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Dendrite-free lithium metal anodes: stable solid electrolyte interphases for high-efficiency batteries

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Li metal anodes are the 'Holy Grail' of energy storage systems and they have shown significant advances recently. A more superior cycling stability and a higher utilization ratio of the Li metal anode have been achieved by additive- and nanostructure-stabilized SEI layers. A profound understanding of the composition, internal structure, and evolution of the SEI film sheds new light on dendrite-free high-efficiency lithium metal batteries.

Modern portable electronics, electric vehicles, and grid energy storage put forward an urgent requirement for high-energy-density energy storage systems. Lithium metal batteries (LMBs) are the "Holy Grail" of energy storage systems due to their extremely high theoretical specific capacity (3860 mA h g^{-1}) and low negative redox potential (-3.040 V *vs.* a standard hydrogen electrode). They have sparked global interest in the next generation of rechargeable batteries.[1] In 2009, IBM launched the "Battery 500" project with an ambitious aim of developing a LMB system that could ensure a 500 mile driving range for electric vehicles.[2] However, the initial excitement soon dwindled as the task was much more complex than initially thought. Differing from Li-ion batteries which are based on the rocking-chair concept between intercalated cathode/anode pairs, one of the toughest challenges in LMBs is the formation of Li dendrites, which induce a severe security risk and low efficiency (Fig. 1), and hinder the practical use of high-energy-density LMBs.

The Li dendrite refers to a branched or tree-like structure of Li metal where the Li ions are deposited inhomogeneously on the anode surface. The dendritic growth of Li metal has been known since the 1960s. However, there is only a limited mechanistic understanding on Li metal growth in a working cell. A diffusion model has been proposed as the "Sand's time" (τ) to correlate the dendrite nucleation to the transfer nature of the ions/electrons empirically near the solid electrolyte interphase (SEI):[3]

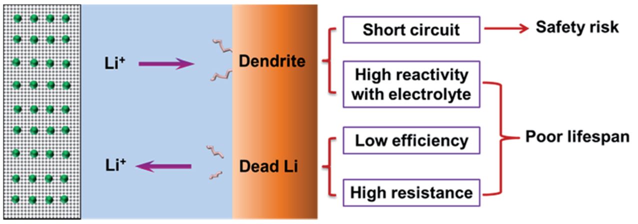

Fig. 1 Schematic diagram of the typical morphology of Li dendrites, and the related safety risks and poor lifespan.

$$\tau = \pi D \frac{eC_0 + (\mu_a + \mu_{Li^+})^2}{2J\mu_a} \tag{1}$$

where D is the diffusion coefficient, e is the electronic charge, C_0 is the initial concentration of Li salt, μ_a and μ_{Li^+} are the anionic and Li^+ mobilities, and J is the effective electrode current density. The large migration rate of the Li ion (D and μ_{Li^+}) and the small effective electrode current density (J) lead to a large Sand's time (τ), which indicates that the cell has a long lifespan before the growth of lithium dendrites.

Once the dendrites nucleate, continuous growth of the Li dendrites can not be avoided due to the intensified charge density and electric fields in and at the protrusion areas (such as the tip of the Li dendrites).[4,5] Such growth is self-enhancing: as the Li deposition at the tip of a protrusion further increases in length, the local inhomogeneity of the anode surface and the local electric field increase as well. The ever-enhancing growth of the dendrites can be stopped if the SEI holds a shear modulus of about twice that of the Li dendrite ($\sim 10^9$ Pa).[6] Thus, the SEI is of prime importance to inhibit dendrite formation at the initial nucleation stage and the final short circuit stage. Among the many effective strategies to improve the cycling performance of the lithium metal anode by modifying the SEI composition and the anode structure, the achievements from Archer's group[7] and Cui's group[8] demonstrated two pioneering works on the Li metal anode. They shed new light on the formation mechanism and the function of SEIs to stabilize the anode and inhibit the formation of dendrites.

The composition, properties, and stability of the surface layer on the anode determine the morphology of the re-deposited Li, thus guiding the cell performance of the LMB. Electrolyte additives are deemed to have a positive effect on building a

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stable SEI and a family of additives with higher reduction voltages than solvents and salts has been widely employed to reinforce the interfaces on the Li metal. Archer and co-workers reported that simple liquid electrolytes reinforced with halogenated salt blends exhibited stable long-term cycling at room temperature, often with no signs of deposition instabilities over hundreds of charge/discharge cycles and thousands of operating hours, and impedance spectroscopy indicated a decreased diffusion resistance of the Li ions through the SEI.[7,9] With halogenated salt additives in the electrolyte, the deposits on the electrode are fluorine-rich (most likely LiF). LiOH and Li_2CO_3 were also found in the SEI. The *in situ* formed SEI (Fig. 2a) driven by reactions between active Li metal and the organic and inorganic components in the electrolyte solution at the anode interphase plays a key role in removing the solvent molecules and can act as a "catalyst" to decrease the activation energy of the Li ions crossing the SEI and depositing on the anode.[10]

As well as halides, FSI^-, the "magic anion", can also help to build a unique SEI layer to achieve a remarkably enhanced Coulombic efficiency (*ca.* 99%) and a superior cycling stability of lithium deposition/dissolution, and the favorable lithium morphology can be retained even at the high current density of 10 mA cm^{-2}.[11] Zhang *et al.* found that Cs^+ additives in an appropriate concentration in the electrolyte can form a positively charged electrostatic shield around the initial tip of the protuberances, which forces further deposition of Li to adjacent regions of the anode and eliminates anisotropic formation of dendrites in the LMB *via* a self-healing electrostatic shield mechanism.[5] Smooth and dendrite-free Li deposition films with vertically grown, self-aligned, and highly compacted Li nanorods were observed.[12] 'Solvent-in-Salt' electrolytes with high salt concentrations and large Li ion transference numbers were also efficient to prevent the depletion of anions in the vicinity of the anode and suppress Li dendrite formation.[13]

In addition to the *in situ* formed SEI from the reactions between Li metal and solvents, and salts or additives in the electrolytes, another approach to suppressing dendrite growth is to cover the Li electrode with an *ex situ* formed protective layer (or "artificial" SEI layer) by treating the Li metal with chosen chemicals prior to its use in battery electrolytes. Cui and co-workers created a monolayer of nanostructured and interconnected amorphous hollow carbon nanospheres to act as an artificial SEI (Fig. 2b).[8] The amorphous hollow carbon nanospheres had a conductivity of ~7.5 S m^{-1} and there were no large pores on the artificial SEI for the electrolyte with a molecular size ranging from a few tenths of an angstrom to a few angstroms to permeate.[14] With the continuous electrodeposition of Li metal, granular Li began to grow and elevated the hollow carbon nanosphere film, confirming the design of depositing Li metal underneath the carbon. The formation of a stable SEI facilitated by the hollow carbon nanospheres on the Cu substrate promotes a low and stable hysteresis in the voltage–capacity curves with the cell showing a high Coulombic efficiency of ~99.5% at 0.25 mA cm^{-2} after 150 cycles. The use of hexagonal boron nitride and graphene directly on Cu metal current collectors can also serve as interfacial protection of the Li metal.[15]

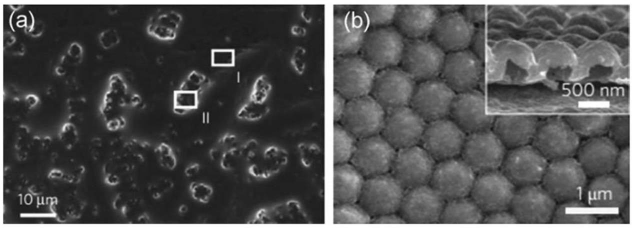

Fig. 2 The morphology of the SEI on the anode: (a) SEM image of the *in situ* formed SEI from the salt clusters on Li foil;[7] (b) Top-view SEM image of the hollow carbon nanospheres after the initial SEI formation process. Inset: the hollow carbon nanosphere structure is preserved after SEI coating.[8]

Nanoscale interfacial engineering provides a promising strategy to tackle the intrinsic problems of Li metal anodes. However, relative to the cost-effective electrochemical approaches with a small amount of additives in the electrolyte, the elaborately modified *ex situ* SEI layer has several problems for the practical applications of LMBs, such as the high cost, difficulty in obtaining a layer with a large area, complex synthesis routes, *etc.* To address the issues, several simple "artificial" SEI layers have been developed for Li metal-based batteries, such as a Li_3N protection layer or a PEDOT-*co*-PEG coating layer.[16] As well as nanostructured SEIs, some creative ideas for dendrite-free nanostructures (*e.g.* a coated Li powder electrode,[17] mechanical surface modification of Li metal,[18] a hybrid anode using electrically connected graphite and lithium metal,[19] Li metal within porous graphene networks,[20] and self-limited Li deposited in an inert Li_7B_6 framework[21]) have recently been proposed for LMBs.

In summary, a more superior cycling stability and a higher utilization ratio for Li metal anodes have been achieved recently by *in situ* SEI layers formed by additives and "artificial" SEI layers formed by nanocarbon. New insights into the high-energy-density metallic Li anode with an appropriate combination of electrochemistry and nanostructures at the interfaces are provided. More fundamental investigations are urgently required to fully understand the formation and performance of SEIs, and the behavior of Li ions crossing through the SEI are expected to be observed *in situ* in a working cell. The profound understanding of the composition, internal structure, and evolution of SEI films may lead to new approaches to stabilize the long-term cycling stability of Li metal and other metal anodes for energy storage applications. Thus, more and more scientific exploration should be ignited from chemistry, nanomaterials, physics, as well as engineering communities to achieve the practical applications of Li metal for high-energy-density LMBs.

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