

Impact of Fluorination Degree of Ether-Based Electrolyte Solvent on Li-metal Battery Performance

Yangju Lin,^{1‡} Zhiao Yu,^{1,2‡} Weilai Yu,¹ Sheng-Lun Liao,¹ Zhuojun Huang,^{1,3} Yuelang Chen,^{1,2} Elizabeth Zhang,^{1,3} Jian Qin,^{*1} Yi Cui^{*3,4,5} and Zhenan Bao^{*1}

¹Department of Chemical Engineering, ²Department of Chemistry, and ³Department of Materials Science and Engineering, ⁴Department of Energy Science and Engineering, Stanford University, Stanford, California 94305, United States.

⁵Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States.

ABSTRACT: Electrolytes using fluorinated solvents have proven effective in improving the cycling life of Li-metal batteries, by forming a robust solid-electrolyte interphase through decomposition of anion and fluorinated solvent molecules. Herein, we modulated the fluorination degree of ether-based electrolyte solvents to investigate their performance in Li-metal batteries. We tuned the fluorination degree by installing a monofluorine substituent on one ethoxy group of 1,2-diethoxyethane (DEE) and varying the fluorination degree on the other one, providing three fluorinated DEE solvent molecules (i.e., **F1F0**, **F1F1** and **F1F2**) with a relatively low fluorination degree. All the three electrolytes showed improved solvation strength and ionic conductivities compared with previous highly fluorinated DEE electrolytes, while retaining good oxidative stability. Full cell test using Li-metal anode and nickel-rich cathode revealed that a higher degree of fluorination is beneficial to the cycling performance, and the cycling stability follows **F1F0** < **F1F1** < **F1F2**. Specifically, **F1F0** exhibited poor cycling stability due to its instability against both anode and cathode. While **F1F1** and **F1F2** both showed good stability against Li-metal anode, their relative long-term oxidative stability was responsive for the distinct performance, in which the cycle numbers at 80% capacity retention for **F1F1** and **F1F2** were ~20 and ~80, respectively. This work shows the importance to modulate the fluorination degree of electrolyte solvents, and this approach is suitable for various cathode materials.

The high number of transferring electron per atomic mass and low electrochemical potential in Li⁺/Li redox reaction render Li metal an ideal anode material for high-energy-density batteries.¹⁻³ Despite these merits, the Li-electrolyte side reactions, inaccessible lithium (or called dead lithium) generated during the plating/stripping cycles^{4, 5} and, thus, the poor Coulombic efficiency (CE) and cyclability have significantly impeded the practical implementation.⁶ A key factor enabling stable Li deposition is the formation of a robust solid electrolyte interphase (SEI) that allows for efficient Li⁺ transfer and uniform Li deposition.^{7, 8} Typically, this SEI layer is composed of species associated with electrochemical and chemical decomposition of salt and solvent molecules, and a SEI layer that is rich in inorganic components (e.g., LiF, LiO₂ and LiN₃) has been found beneficial.⁹

A variety of molecular engineering strategies for electrolytes have been explored in order to achieve robust SEI layers in Li-metal batteries,^{10, 11} including additive-reinforced electrolytes (AREs),¹² high concentration electrolytes (HCEs),¹³ localized high concentration electrolytes (LHCEs),¹⁴ weakly solvating electrolytes (WSEs),¹⁵⁻²² and electrolytes with fluorinated solvents,²³⁻²⁹ etc. In these approaches, the formation of a robust SEI layer is promoted through decomposition of either additive, anion or/and fluorinated molecules. In particular, the fluorinated solvents were found to simultaneously provide several merits

in electrolytes, including 1) improved oxidative stability resulted from the high electron-withdrawing capability of fluorine that lowers the highest occupied molecular orbital (HUMO),^{30, 31} 2) promotion of anion-derived SEI layer due to the weakened solvation ability associated with the reduced electron density of binding atoms,³² 3) improved flame retardance,³³ and 4) enriched LiF component in SEI layer through potential decomposition of solvent molecules.^{34, 35} Notably, the strategy of solvent fluorination allows for a single-solvent low-concentration electrolyte system without compromising ionic conductivity.³⁶

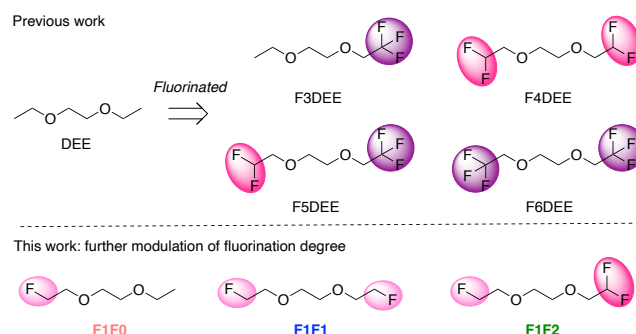


Figure 1 Chemical structures of fluorinated 1,2-diethoxyethane solvent molecules.

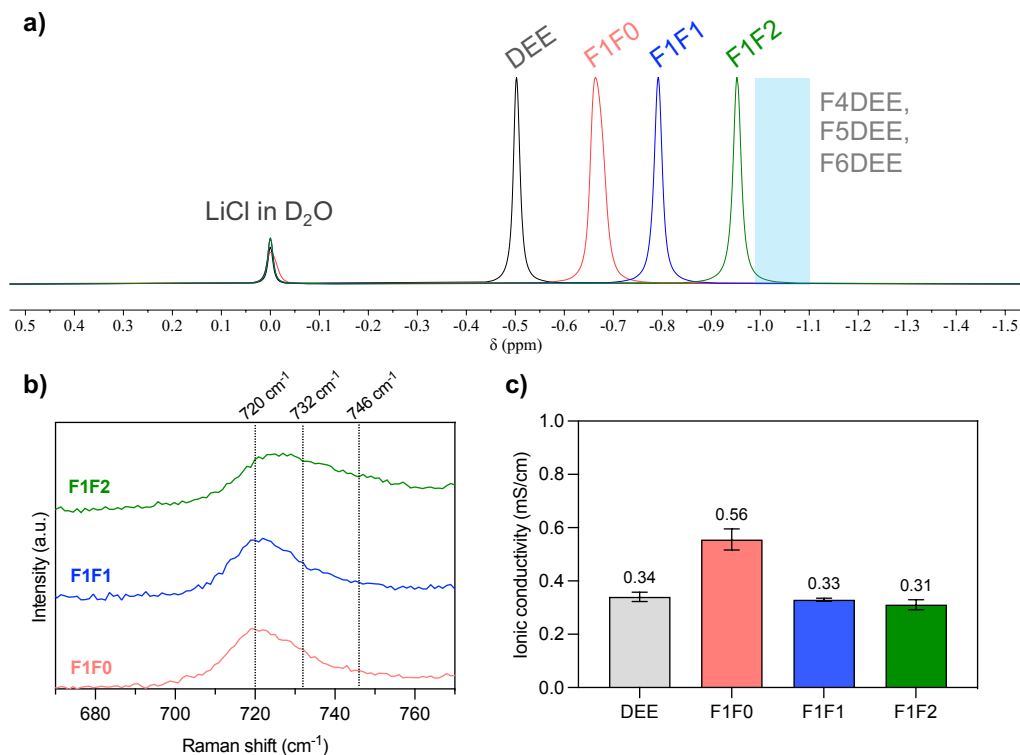


Figure 2 a) Overlay of normalized ${}^7\text{Li}$ NMR spectra of electrolyte solutions containing 1.2 mole of LiFSI salt, and LiCl in D_2O was applied as an external standard. The pale blue region indicates the chemical shift of F4DEE, F5DEE and F6DEE electrolytes in previous report. b) Raman spectra of electrolytes in this study showing the solvation conditions of LiFSI salt. c) Comparison of ionic conductivity in the stainless steel-separator-stainless steel sandwich structure using Celgard2325 trilayer separator. Each electrolyte was measured three times (see Table S2).

Examples of using fluorinated molecule as a single electrolyte solvent include a series of long-chain fluorinated glymes,^{37,38} fluorinated 1,4-dimethoxybutane (FDMB),³² *N,N*-dimethylsulfamoyl fluoride (FSA),³⁴ *N,N*-dimethyltrifluoromethane-sulfonamide (DMTMSA),³¹ fluorinated-1,2-diethoxyethane (FDEE)³⁹ and, more recently, 1,1,1-trifluoro-2,3-dimethoxypropane (TFDMP)⁴⁰ and bis(2-fluoroethyl) ethers (BFE).⁴¹ In addition to improved oxidative stability, all these electrolytes showed excellent CE and cyclability using nickel-rich high-voltage cathodes. We recently showed that an exciting family of electrolyte based on FDEE (Figure 1 top row) can achieve Li-cycling CE as high as 99.9% and ~ 200 cycles of full battery cycling at high-loading capacity (4.8 mAh/cm^2) under hash cycling conditions (0.2C charge, 0.3C discharge).³⁹ This series electrolytes have fluorine content of 3-6 fluorine atoms per molecule and show moderate ionic conductivities, and a higher ionic conductivity is necessary for fast charging/discharging. Therefore, we sought to fine-tune the degree of fluorination of DEE in the lower fluorine regime (Figure 1 bottom row) to optimize the ionic conductivity with the hope to not compromise their oxidative stability.

It is known that increased fluorination degree in ether molecule improves oxidative stability but simultaneously reduces the solvation/binding strength, resulting in formation of larger size of salt-anion clusters and so reduced ionic conductivity.³⁹ We therefore further reduced the fluorination degree on the ether molecules, by applying the monofluoro-substitution on the one ethoxy group of 1,2-diethoxyethane (DEE) and varying the number of fluorine substituent on the other one (Figure 1 bottom row).

Results and discussions

The fluorinated ether molecules (i.e., **F1F0**, **F1F1**, and **F1F2**) are synthesized through $\text{S}_{\text{N}}2$ reactions and can be obtained in $> 10 \text{ g}$ scale (see Supporting Information). Three single-solvent electrolytes were prepared by adding 1.2 mmol of lithium bis(fluoromethanesulfonyl)imide (LiFSI) into 1 mL of each of the solvent molecules. We then performed ${}^7\text{Li}$ NMR to analyze the solvation structure of salt in the electrolyte using LiCl in D_2O as an external reference. As can be seen in Figure 2a, the chemical shift of ${}^7\text{Li}$ gradually moved up field upon increasing the degree of fluorination. This increased electron shielding is attributed to more compact cation-anion interaction resulted from weakened solvation ability, as has been observed in other fluorinated solvents, HCEs, LHCEs and WSEs.^{16,39,41} Herein, consistent with our expectation, increasing the fluorination degree of ether solvent reduces its solvation ability; however, the impact on chemical shifts are not as pronounced as those of highly fluorinated FDEE electrolytes (Figure 1, top),³⁹ indicating improved salt solvation (or cation-anion dissociation) in our new electrolytes. Additional evidence from Raman measurement (Figure 2b) showed that **F1F0** and **F1F1** electrolytes exhibit mainly solvent separated ion pairs (SSIPs, 720 cm^{-1}), while trivial contact ion pairs (CIPs, 732 cm^{-1}) and aggregates (AGGs, 746 cm^{-1}).⁴² In the case of **F1F2**, the broad shoulder peak indicated significant portion of CIPs and AGGs, suggesting the weakened solvation strength.

To evaluate the ionic conductivity, we inflated the electrolyte solution into a Celgard2325 separator and used stainless-steel-sandwich configuration to mimetic the

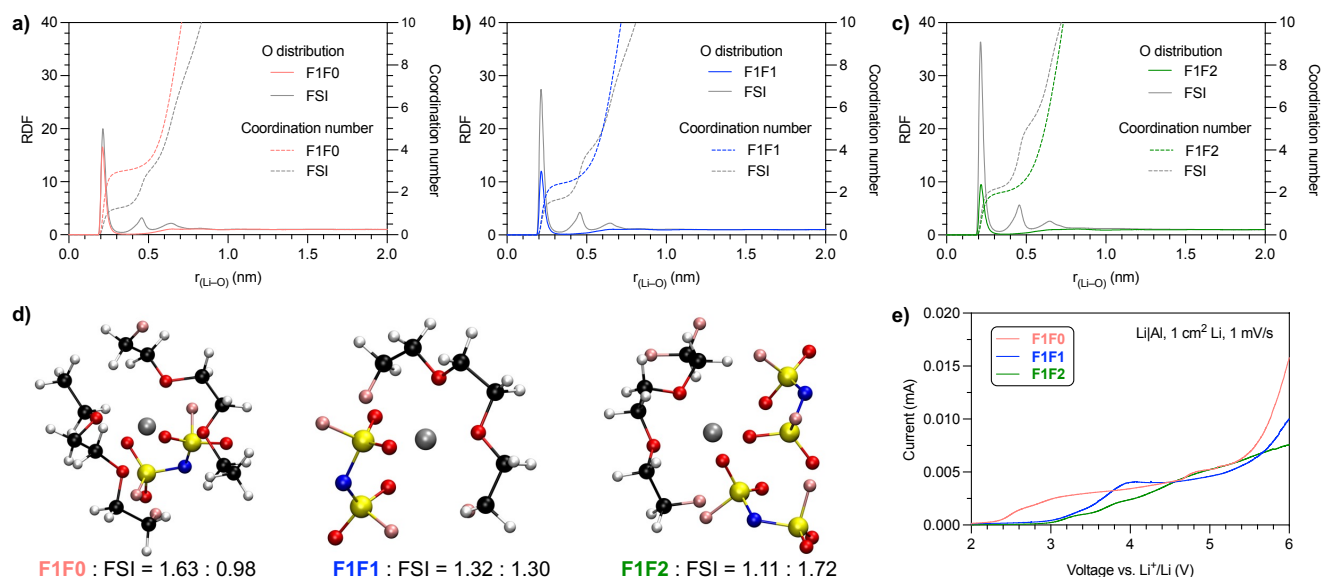


Figure 3 Radial distribution function of O atoms of a) **F1F0**, b) **F1F1** and c) **F1F2** solvent and anion over the distance from Li⁺ cation center. d) Representative solvation structure of electrolytes with 1.2 mol/L LiFSI salt, and the average numbers of solvent and anion in the solvation structure are indicated at the bottom. e) Oxidative stability of electrolytes against Al current collector (scanning rate: 1 mV/s).

conditions of coin-cell tests. As shown in Figure 2c, all three electrolytes exhibited relatively higher ionic conductivities compared with previous FDEE counterparts (0.05–0.17 mS/cm),³⁹ and they follow the trend **F1F0** > **F1F1** > **F1F2**, in alignment with the solvation strength. Interestingly, **F1F0** showed ionic conductivity that is even higher than the nonfluorinated DEE electrolyte. We reasoned that the F substituent increases the polarity of molecule and provides an additional binding to the Li⁺, giving rise to less compact cation-anion cluster, as indicated by ¹⁹F NMR spectra (Figure S1) and some previous studies.^{41, 43}

We further performed molecular dynamics (MD) simulation to gain insight into the solvation behavior. Figure 3a-c showed the probability of coordinating O atom as a function of distance from the Li⁺ center, or radial distribution function (RDF). We compared the O atom from both solvent and anion molecules. The first solvation shell peaked at $r_{(\text{Li}-\text{O})} \sim 0.22$ nm, which indicates the length of Li–O dative bond,⁴⁴ for both solvent and anion in all three electrolyte systems.

Notably, the composition of solvating O atom from solvent and anion molecules varied with the fluorination degree of electrolyte solvent. The fraction of solvating O atom from FSI anion increases in the order **F1F0** < **F1F1** < **F1F2**, and that from solvent molecule decreases accordingly. This trend is consistent with the ordering of the solvation strength. Consequently, the overall cation-anion interaction is stronger in less solvated electrolyte system, as also evidenced by ⁷Li NMR and Raman spectra analysis (Figure 2a and 2b).

To present a quantitative picture of solvation shell, we integrated the RDF to get the coordinating number (CN) of O atoms from solvent and FSI anion. The presence of a plateau at $r_{(\text{Li}-\text{O})} \sim 0.36$ nm for both solvent and FSI anion suggested the radius of first solvation sheath, and the corresponding CN in the sheath was estimated. For **F1F0** electrolyte, the CNs of O from solvent and FSI anion are 3.03 and 1.34, respectively. The numbers became 2.46 and 1.76 for

F1F1 electrolyte, and 2.03 and 2.31 for **F1F2** electrolyte. We further counted the number of solvent and FSI anion molecules in the first solvation shell and found, on average, 1.63 solvent and 0.98 FSI in **F1F0** electrolyte, 1.32 solvent and 1.30 FSI in **F1F1** electrolyte, and 1.11 solvent and 1.72 FSI in **F1F2** electrolyte. It is worth noting that for electrolytes with 1.2 mmol of LiFSI in 1 mL solvent, the solvent/LiFSI molar ratios are 6.01, 6.03 and 5.78 for **F1F0**, **F1F1** and **F1F2**, respectively. Hence, there are both “binding” and “free” solvent molecules in the electrolytes. The above quantitative analysis is further highlighted by the typical solvation structures shown in Figure 3d. Again, this observation is in alignment with the relative solvation strength of solvent molecules.

Previous work have found strong correlation between solvation structure and the oxidative stability of electrolytes.¹³⁻²⁹ We then scrutinized the impact of fluorination degree of solvent on the oxidative stability and, hence, the feasibility to be used in high-voltage battery systems. Figure 3e shows the screening of leakage current through linear sweep voltammetry of Li||Al half cells at the scanning rate of 1 mV/s. Interestingly, all three electrolytes exhibit a relatively small current (< 5 μ A) at up to 5 V, and these observed low leakage current are comparable to previous FDEE electrolytes.³⁹

Encouraged by the improved ionic conductivity and retained anodic stability while reducing the fluorination degree, we performed Li||NMC811 full battery tests of the three electrolytes using the same conditions as reported for FDEE electrolytes, i.e., pairing 50- μ m-thick Li foil (10.3 mAh/cm²) with high-loading NMC811 cathode (4.8 mAh/cm²) to yield a negative-to-positive electrode ratio (N/P) of \sim 2.1; using electrolyte-to-cathode ratio (E/C) of \sim 8 g/Ah; and cycling at C/5 charging and C/3 discharging rates, for the purpose of comparison with previous studies and so evaluation of fluorination effects.

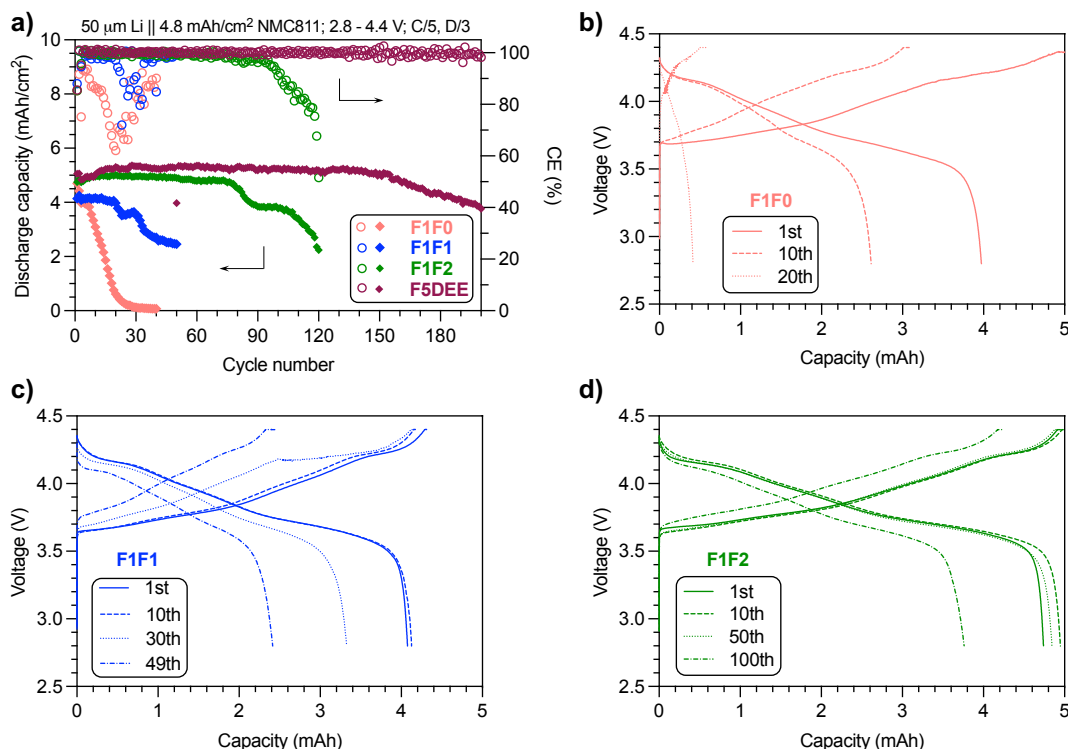


Figure 4 a) Capacity and CE retention of **F1F0**, **F1F1** and **F1F2** electrolytes over cycling number. The data of **F5DEE** was adapted from previous results.³⁹ The charge/discharge curves of b) **F1F0**, c) **F1F1** and d) **F1F2** at various cycles. Note: cycling of full cells were repeated and results can be found in Figure S4-7.

A representative set of battery cycling results is provided in Figure 3a (repeated results are provided in Figure S4-7), and a clear trend of cycling life was observed: **F1F0** < **F1F1** < **F1F2**. The capacity of **F1F0** decayed quickly to near zero within 30 cycles, and its CE dropped significantly despite the presence of excess Li reservoir, indicating the instability of **F1F0** against both anode and cathode. Additionally, the decay pattern is in contrast to the DEE electrolyte (non-fluorinated electrolyte), which presents a steady

capacity without significant reduction in the beginning 18 cycles and then drop quickly to 80% capacity in the following 37 cycles.¹⁶ Herein, the continuous capacity decay in **F1F0** suggested the negative impact of mono-fluorination on DEE. As for **F1F1**, the capacity remained almost unchanged in the first 20 cycles but then quickly reduced over cycles. In stark contrast, **F1F2** exhibited stable cycling without substantial capacity decay for ~80 cycles, which is

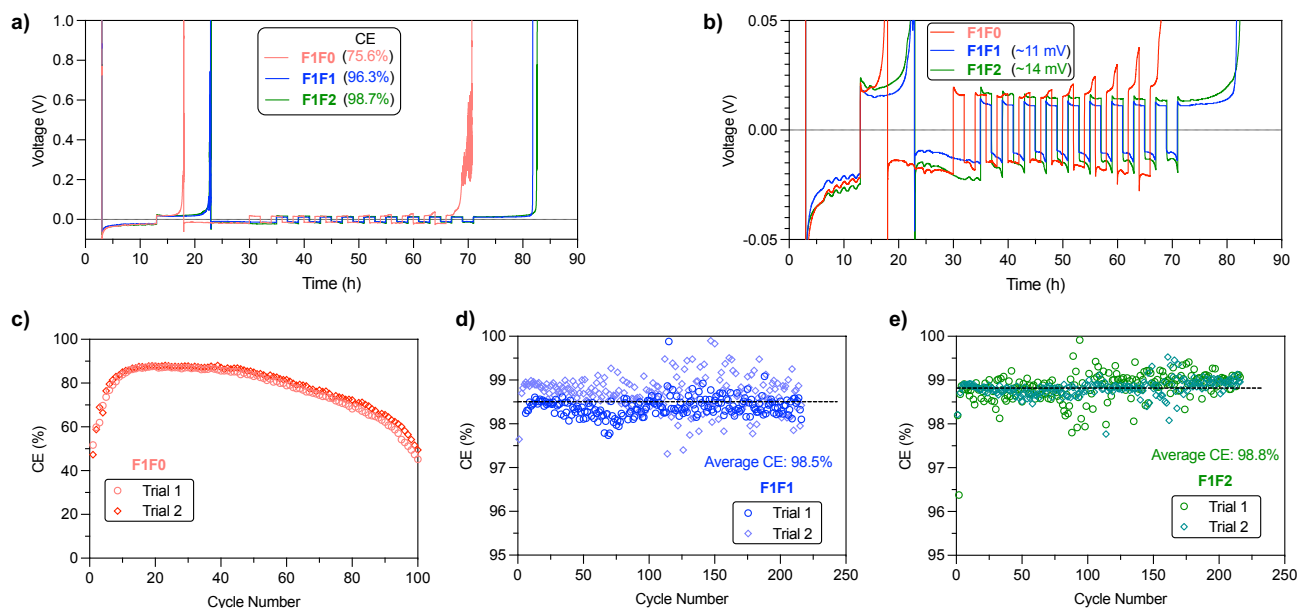


Figure 5 a) CE evaluation of Li||Cu half cells using modified Aurbach method. b) Zoom-in view of voltage-time profiles in CE measurements. CE values of c) **F1F0**, d) **F1F1** and e) **F1F2** electrolytes over long-term cycling of Li||Cu half cells. The average CE of **F1F1** and **F1F2** from two trials over > 200 cycles are indicated in d) and e), respectively.

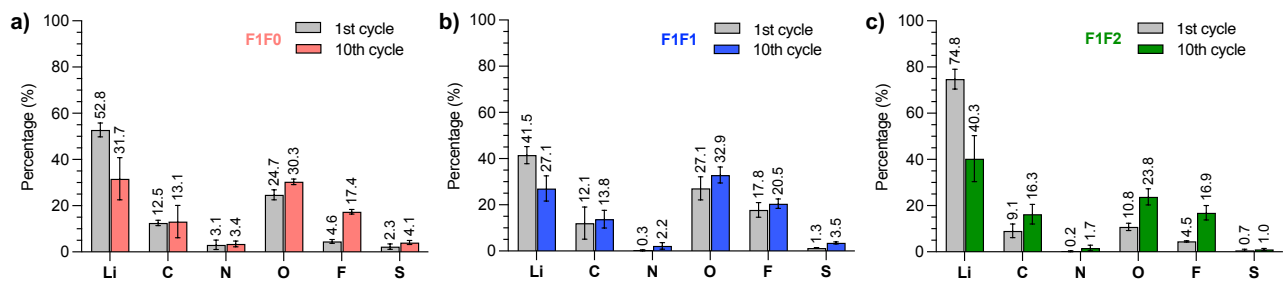


Figure 6 XPS analysis of SEI composition of a) **F1F0**, b) **F1F1**, and c) **F1F2** electrolytes at the 1st and 10th cycles of lithium deposition using Li||Cu half cells. The results were obtained by averaging the signals from 4 different sputtering times.

comparable to F3DEE and F6DEE but less than F4DEE and F5DEE in previous report.³⁹

We further studied the charge/discharge curves at different cycles. Figure 4b shows the charge/discharge curves of **F1F0** at 1st, 10th and 20th cycles, where the overpotential at the start of charge/discharge remains nearly unchanged while the capacity fades quickly over cycles, indicating the retained bulk and interfacial resistance yet instability against electrodes. Specifically, the 10th discharge process only gave ~2.6 mAh, which corresponds to ~84% of the 10th charging capacity (~3.1 mAh). Because the high initial Li reservoir (N/P ~ 2.1) would guarantee the 3.1 mAh capacity when discharge at the 10th cycle, the observed capacity loss highly suggested the cathode degradation during the 10th discharge cycle. This instability can be ascribed to the intrinsic low oxidative stability of **F1F0** (as will be discussed later), and the resulting side reactions deteriorates the cathode integrity. In contrast, **F1F1** showed slightly less capacity loss over cycles, but a substantial polarization (decrease in the initial discharge voltage or increase in charge voltage) imply the raised bulk and interfacial resistance. In the case of **F1F2**, the capacity loss is even less and the polarization over cycles is not as pronounced. Therefore, compared with **F1F0**, the improved oxidative stability of **F1F1** benefited the cathode performance but induced polarization, and **F1F2** overcame both drawbacks. We postulated that the combined compact Li⁺-anion pairs associated with weak solvation and improved oxidative stability resulted from increased fluorination degree contributed to the overall improved cycling performance.

We then examined the stability of Li metal cycling through Li||Cu half cells. Typical evaluation of CE using the modified Aurbach method⁴⁵ indicated that the CEs for **F1F0**, **F1F1**, and **F1F2** are 75.8%, 96.3% and 98.7%, respectively (Figure 5a). A close scrutinization of the overpotential curves reveals a “yielding” peak in the stripping cycle for all three electrolytes (Figure 5b), which is ascribed to the transformation of interphase kinetics.⁴⁶ Meanwhile, we noticed a significant capacity loss in the beginning cleaning cycle of **F1F0**, along with slowly increased stripping overpotential in the later cycles, indicating cathodic instability of **F1F0** and impedance increase. Notably, the overpotential curve of stripping cycle presents spike features, which could be related to the reconnection of “dead” Li upon stripping.⁴⁷ We therefore reasoned that **F1F0** presents poor electrochemical stability and unstable/nonuniform Li deposition. By contrast, **F1F1** and **F1F2** showed relatively high CE of 96.3% and 98.7%, respectively, and the average overpotential of **F1F1** and **F1F2** under 0.5 mA/cm² current are

respectively 11 mV and 13 mV, both of which are lower than F5DEE (~20 mV)³⁹ owing to their higher ionic conductivity.

Long-term cycling of Li||Cu half cells was applied to further validate the Li cycling stability (Figure 5c-e). Interestingly, **F1F0** showed extremely low CE of ~50% in the first cycle, and it then increased and reached a plateau value of ~88% in the following 20 cycles. However, this value slowly decreased to ~50% after 100 cycles. It was found that the average CE of initial 12 cycles is ~75%, which is consistent with the CE value obtained from the modified Aurbach measurement that includes 12 cycles of Li plating/stripping. Herein, **F1F0** shows poor stability against Li cycling and thus cycling of full battery. On the other hand, both **F1F1** and **F1F2** showed stable Li cycling over 200 cycles and average CE of 98.5% and 98.8%, respectively. It is worth noticing that the CE of both **F1F1** and **F1F2** quickly reached to stable values during the initial 3 cycles, which suggests a quick passivation and formation of robust SEI layers (Figure S8).

Despite the similar Li||Cu cycling performance between **F1F1** and **F1F2**, they show different full battery performance. To understand the underlying mechanism, we compared the Li deposition morphology of **F1F1** and **F1F2**. However, no substantial difference in the grain size and morphology was found (Figure S9). Further, the SEI composition after one cycle was analyzed by XPS, which showed signals from LiOH, Li₂O, LiF, Li₂SO_x, Li₂S and organic species for both electrolytes (Figure S10-12). While the species are similar, a closer comparison of relative abundance of each element revealed that **F1F1** present more O and F contents than **F1F2** in the first cycle (27.1% vs. 10.8% and 17.8% vs. 4.5%, Figure 6). The difference could be due to the higher electrochemical susceptibility of monofluoride substituent than difluoro one. More O and F contents may suggest more beneficial Li₂O and LiF compositions in the SEI. We next scrutinized the SEI at the 10th cycle. It was found that the O and F contents in **F1F1** slightly increased to 32.9% and 20.5%, respectively. Interestingly, this raise was more significant in **F1F2**, which showed 23.8% for O and 16.9% for F at the 10th cycle. The more increase of O and F contents in **F1F2** over cycling indicated more accumulation of robust components (possibly Li₂O and LiF) in the SEI, which we hypothesized could be a consequence of less SEI dissolution over cycling, and the dissolved SEI components could potentially migrate to the cathode side and affect the cathode performance.⁴⁸

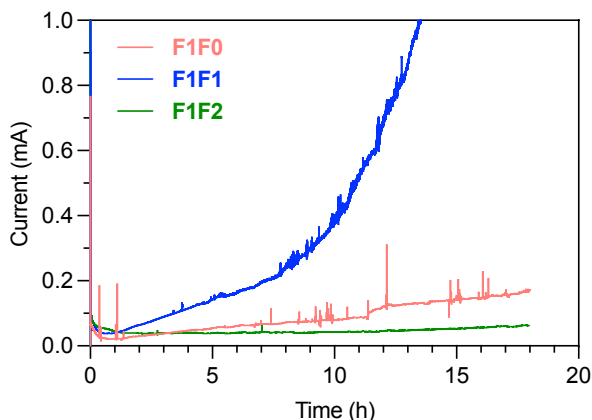


Figure 7 The leakage current of electrolytes under 4.4V constant voltage holding.

The SEI composition and Li||Cu half-cell cycling performance of **F1F1** and **F1F2** are rather similar, and albeit thin, the Li metal foil in the full cell still provides excess Li reservoir. Therefore, with an average CE of > 98% for Li plating/stripping, the full cell performance is more limited by the cathode side. Because full cell cycling is a long-term process, the oxidation of electrolytes occurs in an accumulating manner and the side reactions could diminish the cathode integrity over time. We therefore performed chronoamperometry to understand the long-term oxidative stability of electrolytes under high voltage. Figure 7 shows the leakage current of electrolytes under 4.4 V constant voltage over time using Li||Pt half cells. Significant leakage current was observed in **F1F0** and **F1F1** over long-term high-voltage holding, and the situation devastated over time. By contrast, there was minimal leakage current in **F1F2**, and it remained steady over more than 18 h. Herein, compared with **F1F1**, the superior oxidative stability of **F1F2** is responsible for its much more stable cycling of full batteries.

Conclusion

To conclude, the modulation of fluorination degree in ether-based electrolyte solvents allows for fine-tuning of solvation strength and long-term oxidative stability. A general trend that low degree of fluorination presents relatively strong solvation but poor oxidative stability and increasing fluorination degree improves the oxidative stability at the expense of solvation strength has been observed. Among these ether solvents with relatively low fluorination degree, **F1F0** exhibited particularly both poor stability against Li-metal anode and NMC cathode, while **F1F1** and **F1F2** showed improved anodic and cathodic stability, contributing to the enhanced battery cyclability. While the performance of this series of electrolytes does not outperform our previous FDEE electrolytes, the improved ionic conductivity might be beneficial to fast charging of battery systems that possess relatively low overpotential (e.g., Li-LiFePO₄ and Li-S batteries).

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, cell fabrications, repeated cell test, XPS, SEM, and NMR spectra are included in the Supporting Information.

AUTHOR INFORMATION

Corresponding Author

Jian Qin – Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States. Email: jiang@stanford.edu

Yi Cui – Department of Materials Science and Engineering, Department of Energy Science and Engineering, Stanford University, Stanford, California 94305, United States. Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States. Email: yicui@stanford.edu

Zhenan Bao – Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States. Email: zbao@stanford.edu

Authors

Yangju Lin – Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States. Email: yl2020@stanford.edu

Zhiao Yu – Department of Chemical Engineering Department of Chemistry, Stanford University, Stanford, California 94305, United States. Email: zhiaoyu@stanford.edu

Weilai Yu – Department of Chemical Engineering Department of Chemistry, Stanford University, Stanford, California 94305, United States. Email: wyyu@stanford.edu

Sheng-Lun Liao – Department of Chemical Engineering Department of Chemistry, Stanford University, Stanford, California 94305, United States. Email: shenglun@stanford.edu

Zhuojun Huang – Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, United States. Email: zjhuang@stanford.edu

Yuelang Chen – Department of Chemical Engineering and Department of Chemistry, Stanford University, Stanford, California 94305, United States. Email: ylc@stanford.edu

Elizabeth Zhang – Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States. Email: eliz2000@stanford.edu

Author Contributions

‡These authors contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy, under the Battery 500 Consortium and the Battery Materials Research (BMR) programs.

Conflict of Interest

Zhenan Bao, Yi Cui, Yangju Lin, Zhiao Yu and Yuelang Chen declare that this work is part of US Provisional Patent Application No. 63/283,828 filed in 11/29/2021. The remaining authors declare no competing interests.

REFERENCES

- (1) Guo, Y.; Li, H.; Zhai, T. Reviving Lithium-Metal Anodes for Next-Generation High-Energy Batteries. *Adv Mater* **2017**, *29* (29). DOI: 10.1002/adma.201700007.
- (2) Lin, D.; Liu, Y.; Cui, Y. Reviving the lithium metal anode for high-energy batteries. *Nat Nanotechnol* **2017**, *12* (3), 194-206. DOI: 10.1038/nnano.2017.16.
- (3) Xu, W.; Wang, J.; Ding, F.; Chen, X.; Nasybulin, E.; Zhang, Y.; Zhang, J.-G. Lithium metal anodes for rechargeable batteries. *Energy & Environmental Science* **2014**, *7* (2), 513-537. DOI: 10.1039/C3EE40795K.
- (4) Paul, P. P.; McShane, E. J.; Colclasure, A. M.; Balsara, N.; Brown, D. E.; Cao, C.; Chen, B.-R.; Chinnam, P. R.; Cui, Y.; Dufek, E. J.; et al. A Review of Existing and Emerging Methods for Lithium Detection and Characterization in Li-Ion and Li-Metal Batteries. *Advanced Energy Materials* **2021**, *11* (17), 2100372. DOI: <https://doi.org/10.1002/aenm.202100372>.
- (5) Fang, C.; Li, J.; Zhang, M.; Zhang, Y.; Yang, F.; Lee, J. Z.; Lee, M. H.; Alvarado, J.; Schroeder, M. A.; Yang, Y.; et al. Quantifying inactive lithium in lithium metal batteries. *Nature* **2019**, *572* (7770), 511-515. DOI: 10.1038/s41586-019-1481-z.
- (6) Cheng, X. B.; Zhang, R.; Zhao, C. Z.; Zhang, Q. Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review. *Chem Rev* **2017**, *117* (15), 10403-10473. DOI: 10.1021/acs.chemrev.7b00115.
- (7) Tikekar, M. D.; Choudhury, S.; Tu, Z.; Archer, L. A. Design principles for electrolytes and interfaces for stable lithium-metal batteries. *Nature Energy* **2016**, *1* (9), 16114. DOI: 10.1038/nenergy.2016.114.
- (8) Peled, E.; Menkin, S. Review—SEI: Past, Present and Future. *Journal of The Electrochemical Society* **2017**, *164* (7), A1703. DOI: 10.1149/2.1441707jes.
- (9) Cheng, X. B.; Zhang, R.; Zhao, C. Z.; Wei, F.; Zhang, J. G.; Zhang, Q. A Review of Solid Electrolyte Interphases on Lithium Metal Anode. *Adv Sci (Weinh)* **2016**, *3* (3), 1500213. DOI: 10.1002/advs.201500213.
- (10) Li, S.; Jiang, M.; Xie, Y.; Xu, H.; Jia, J.; Li, J. Developing High-Performance Lithium Metal Anode in Liquid Electrolytes: Challenges and Progress. *Adv Mater* **2018**, *30* (17), e1706375. DOI: 10.1002/adma.201706375.
- (11) Jie, Y.; Ren, X.; Cao, R.; Cai, W.; Jiao, S. Advanced Liquid Electrolytes for Rechargeable Li Metal Batteries. *Advanced Functional Materials* **2020**, *30* (25), 1910777. DOI: <https://doi.org/10.1002/adfm.201910777>.
- (12) Zhang, H.; Eshetu, G. G.; Judez, X.; Li, C.; Rodriguez-Martinez, L. M.; Armand, M. Electrolyte Additives for Lithium Metal Anodes and Rechargeable Lithium Metal Batteries: Progress and Perspectives. *Angewandte Chemie International Edition* **2018**, *57* (46), 15002-15027. DOI: <https://doi.org/10.1002/anie.201712702>.
- (13) Yamada, Y.; Wang, J.; Ko, S.; Watanabe, E.; Yamada, A. Advances and issues in developing salt-concentrated battery electrolytes. *Nature Energy* **2019**, *4* (4), 269-280. DOI: 10.1038/s41560-019-0336-z.
- (14) Cao, X.; Jia, H.; Xu, W.; Zhang, J.-G. Review—Localized High-Concentration Electrolytes for Lithium Batteries. *Journal of The Electrochemical Society* **2021**, *168* (1), 010522. DOI: 10.1149/1945-7111/abd60e.
- (15) Zhang, J.; Li, Q.; Zeng, Y.; Tang, Z.; Sun, D.; Huang, D.; Tang, Y.; Wang, H. Weakly Solvating Cyclic Ether Electrolyte for High-Voltage Lithium Metal Batteries. *ACS Energy Letters* **2023**, *8* (4), 1752-1761. DOI: 10.1021/acscenergylett.3c00181.
- (16) Chen, Y.; Yu, Z.; Rudnicki, P.; Gong, H.; Huang, Z.; Kim, S. C.; Lai, J.-C.; Kong, X.; Qin, J.; Cui, Y.; et al. Steric Effect Tuned Ion Solvation Enabling Stable Cycling of High-Voltage Lithium Metal Battery. *Journal of the American Chemical Society* **2021**, *143* (44), 18703-18713. DOI: 10.1021/jacs.1c09006.
- (17) Park, E.; Park, J.; Lee, K.; Zhao, Y.; Zhou, T.; Park, G.; Jeong, M.-G.; Choi, M.; Yoo, D.-J.; Jung, H.-G.; et al. Exploiting the Steric Effect and Low Dielectric Constant of 1,2-Dimethoxypropane for 4.3 V Lithium Metal Batteries. *ACS Energy Letters* **2023**, *8* (1), 179-188. DOI: 10.1021/acscenergylett.2c02003.
- (18) Zhang, H.; Zeng, Z.; Ma, F.; Wu, Q.; Wang, X.; Cheng, S.; Xie, J. Cyclopentylmethyl Ether, a Non-Fluorinated, Weakly Solvating and Wide Temperature Solvent for High-Performance Lithium Metal Battery. *Angew Chem Int Ed Engl* **2023**, e202300771. DOI: 10.1002/anie.202300771.
- (19) Pham, T. D.; Lee, K.-K. Simultaneous Stabilization of the Solid/Cathode Electrolyte Interface in Lithium Metal Batteries by a New Weakly Solvating Electrolyte. *Small* **2021**, *17* (20), 2100133. DOI: <https://doi.org/10.1002/smll.202100133>.
- (20) Xu, R.; Ding, J.-F.; Ma, X.-X.; Yan, C.; Yao, Y.-X.; Huang, J.-Q. Designing and Demystifying the Lithium Metal Interface toward Highly Reversible Batteries. *Advanced Materials* **2021**, *33* (52), 2105962. DOI: <https://doi.org/10.1002/adma.202105962>.
- (21) Ding, K.; Xu, C.; Peng, Z.; Long, X.; Shi, J.; Li, Z.; Zhang, Y.; Lai, J.; Chen, L.; Cai, Y.-P.; et al. Tuning the Solvent Alkyl Chain to Tailor Electrolyte Solvation for Stable Li-Metal Batteries. *ACS Applied Materials & Interfaces* **2022**, *14* (39), 44470-44478. DOI: 10.1021/acsami.2c13517.
- (22) Li, Z.; Rao, H.; Atwi, R.; Sivakumar, B. M.; Gwalani, B.; Gray, S.; Han, K. S.; Everett, T. A.; Ajantiwalay, T. A.; Murugesan, V.; et al. Non-polar ether-based electrolyte solutions for stable high-voltage non-aqueous lithium metal batteries. *Nature Communications* **2023**, *14* (1), 868. DOI: 10.1038/s41467-023-36647-1.
- (23) von Aspern, N.; Rösenthaller, G. V.; Winter, M.; Cekic-Laskovic, I. Fluorine and Lithium: Ideal Partners for High-Performance Rechargeable Battery Electrolytes. *Angew Chem Int Ed Engl* **2019**, *58* (45), 15978-16000. DOI: 10.1002/anie.201901381.
- (24) Zhao, Y.; Zhou, T.; Ashirov, T.; Kazzi, M. E.; Cancellieri, C.; Jeurgens, L. P. H.; Choi, J. W.; Coskun, A. Fluorinated ether electrolyte with controlled solvation structure for high voltage lithium metal batteries. *Nature Communications* **2022**, *13* (1), 2575. DOI: 10.1038/s41467-022-29199-3.
- (25) Zhao, Y.; Zhou, T.; El Kazzi, M.; Coskun, A. Fluorinated Cyclic Ether Co-solvents for Ultra-high-Voltage Practical Lithium-Metal Batteries. *ACS Applied Energy Materials* **2022**, *5* (6), 7784-7790. DOI: 10.1021/acsaem.2c01261.
- (26) Holoubek, J.; Yu, M.; Yu, S.; Li, M.; Wu, Z.; Xia, D.; Bhaladhare, P.; Gonzalez, M. S.; Pascal, T. A.; Liu, P.; et al. An All-Fluorinated Ester Electrolyte for Stable High-Voltage Li Metal Batteries Capable of Ultra-Low-Temperature Operation. *ACS Energy Letters* **2020**, *5* (5), 1438-1447. DOI: 10.1021/acscenergylett.0c00643.
- (27) Zhao, Y.; Zhou, T.; Jeurgens, L. P. H.; Kong, X.; Choi, J. W.; Coskun, A. Electrolyte engineering for highly inorganic solid electrolyte interphase in high-performance lithium metal batteries. *Chem* **2023**, *9* (3), 682-697. DOI: 10.1016/j.chempr.2022.12.005 (accessed 2023/04/29).
- (28) Yang, Y.; Davies, D. M.; Yin, Y.; Borodin, O.; Lee, J. Z.; Fang, C.; Olguin, M.; Zhang, Y.; Sablina, E. S.; Wang, X.; et al. High-Efficiency Lithium-Metal Anode Enabled by Liquefied Gas Electrolytes. *Joule* **2019**, *3* (8), 1986-2000. DOI: <https://doi.org/10.1016/j.joule.2019.06.008>.
- (29) Shi, J.; Xu, C.; Lai, J.; Li, Z.; Zhang, Y.; Liu, Y.; Ding, K.; Cai, Y. P.; Shang, R.; Zheng, Q. An Amphiphilic Molecule-Regulated Core-Shell Solvation Electrolyte for Li-Metal Batteries at Ultra-Low Temperature. *Angew Chem Int Ed Engl* **2023**, *62* (13), e202218151. DOI: 10.1002/anie.202218151 From NLM.
- (30) Fan, X.; Chen, L.; Borodin, O.; Ji, X.; Chen, J.; Hou, S.; Deng, T.; Zheng, J.; Yang, C.; Liou, S.-C.; et al. Non-flammable electrolyte enables Li-metal batteries with aggressive cathode chemistries. *Nature Nanotechnology* **2018**, *13* (8), 715-722. DOI: 10.1038/s41565-018-0183-2.
- (31) Xue, W.; Huang, M.; Li, Y.; Zhu, Y. G.; Gao, R.; Xiao, X.; Zhang, W.; Li, S.; Xu, G.; Yu, Y.; et al. Ultra-high-voltage Ni-rich layered cathodes in practical Li metal batteries enabled by a sulfonamide-based electrolyte. *Nature Energy* **2021**, *6* (5), 495-505. DOI: 10.1038/s41560-021-00792-y.
- (32) Yu, Z.; Wang, H.; Kong, X.; Huang, W.; Tsao, Y.; Mackanic, D. G.; Wang, K.; Wang, X.; Huang, W.; Choudhury, S.; et al. Molecular design for electrolyte solvents enabling energy-dense and long-cycling lithium metal batteries. *Nature Energy* **2020**, *5* (7), 526-533. DOI: 10.1038/s41560-020-0634-5.
- (33) Zhang, Z.; Hu, L.; Wu, H.; Weng, W.; Koh, M.; Redfern, P. C.; Curtiss, L. A.; Amine, K. Fluorinated electrolytes for 5 V lithium-ion battery chemistry. *Energy & Environmental Science* **2013**, *6* (6), 1806-1810. DOI: 10.1039/C3EE24414H.

- (34) Xue, W.; Shi, Z.; Huang, M.; Feng, S.; Wang, C.; Wang, F.; Lopez, J.; Qiao, B.; Xu, G.; Zhang, W.; et al. FSI-inspired solvent and “full fluorosulfonyl” electrolyte for 4 V class lithium-metal batteries. *Energy & Environmental Science* **2020**, *13* (1), 212-220. DOI: 10.1039/C9EE02538C. DOI: 10.1039/C9EE02538C.
- (35) Zhang, W.; Yang, T.; Liao, X.; Song, Y.; Zhao, Y. All-fluorinated electrolyte directly tuned Li⁺ solvation sheath enabling high-quality passivated interfaces for robust Li metal battery under high voltage operation. *Energy Storage Materials* **2023**, *57*, 249-259. DOI: <https://doi.org/10.1016/j.ensm.2023.02.027>.
- (36) Chen, X.; Zhang, Q. Atomic Insights into the Fundamental Interactions in Lithium Battery Electrolytes. *Accounts of Chemical Research* **2020**, *53* (9), 1992-2002. DOI: 10.1021/acs.accounts.0c00412.
- (37) Ma, P.; Mirmira, P.; Amanchukwu, C. V. Effect of Building Block Connectivity and Ion Solvation on Electrochemical Stability and Ionic Conductivity in Novel Fluoroether Electrolytes. *ACS Central Science* **2021**, *7* (7), 1232-1244. DOI: 10.1021/acscentsci.1c00503.
- (38) Amanchukwu, C. V.; Yu, Z.; Kong, X.; Qin, J.; Cui, Y.; Bao, Z. A New Class of Ionically Conducting Fluorinated Ether Electrolytes with High Electrochemical Stability. *Journal of the American Chemical Society* **2020**, *142* (16), 7393-7403. DOI: 10.1021/jacs.9b11056.
- (39) Yu, Z.; Rudnicki, P. E.; Zhang, Z.; Huang, Z.; Celik, H.; Oyakhire, S. T.; Chen, Y.; Kong, X.; Kim, S. C.; Xiao, X.; et al. Rational solvent molecule tuning for high-performance lithium metal battery electrolytes. *Nature Energy* **2022**, *7* (1), 94-106. DOI: 10.1038/s41560-021-00962-y.
- (40) Zhao, Y.; Zhou, T.; Mensi, M.; Choi, J. W.; Coskun, A. Electrolyte engineering via ether solvent fluorination for developing stable non-aqueous lithium metal batteries. *Nature Communications* **2023**, *14* (1), 299. DOI: 10.1038/s41467-023-35934-1.
- (41) Zhang, G.; Chang, J.; Wang, L.; Li, J.; Wang, C.; Wang, R.; Shi, G.; Yu, K.; Huang, W.; Zheng, H.; et al. A monofluoride ether-based electrolyte solution for fast-charging and low-temperature non-aqueous lithium metal batteries. *Nature Communications* **2023**, *14* (1), 1081. DOI: 10.1038/s41467-023-36793-6.
- (42) Yamada, Y.; Yaegashi, M.; Abe, T.; Yamada, A. A superconcentrated ether electrolyte for fast-charging Li-ion batteries. *Chemical Communications* **2013**, *49* (95), 11194-11196. DOI: 10.1039/C3CC46665E. DOI: 10.1039/C3CC46665E.
- (43) Ruan, D.; Tan, L.; Chen, S.; Fan, J.; Nian, Q.; Chen, L.; Wang, Z.; Ren, X. Solvent versus Anion Chemistry: Unveiling the Structure-Dependent Reactivity in Tailoring Electrochemical Interphases for Lithium-Metal Batteries. *JACS Au* **2023**, *3* (3), 953-963. DOI: 10.1021/jacsau.3c00035.
- (44) Gagné, O. C.; Hawthorne, F. C. Bond-length distributions for ions bonded to oxygen: alkali and alkaline-earth metals. *Acta Crystallogr B Struct Sci Cryst Eng Mater* **2016**, *72* (Pt 4), 602-625. DOI: 10.1107/S2052520616008507.
- (45) Adams, B. D.; Zheng, J.; Ren, X.; Xu, W.; Zhang, J.-G. Accurate Determination of Coulombic Efficiency for Lithium Metal Anodes and Lithium Metal Batteries. *Advanced Energy Materials* **2018**, *8* (7), 1702097. DOI: <https://doi.org/10.1002/aenm.201702097>. DOI: <https://doi.org/10.1002/aenm.201702097> (accessed 2023/05/08).
- (46) Wood, K. N.; Kazyak, E.; Chadwick, A. F.; Chen, K.-H.; Zhang, J.-G.; Thornton, K.; Dasgupta, N. P. Dendrites and Pits: Untangling the Complex Behavior of Lithium Metal Anodes through Operando Video Microscopy. *ACS Central Science* **2016**, *2* (11), 790-801. DOI: 10.1021/acscentsci.6b00260.
- (47) Chen, K.-H.; Wood, K. N.; Kazyak, E.; LePage, W. S.; Davis, A. L.; Sanchez, A. J.; Dasgupta, N. P. Dead lithium: mass transport effects on voltage, capacity, and failure of lithium metal anodes. *Journal of Materials Chemistry A* **2017**, *5* (23), 11671-11681. DOI: 10.1039/C7TA00371D. DOI: 10.1039/C7TA00371D.
- (48) Wu, H.; Jia, H.; Wang, C.; Zhang, J.-G.; Xu, W. Recent Progress in Understanding Solid Electrolyte Interphase on Lithium Metal Anodes. *Advanced Energy Materials* **2021**, *11* (5), 2003092. DOI: <https://doi.org/10.1002/aenm.202003092>. DOI: <https://doi.org/10.1002/aenm.202003092> (accessed 2023/05/05).