LITHIUM METAL BATTERIES

Make ion–solvent interactions weaker

Low-temperature operation of lithium batteries is notoriously challenging. However, tailoring the electrolyte structure may provide a pathway toward uniform lithium deposition and reversible operation of lithium metal anodes at low temperatures.

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Rechargeable batteries that can operate at extremely low temperatures (−40 to −180 °C) are necessary for orbital missions and in electric vehicles in cold environments. Liquid-based electrolytes facilitate ion transport between the anode and cathode and typically comprise a salt and a solvent. The freezing and boiling temperature of the liquid solvent in the electrolyte limits the operating temperature window (between around −20 °C to 40 °C).

To overcome this challenge, state-of-the-art electrolytes employ mixtures of co-solvents and additives. Co-solvents such as vinylene carbonate, ethylene sulfite and a variety of ester-based systems aid in building protective layers on the electrode that prolong its lifetime in ambient conditions[1]. However, the protective layers can impede ion intercalation kinetics at low temperatures.

Most co-solvents fundamentally act to improve the ion transport properties at the cathode surface but at the cost of increasing the anode–electrolyte interface resistance. The imbalance can result in irreversible lithium plating at low temperatures. Thus, there are fundamental challenges between designing an electrolyte for simultaneous performance parameters such as low viscosity, high ionic conductivity, low boiling point, and designing an electrolyte that produces adequate electrode kinetics[2]. A recent innovative approach used liquefied gas electrolytes, offering an interesting route toward ultra-low temperature battery systems[3]. A potential challenge with liquefied electrolyte gas systems is the need for high-pressure containment.

Now, writing in *Nature Energy*[4], Ping Liu and co-workers from University of California San Diego identify an electrolyte formula for a high-performance Li metal battery operating at ultra-low temperatures (<−30 °C). The team explored the performance of 1M lithium bis(flurosulfonyl)imide in two solvents, diethyl ether (DEE) and a mixture of 1,3-dioxolane and 1,2-dimethyoxyethane (DOL/DME), at temperatures ranging between −60 and 23 °C. At room temperature the two electrolytes demonstrate very similar behaviours with greater than 98% coulombic efficiency (CE). However, the electrolyte with DEE (98.4% CE at −60 °C) demonstrated markedly better performance at low temperatures than the electrolyte with DOL/DME (27.5% CE at −60 °C). The morphology of the plated lithium metal from DEE was dense and uniform at all temperatures, whereas the lithium plated from the DOL/DME formed porous and dendritic structures at low temperatures.

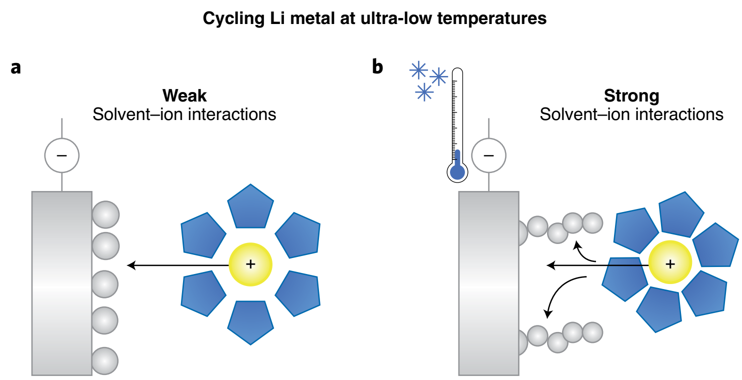

Fig. 1 | Impact of electrolyte structure on lithium deposition morphology. a, In the work of Liu and team, the weak interaction between the solvent and lithium ions at low temperatures led to fast desolvation and uniform electrodeposition. **b**, The solvent–ion interactions in conventional electrolytes are strong, leading to sluggish desolvation and dendritic lithium deposition morphologies. The Li ions and solvation shells are represented by yellow spheres and blue pentagons, respectively.

With the help of Raman spectroscopy and molecular dynamic simulations the team of researchers probe the impact of electrolyte structure on plating morphology. Specifically, Liu and team demonstrate how weak interactions between the lithium ion and solvent led to facile desolvaton and homogeneous lithium deposition across all temperatures for the DEE electrolyte (Fig. 1a). In contrast, strong binding between the solvent and cation lead to sluggish desolvation, the formation of lithium filaments and dendrites, and consequently the cycling irreversibility (Fig. 1b).

In addition to the low-temperature cycling requirements, there is a simultaneous need for energy-dense batteries to extend the driving range for electric vehicles and a range of space applications (for example, space robotic instrumentation). The use of Li metal anodes (3860 mAh g^{-1}) in the work of Liu and team represents a potential pathway toward achieving energy densities greater than 300 Wh kg^{-1}. However, high reactivity of Li metal in liquid electrolytes and non-uniform electrodeposition (microstructure heterogeneity) not only limit the cycle life, but also reduce battery capacity and energy due to the Li inventory loss during cycling.

For high-energy applications, Liu and team constructed a full-cell configuration with a metallic Li anode and a sulferized polyacrylonitrile cathode. In particular, the anode has just one-fold excess capacity and the cathode has a high loading of 3.5 mAh cm^{-2}, both approaching the practical operating requirements. The full cell with the DEE electrolyte achieved discharge capacities of 519 mAh g^{-1} and 474 mAh g^{-1} at a 0.1C at −40 °C and −60 °C, respectively, which correspond to exceptionally high cell-level energy densities of 143 and 126 Wh kg^{-1} at these low temperatures.

The work of Liu and team demonstrates the first lithium metal battery with practical electrode loadings that has been cycled at ultra-low temperatures and thus represents a significant accomplishment within the low-temperature battery field. Ultimately, it highlights the importance of electrolyte structure on desolvation, deposition and effective electron-transfer reactions at solid–liquid interfaces. The concept of having weak interactions between the charge carrier and solvent for uniform deposition provides a framework for future exploration in electrolyte design for batteries in extreme environments. However, for practical applications, it is unclear whether control over these electrolyte interactions will enable high-rate cycling. Furthermore, the safety of diethyl ether may make application of this electrolyte challenging. Nevertheless, the fundamental principles may inspire future directions in electrolyte design. ❐

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Competing interests

The author declares no competing interests.