Interfacial Chemistry Regulation via a Skin-Grafting Strategy Enables High-Performance Lithium-Metal Batteries

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ABSTRACT: The lithium (Li) metal anode suffers severe interfacial instability from its high reactivity toward liquid electrolytes, especially carbonate-based electrolytes, resulting in poor electrochemical performance of batteries that use 4 V high-capacity cathodes. We report a new skin-grafting strategy that stabilizes the Li metal—liquid electrolyte interface by coating the Li metal surface with poly((N-2,2-dimethyl-1,3-dioxolane-4-methyl)-S-norbornene-exo-2,3-dicarboximide), a chemically and electrochemically active polymer layer. This layer, composed of cyclic ether groups with a stiff polycyclic main chain, serves as a grafted polymer skin on the Li metal anode not only to incorporate ether-based polymeric components into the solid-electrolyte interphase (SEI) but also to accommodate Li deposition/dissolution under the skin in a dendrite/moss-free manner. Consequently, a Li-metal battery employing a Li metal anode with the grafted skin paired with LiNi0.5Co0.2Mn0.3O2 cathode has a 90.0% capacity retention after 400 charge/discharge cycles and a capacity of 1.2 mAh/cm² in a carbonate-based electrolyte. This proof-of-concept study provides a new direction for regulating the interfacial chemistry of Li metal anodes and for enabling high-performance Li-metal batteries.

Lithium-ion batteries (LIBs) have achieved great success as one of the most important energy storage systems for portable electronics and electric vehicles. Lithium (Li) metal is considered to be the ultimate anode material, owing to its high theoretical capacity (3860 mAh g⁻¹), low chemical potential (−3.04 V vs the standard hydrogen electrode), low density (0.59 g cm⁻³), and irreplaceable role in Li−sulfur and Li−air battery systems. Unfortunately, metallic Li is very reactive with most liquid organic electrolytes, especially the carbonate-based electrolytes that are compatible with current 4 V Li-ion cathodes technology. The solid-electrolyte interphase (SEI) of Li metal anodes with carbonate-based electrolytes is unstable and creates an unfavorable environment for Li deposition/dissolution. As a result, Li metal anodes suffer from dendritic/mossy Li growth, huge interfacial fluctuations, and severe electrolyte consumption by SEI formation during cycling (Figure 1a).

These interfacial issues are mainly responsible for the poor electrochemical performance of Li-metal batteries including their low Coulombic efficiency (CE), short cycle life, and severe polarization of charging/discharging potentials. Despite much progress in addressing the problem of anode morphology changes by designing structured Li metal anodes and using mechanically robust coating layers on the Li-metal surface, the control of Li interfacial chemistry is still pivotal for enabling higher performance Li metal anodes. Currently, most efforts to enhance the interfacial stability have focused on engineering the liquid electrolyte, including ether-based electrolytes, ionic liquid electrolytes, superconcentrated electrolytes, and additives. However, carbonate-based electrolytes, which exhibit excellent compatibility with current 4 V cathodes, are still plagued by interfacial reactions at the Li metal anode.

We report here a grafted-skin strategy that involves coating a chemically and electrochemically active polymer onto the Li metal surface in order to regulate the SEI structure and the Li metal deposition/dissolution behavior. We reasoned that a stiff polymer with a high volume fraction of cyclic ether groups, which have a strong affinity for Li, would compete effectively with monomeric cyclic carbonates from the liquid electrolyte for Li-metal surface sites. Li metal deposits/dissolves in a dendrite-free manner under this polymeric skin, protecting the electrode from over-reaction with the liquid electrolyte (Figure 1b). Li metal anodes with the grafted skin show significantly improved CE and stability over many Li deposition/dissolution cycles. Li-metal batteries employing LiFePO4 (LFP) and LiNi0.5Co0.2Mn0.3O4 (NCM 523) cathodes both show dramatically enhanced cycling performance in a carbonate electrolyte compared to batteries without the polymeric grafted skin.

Figure 1c illustrates the structure of the polymer, poly((N-2,2-dimethyl-1,3-dioxolane-4-methyl)-S-norbornene-exo-2,3-dicarboximide). The cyclic ether group (pink) has high affinity for the Li metal surface, reductively adsorbing and competing for surface sites with the carbonate-based electrolyte components in the SEI. This results in a more uniform SEI with improved density and flexibility. The polycyclic main chain imparts stiffness, resulting in a modulus of 0.37 GPa as measured by nanoindentation (Figure S21, S22), modulating the morphology of Li deposition and enabling lasting protection of the Li metal surface against over-reaction with the carbonate electrolyte. The skin polymer was synthesized via...
ring-opening metathesis polymerization (Figure S1), and its structure was confirmed by proton nuclear magnetic resonance spectroscopy (1H NMR), high-resolution X-ray photoelectron spectroscopy (XPS), and gel permeation chromatography (GPC) (Figure S2, S3). In addition, the skin polymer, which has good compatibility with carbonate electrolytes, is not soluble in or reactive with the electrolyte, as confirmed by NMR (Figures S17, S18).

The cyclic ether group is designed to be chemically reactive with Li metal, enabling the polymer to be grafted to Li and to act as a component of the SEI after electrochemical activation. After reacting the polymer with metallic Li, the broad peak from −0.3 to −0.9 ppm in the 7Li NMR spectrum (Figure 2a) and the peak at 53.6 eV in the high-resolution XPS spectrum (Figure S4) can be assigned to the R−O−Li bond, indicating ring opening of cyclic ether groups. Figure 2b displays the cyclic voltammogram of the polymer on a Cu electrode in the carbonate electrolyte. When no polymer was applied to the working electrode, an SEI formation peak was observed from +0.2 to −0.05 V vs Li+/Li. When the polymer was added, SEI formation shifted by ∼0.14 V in the positive direction, indicating that a chemically different SEI layer forms prior to deposition of the carbonate-based electrolyte derived SEI. This is consistent with our hypothesis that the polymer was deposited in the new SEI layer. The affinity of the cyclic ether group (2,2-dimethyl-1,3-dioxolane, DMDOL) for metallic Li was also investigated, and similar results were obtained (Figure S5, S6).

The Li deposition/dissolution behaviors of the Li metal anode with and without the grafted skin were compared in scanning electron microscopy (SEM) images. The grafted skin forms a uniform coating on the Li metal anode surface, owing to its strong affinity for metallic Li (Figure S7). The coating thickness was optimized by measurement of the Li deposition overpotential (Figure S14) and was found to be 2.2 μm from SEM images (Figure S16). The bare Li metal electrode displays a typical dendritic and loose morphology after 30 cycles (Figure 3b,c) and 50 cycles (Figure S8) in the carbonate electrolyte. In contrast, the Li metal anode with the grafted skin presents a flat surface, which is a typical polymer coated morphology, and no dendritic or mossy Li can be observed after 30 cycles (Figure 3e,f) or 50 cycles (Figure S9), suggesting that Li deposition/dissolution occurs underneath the skin. We note that the polymer skin is not very dense from a top-view of the surface, thus allowing an electrolyte permeation and participation in the SEI formation.

To investigate the SEI structure of Li metal with and without the grafted skin, we conducted XPS analyses on Li metal anode surfaces after 30 cycles in the carbonate electrolyte. Figure 4a−d shows high-resolution F 1s, N 1s, C 1s, and Li 1s of (a−d) bare Li anode surface and (e−h) Li metal with grafted skin.
F, peaks at 286.3 and 284.6 eV in the C 1s spectrum are related to C—O and C/C—C/H, respectively, and the peak at 53.2 eV in the Li 1s spectrum corresponds to Li—O. The N 1s signal is absent in this system. Interestingly, new peaks appeared in the spectra of the SEI of a Li metal anode with the polymeric grafted skin. As shown in Figure 4e–h, the peaks at 400.0 and 288.2 eV in the N 1s and C 1s spectra correspond to C—N and C═O, respectively, which are the characteristic peaks of the polymer (Figure S10). This result verifies the presence of the polymeric grafted skin-derived components in the SEI. Meanwhile, the concentrations of C—O and C—N groups in the C 1s spectra and Li—O in the Li 1s spectra are much higher than those of the bare Li SEI, and very little LiPO4F or C—F was detected in the F 1s spectrum, indicating that the SEI is composed of a high concentration of ether-based species. There is relatively little of the components derived from the carbonate electrolyte in the new SEI layer.

XPS depth profiling was employed to investigate the different Li chemical environments from the top surface of the grafted skin to the Li surface underneath. As shown in Figure 5, the curves from top (light blue) to bottom (green) represent the spectra acquired after sputtering for 0, 30, 60, 90, 120, 150, 155, 160, 180, and 200 min.

Figure 5. XPS depth profiling of N 1s, Li 1s, and C 1s of Li metal with grafted skin after 30 cycles. Curves from top (light blue) to bottom (green) represent the spectra acquired after sputtering for 0, 30, 60, 90, 120, 150, 155, 160, 180, and 200 min.

In conclusion, we report a new skin-grafting strategy, incorporating a chemically and electrochemically active polymer on the Li metal surface to regulate the SEI structure and Li deposition/dissolution behavior. An SEI containing a high concentration of cyclic ether groups and a durable and dendrite-free Li deposition/dissolution morphology were achieved. This strategy enables dramatically increased CE of the Li metal anode and long cycling lives of Li-metal batteries with 4 V Li-ion cathodes in a carbonate electrolyte. Moreover, this proof-of-concept study illustrates a new strategy for designing and optimizing the SEI structure of the Li metal anode. Additional polymer skin candidates can be investigated to further stabilize the Li metal anode in liquid electrolytes.

ASSOCIATED CONTENT

Supporting Information
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Elemental details and additional characterizations (PDF)

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