Check for updates

A criterion for evaluating Li-dendrite-suppression capability for the design of solid electrolyte interphases

The critical interphase overpotential (CIOP) represents the capability of the interphase on solid-state electrolyte surfaces to suppress Li-dendrite penetration. An interphase with a high CIOP is shown to enable an all-solid-state Li-metal battery to operate at high current and high capacity.

This is a summary of:
Wan, H. et al. Critical interphase overpotential as a lithium dendrite-suppression criterion for all-solid-state lithium battery design. *Nat. Energy* https://doi.org/10.1038/s41560-023-01231-w (2023).

Published online: 20 March 2023

The problem

Suppressing Li dendrite growth is a crucial challenge in the development of all-solid-state Li-metal batteries (ASSLBs). Penetration of Li dendrites through the solid-state electrolyte (SSE) can lead to short circuiting of the cells, presenting a safety concern. The current density at which Li dendrites penetrate through the SSE and cause short circuiting is termed the critical current density (CCD). The CCD not only depends on the intrinsic properties of the SSE but also on the thickness of the SSE. Furthermore, as the Li plating or stripping capacity, stack pressure and interfacial resistance change the overpotential, which is the driving force for Li plating and stripping[1], these factors also change the CCD. Thus, because the CCD is not an intrinsic property of an SSE, it is difficult to use CCDs to design SSEs.

The discovery

Most SSEs are not stable against Li and are reduced during Li plating, leading to the formation of a solid electrolyte interphase (SEI) between the Li anode and the SSE. At a low applied interphase overpotential (AIOP) during Li plating, plated Li diffuses along the Li/SEI interface and maintains planar growth. However, when the AIOP is higher than a critical interphase overpotential (CIOP), Li starts to penetrate the SEI, forming dendrites (Fig. 1a). Upon further increase in the applied overpotential to increase the current density to the CCD, Li dendrites grow through the SSE, shorting the cell. The CIOP is therefore the critical overpotential at which Li starts to penetrate the interphase. Unlike the CCD, which is controlled by the properties of the SSE and engineering parameters, the CIOP is an intrinsic property of the SEI and is determined by the lithiophobicity and mechanical properties of the SEI.

To achieve a Li-dendrite-free ASSLB with a high energy density, the SEI should have a high CIOP (and thus have high lithiophobicity and high mechanical strength) to suppress Li-dendrite penetration and a low AIOP (requiring a low SEI resistance and low interfacial resistance). Because the CIOP of most SEIs formed by the reduction of the SSE is low, an artificial interphase with a high CIOP is required at the Li/SSE interface.

Guided by these criteria, we designed a mixed-conductive Li_2NH–Mg interlayer, which was inserted between a Li_6PS_5Cl SSE and a Li–1.0 wt%La anode. During annealing, the Mg in Li_2NH–Mg reacts with the SSE to form a $LiMgS_x$ interphase, while migration of Mg during annealing and cycling results in the formation of a LiMgLa alloy on the anode (Fig. 1b). Moreover, Li_2NH decomposes during heat treatment to form porous, lithiophobic LiH–Li_3N. The $LiMgS_x$ interphase increases the CIOP from about 10 mV (for the SEI of Li_6PS_5Cl) to about 220 mV. Furthermore, the Li plates on the LiMgLa surface and reversibly penetrates into porous LiH–Li_3N, decreasing the AIOP.

In evaluations of the electrochemical performance of a ASSLB with our interphase, a $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622)|Li_6PS_5Cl|Li full cell showed a high reversible capacity of 1.9 mAh cm^{-2} after 100 cycles at a current density of 0.76 mA cm^{-2} at 25 °C and under a low stack pressure.

Future directions

As the CIOP is an intrinsic property of the interphase, it could be used to design interphases for Li-dendrite suppression. The CIOP concept can also be used in other solid-state metal batteries, which also feature SEIs.

We determined CIOP values by monitoring the potential evolution during Li plating or stripping in three-electrode cells. However, the widespread application of this testing protocol is limited by the difficulty of assembling the three-electrode cell. Alternatively, the CIOP could be determined by measuring the resistance of the interphase using electrochemical impedance spectroscopy and the current before voltage drop, because the interphase at the working electrode and counter electrode is the same.

Another problem we have not yet fully addressed is how to ensure that the AIOP does not surpass the CIOP. The AIOP is affected by the electronic and ionic conductivity of the interphase, Li diffusivity in the Li anode, and void formation at the Li/SSE interface[2,3]. We are systematically investigating the impact of these factors on the AIOP.

Hongli Wan & Chunsheng Wang
University of Maryland, College Park, MD, USA.

EXPERT OPINION

"This study identified a critical interphase overpotential (CIOP) for the evaluation of the capability of the interphase (or solid-state electrolyte (SSE) if no interphase is formed) to suppress Li-dendrite penetration; this differs from the critical current density, which represents the capability of SSEs to suppress Li-dendrite penetration through the SSE. The CIOP is an intrinsic property of the interphase and can be used to design the interphase in all-solid-state lithium batteries." **Dalin Sun, Fudan University, Shanghai, China.**

FIGURE

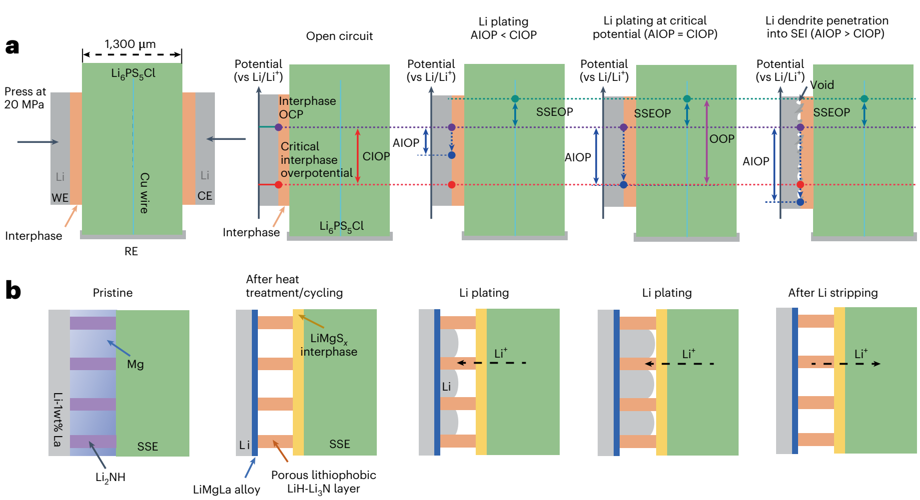

Fig. 1 | CIOP concept for the development of a Li-dendrite-free interlayer. a, The three-electrode cell used to accurately monitor the potential evolution at the working electrode (WE) and counter electrode (CE) during the Li plating or stripping process is shown on the far left. The other schematics show the relationship between the CIOP, AIOP, SSE overpotential (SSEOP), and the overall overpotential (OOP) when Li dendrites are formed at the WE or CE. CIOP = OOP − SSEOP. **b**, Illustration of the Li plating and stripping process with the Li_2NH–Mg interphase. The in situ formation of the $Li_6PS_5Cl/LiMgS_x/LiH–Li_3N/LiMgLa$ structure from $Li_6PS_5Cl/Li_2NH–Mg/Li–1wt\%La$ enables the realization of a high CIOP and low AIOP. RE, reference electrode. © 2023, Wan, H. et al.

BEHIND THE PAPER

We previously found that when decreasing the area-specific resistance of the Li||Li cell, the CCD increased but the overpotential before the voltage drop did not markedly change, which led us to think that it should be the overpotential, not CCD, that determines the Li-dendrite-suppression capability of the SSE.

One challenge was to accurately measure the CIOP. To do so, we inserted a Cu wire into the Li_6PS_5Cl electrolyte and connected the end of the wire to the Li metal to serve as the reference electrode (Fig. 1a, left), enabling us to measure the true potential of the anode and cathode.

One question is whether it is rational to link dendrite formation — a local event — to a global critical overpotential over the whole SSE. However, a similar strategy has been reported in which the dielectric strength was used to evaluate the capability of a solid insulator to withstand dielectric breakdown[4]. **H.W. & C.W.**

REFERENCES

1. Porz, L. et al. Mechanism of lithium metal penetration through inorganic solid electrolytes. *Adv. Energy Mater.* **7**, 1701003 (2017).
This paper reports that a small overpotential can lead to SSE fracture caused by Li plating.
2. Kasemchainan, J. et al. Critical stripping current leads to dendrite formation on plating in lithium anode solid electrolyte cells. *Nat. Mater.* **18**, 1105–1111 (2019).
This paper shows that void formation at the Li–SSE interface leads to Li-dendrite growth.
3. Park, R. J. Y. et al. Semi-solid alkali metal electrodes enabling high critical current densities in solid electrolyte batteries. *Nat. Energy* **6**, 314–322 (2021).
This paper reports that Li-dendrite penetration can be suppressed by avoiding the formation of voids at the Li–SSE interface using Na–K liquid metal.
4. Friedrichs, P., Burte, E. P. & Schörner, R. Dielectric strength of thermal oxides on 6H-SiC and 4H-SiC. *Appl. Phys. Lett.* **65**, 1665–1667 (1994).
This paper investigates the dielectric strength of the oxide layer formed on SiC.

FROM THE EDITOR

"When this paper was submitted, it immediately stood out to me because of a new criterion proposed to interpret the dendrite-suppression capability of solid electrolytes — an important metric in the development of solid-state batteries. The work also demonstrates the use of the criterion to design high-performance batteries, which is encouraging."
Alex Zhang, Senior Editor, *Nature Energy*.