

Methylation enables high-voltage ether electrolytes for lithium metal batteries

Ether-based electrolytes are desired for lithium metal batteries owing to their low reduction potentials; however, they suffer from low anodic stability. Strategic methylation of ether solvents is shown to extend their electrochemical stability and facilitate the formation of LiF-rich interphases, enabling high-voltage lithium metal batteries while avoiding the use of fluorinated solvents.

This is a summary of:

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The problem

Lithium metal batteries (LMBs) are promising for next-generation energy storage but suffer from poor cycle life owing to Li dendrite formation and cathode cracking. Li Coulombic efficiencies (CEs) of up to ~99.5% can be achieved with ether-based electrolytes owing to the low solvent reduction potentials. However, ethers are prone to α -hydrogen abstraction, which lowers their oxidation stability. Fluorinated solvents are used to overcome this anodic instability at low salt concentrations, such as through the addition of a fluorinated antisolvent as a diluent or through functionalization of ethers with fluorine groups¹. However, the use of fluorinated solvents is associated with high cost and environmental concerns.

Methylation of the ether α -hydrogen atoms could provide a more sustainable approach to suppressing hydrogen-abstraction under highly oxidizing conditions². However, the Li CE and cell performance with methylated ethers are still below those needed for practical application³. We therefore set out to realize high-efficiency LMBs using the ether methylation strategy.

The solution

To enable LMBs with a long cycle life, inorganic LiF-rich interphases need to be formed to support the Li anode and high-voltage cathode. The formation of LiF-rich interphases requires an electrolyte solvent that is weakly solvating to promote the formation of ionic aggregates, which favours anion reduction and suppresses solvent degradation. To decrease the solvation energy and increase the anodic stability of the solvent, we prepared a series of dimethoxyethane (DME) derivatives in which selected α -positions are methylated to increase steric effects and decrease the possibility of hydrogen abstraction occurring at the high-voltage cathode surface (Ti or LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ (NCA)).

Through successive methylation of the outer α -hydrogens (Fig. 1a), we isolated 1,2-diethoxyethane (DEE), 1,2-dipropoxyethane (DPE) and dibutoxyethane (DBE), which show an incremental increase in oxidation stability. However, the increase in steric effects from DME to DBE decreases the solubility of lithium bis(fluorosulfonyl)imide (LiFSI) and thus decreases the ionic conductivity, excluding DBE as an electrolyte solvent. To balance the oxidation stability and ionic conductivity, we selectively methylated one inner and two outer DME α -hydrogens to form 1,2-diethoxypropane (DEP) (Fig. 1a),

which we hypothesized could promote the formation of ionic aggregates at low LiFSI concentrations while maintaining high ionic conductivity and anodic stability.

Using Raman spectroscopy, NMR spectroscopy and molecular dynamics simulations, we showed that at a low LiFSI concentration (2.0 M), the size and number of ionic aggregates formed in the solvents increase in the order DME < DEE < DPE < DEP (Fig. 1b). The ionic aggregates are preferentially reduced at potentials higher than the solvents, resulting in an increase in the Li CE from 98.3% for DME to 99.7% for DPE. Furthermore, the anodic stability of the electrolytes increased from 4.1 V (LiFSI–DME) to 5.3 V (LiFSI–DEP) in Li||Al half cells. The performance of DEP electrolytes was also validated in 100-mAh Li||NCA pouch cells under practical conditions, and a high capacity retention of >95% was achieved after 150 cycles with a cycle CE of >99.9%.

The implications

Our results demonstrate that methylation of both the outer and inner α -hydrogens of DME increases the molecular oxidation stability, whereas methylation of the inner α -hydrogens alters the solvation structure to increase ionic aggregation. The optimized LiFSI–DEP electrolytes stabilize both the Li metal anode and high-voltage NCA cathode, with superior electrochemical performance to state-of-the-art electrolytes. This strategy could be used for other high-capacity anodes with low operation potentials, such as in Na, Mg and Ca metal batteries.

Nevertheless, we have so far investigated only five methylated ether solvents because of the time-consuming synthesis and unavailability of materials. Additionally, the Li CE of 99.7% is still not satisfactory for realizing anode-free LMBs with a long cycle life, and there is a question about the compatibility of the nonfluorinated ethers with different cathodes. These issues could be resolved with the help of artificial intelligence, which could provide insights into the relationship between steric effects and ionic aggregate formation and accelerate solvent screening.

We now plan to optimize the electrolyte using Li salts other than LiFSI to overcome the corrosion problem of the FSI⁻ anion on the cathode. Additionally, we will perform further synthetic modifications to tune the Li salt solubility of the methylated ethers, targeting high-rate LMBs.

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EXPERT OPINION

"This manuscript describes a class of methyl-substituted ethers to increase the redox stability of ether solvents in lithium battery electrolytes. Substitution decreases the dehydrogenation of the ethers at the α positions, and the hypothesis is very

nicely proven by NMR and electrochemical measurements. The work represents another notable advance in molecular engineering to improve the performance of lithium metal batteries." **An anonymous reviewer**

FIGURE

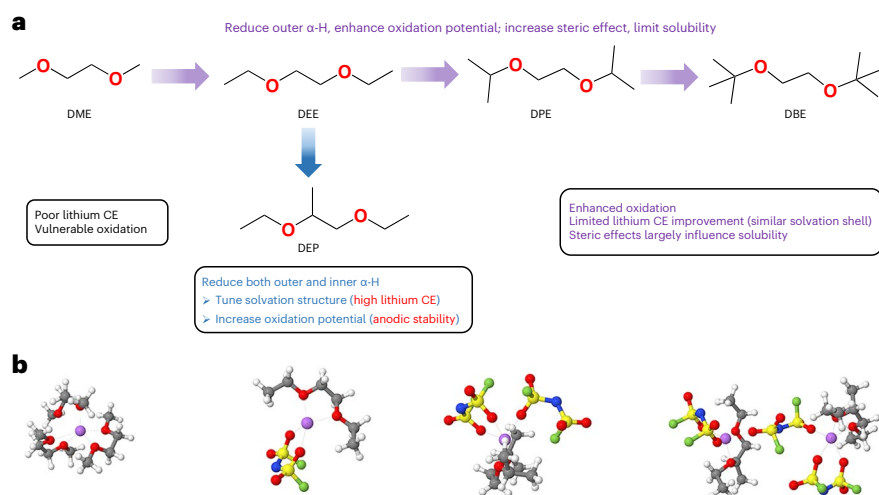


Fig. 1 | Ether methylation to increase the electrochemical performance of electrolytes with the LiFSI salt. a, Stepwise methylation of the outer α -hydrogens of DME (magenta arrows) increases the molecular oxidation stability but the increase in steric effects decreases the LiFSI solubility. Methylation of two outer and one inner α -hydrogen atom of DME (blue arrow) produces DEP, which optimizes the formation of ionic aggregates through steric effects, resulting in a high Li CE and increased anodic stability. **b**, Selected Li solvates with different electrolytes obtained from molecular dynamics simulations. From left to right: a solvent separated ion pair of $[\text{Li}(\text{DME})_3]^+$; a contact ion pair of $\{[\text{Li}(\text{DEE})](\text{FSI})\}^-$; a contact ion pair of $\{[\text{Li}(\text{DPE})](\text{FSI})\}^-$; and an aggregate of $\{[\text{Li}(\text{DEP})(\text{FSI})](\text{FSI})[\text{Li}(\text{DEP})(\text{FSI})]\}^-$. The change of solvation from contact ion pairs to ionic aggregates promotes anion reduction for LiF-rich interphase formation and suppresses solvent degradation, which facilitates high-performance LMBs. © 2024, Li, A.-M. et al.

BEHIND THE PAPER

We aimed to design electrolytes for LMBs that facilitated the formation of inorganic LiF-rich interphases to resolve the issue of Li dendrite growth. After the report of the first generation of fluorinated carbonate electrolytes⁴, we began thinking about developing a class of more environmentally benign electrolytes, in which the solvents are fluorine-free and the LiF interphases form through the reduction of conducting salts only. Our work on developing an electrolyte comprising 2.0M LiPF₆

and a mixture of tetrahydrofuran and 2-methyltetrahydrofuran⁵ that enables high-performance micro-sized silicon anodes inspired us to explore the ether methylation strategy to develop electrolytes for LMBs. This work has been a collaborative effort, and the theoretical expertise of the US Army Laboratory, Oleg Borodin and Travis P. Pollard were crucial in deciphering the solvation mystery and solvent degradation mechanism. **A.-M.L. & C.W.**

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FROM THE EDITOR

"There has been a surge of interest in improving battery performance, but there is a delicate balance between the chemistry, material and engineering aspects. This study stood out because it extensively probes how molecular differences alter ion transport and material phenomena critical to battery operation while also affording promising activities. My hope is that this work develops chemistry-level approaches to resolving system-level challenges in the electrochemical energy storage field."

Adam Weingarten, Senior Editor,
Nature Chemistry.