1:1 by weight ratio) and highly concentrated DMC electrolyte (LiFSI: DMC = 1:1.1 by molar ratio) are also displayed, with ∼10x excess lithium. The constant current of 0.5 mA is applied in all cells, corresponding to the rate of 0.36 C based on the theoretical capacity of LiNi0.5Mn1.5O4 cathode (148 mAhV).
Fig. 5. Performance of LiNi$_{0.5}$Mn$_{1.5}$O$_2$/HFF or SELi system in full cell, where the Li mole ratio of cathode to anode is set up 1 (1.43 mAh): 1.40 (2 mAh) in full cell. The initial Li anode (2 mAh) is prepared by depositing Li on Cu foil at a constant current of 0.05 mA for 40 h. (A) Cycle life and CE. The constant current of 0.5 mA is applied in full cell, corresponding to the rate of 0.36 C based on the theoretical capacity of cathode and the current density of 0.44 mA/cm$^2$ based on the constant collect area of Cu foil. (B) Rate capability of full cell with HFF electrolyte. (C) Estimated output voltage, the real specific capacities of cathodes (Fig. S10 and S12), and gravimetric energy densities based on the total electrode mass (cathode + anode) of different electrochemical couples. Black solid square: rechargeable graphite-based commercial LIBs; red and blue solid squares: rechargeable lithium-metal-free batteries in which red and blue designate 5- and 4-V batteries, respectively. Except for the hollow red squares which represent the real energy density our 5-V lithium metal batteries, all of the other energy densities are calculated based on the theoretical capacity of electrodes.

Further to 11 m (LiFSILDMC = 1:1.1 by molar ratio), the battery shows very low capacity (<50 mAh/g) and much larger polarization due to the kinetic limitation of LiFSI-DMC (Fig. 4C and SI Appendix, Figs. S10 and S124).

To demonstrate that the LMA with excellent CE actually leads to more competitive RLMB, we constructed full-cell battery with high mass loading LNMO (14.7 mg/cm$^2$, 1.83 mAh/cm$^2$, diameter 10 mm) as the cathode. Since LNMO already comes with a full portion of cyclable Li (the “baseline” portion), a truly ideal RLMB battery should use just bare Cu current collector (defined as “0x excess” or “Li-free battery”) at the beginning. We have constructed and tested such a 0x excess RLMB: because Li have certain solubility in Cu and cyclable Li must also be consumed in SEI formation, the capacity fading of this 5-V Li-free battery is fast in the initial cycling with the capacity retention of 50.8% after 50 cycles (SI Appendix, Fig. S13). To demonstrate reasonable cycling, we predeposited some Li on the anode side (“0.5x excess,” “1x excess,” etc.), but not too much. From the Introduction we see that more than “3x excess” (e.g., 3 × 1.83 mAh/cm$^2$ worth of Li metal to start with) LMA would mean the RLMB is no longer competitive against LIB. In half-cell tests, Li metal chips (26 mg, 100 mAh, “~10× excess”) were used as the anode (Fig. 4C), which is far from industrial-use scenarios. We have decided to demonstrate the efficacy of our electrolyte by using no more than “1.5x excess”, which is a very stringent test for long-term cycling. Since any successful, would mean the RLMB can be truly competitive against LIB. In such a parsimonious excess situation (Fig. 5A and SI Appendix, Fig. S14), a small difference in CE could lead to a huge disparity in cycle life. Assuming the cathode is 100% reversible without any capacity fade, the capacity of full cell will fade to zero after 100 cycles if 1% of the original cyclable Li inventory is lost per cycle (CE = 99%) on the LMA. The CE advantage of our FF electrolytes reflects in the limited excess Li anode we can use for long cycling. With commercial carbonate-based electrolytes, the same mass Li anode (2 mAh, 1.77 mAh/cm$^2$, diameter 12 mm) by Li deposition on Cu foil sustains less than 10 cycles due to low CE (<80%) (SI Appendix, Fig. S15), but maintains more than 130 cycles in HFF electrolyte. After 130 cycles, our anode exhausts its own 1.4x excess and begins to dip into the original baseline cyclable Li brought by the LNMO, and the full-cell capacity fades faster. The electrochemical performance of full cell at the different rates (0.2 C ° 0.5 C ° 1 C ° 2 C) is shown in Fig. 5B and SI Appendix, Fig. S16. The highest current density based on cathode electrode is above 3.66 mAh/cm$^2$ at the rate of 2 C, at which point the capacity is still above 70 mAh/g (LNMO). Thus, our 5-V full cell has demonstrated a very good rate capability.

This result demonstrates the unique advantages of our proposed HFF electrolyte in 5-V Li metal full cell which not only has a good compatibility with cathode and wide enough stability window >5 V but also the capability to make the LMA more reversible. HFF is a liquid electrolyte satisfying simultaneously the requirements of a 5-V electrochemical window and >99% Li CE (Table 1). With its utilization, our proposed 5-V lithium metal battery presents much longer cycle life above 130 cycles with the capacity retention of 78% and ensuring an energy density of nearly 600 Wh/kg based on the total electrode masses (Fig. 5C) which is 30+4% higher than graphite-based LNMO batteries and 50+5% higher than the 4-V commercial graphite-based LIBs (SI Appendix, Tables S3 - S6), with parsimonious excess Li (the mole ratio of LNMO/Li equal to 1:1.4) anode and high mass loading LNMO (14.7 mg/cm$^2$) cathode that are close to the industrial requirement. So far, increasing DFC has led to one formulation (LiFSI-EC), demonstrating the feasibility of 5-V-class lithium metal battery. But, other fluorine-containing salts and fluoride solvents could be explored. This could also extend to high-DFC gel polymer electrolyte or the mixture ionic liquid-FF-based electrolytes for improving the full-cell performance, pushing RLMBs into the realm of practical applications.

**Experiment**

The electrolytes are prepared by mol-salt in liter-solvent, which were coded by abbreviated concentrations (1 m, 2 m, 7 m, etc.). The 5-V Spinel

### Table 1. Comparison of electrolytes on 5-V RLMBs

<table>
<thead>
<tr>
<th>Electrolyte components</th>
<th>Stable window, V</th>
<th>Al anticorrosion</th>
<th>Li CE, %</th>
<th>Fitness-for-service</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE: 1 M LiF$_2$ in DEC-DMC-EC</td>
<td>5</td>
<td>Yes</td>
<td>&lt;80</td>
<td>No</td>
</tr>
<tr>
<td>EHC: 4 M LiFSI in DME</td>
<td>&lt;4.5*</td>
<td>—</td>
<td>&gt;99</td>
<td>No</td>
</tr>
<tr>
<td>LFF: 1 m LiFSI in FEC</td>
<td>&lt;4.5</td>
<td>No</td>
<td>&gt;98</td>
<td>No</td>
</tr>
<tr>
<td>HFD: 7 m LiFSI in DMC</td>
<td>5</td>
<td>Yes</td>
<td>&gt;99</td>
<td>Yes</td>
</tr>
<tr>
<td>HFF: 7 m LiFSI in FEC</td>
<td>5</td>
<td>Yes</td>
<td>&gt;99</td>
<td>Yes</td>
</tr>
</tbody>
</table>

*Electrochemical stability of ether-based and carbonate-based highly concentrated electrolyte (EHC and HFD) are evaluated in LNMO/Li cell (SI Appendix, Figs. S12B and S17) which suffers from very serious overcharge and Al corrosion above 4.7 V, respectively."
LiNi0.5Mn1.5S2 electrodes used in this experiment were produced at the US Department of Energy’s (DOE) CAMP (Cell Analysis, Modeling, and Prototyping) Facility, Argonne National Laboratory. Composite electrodes were fabricated by compressing active materials, conductive additive, and binder at weight ratio of 84:8:8 on Al foil (20 μm). The total mass loading of the coating was 14.7 mg/cm², and the theoretical areal capacity was 1.83 mAh/cm². The cell was assembled in a CR2032-type coin cell with glass fiber separator. More details of the materials, characterizations, and electrochemical measurements are provided in SI Appendix.


43. Sand HJS (1901) On the concentration at the electrodes in a solution, with special reference to the liberation of hydrogen by electrolysis of a mixture of copper sulphate and sulphuric acid. Philos Mag 1:A 45-79.


