# Lithium Metal Anodes with an Adaptive "Solid-Liquid" Interfacial **Protective Laver**

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Supporting Information

**ABSTRACT:** Lithium metal is an attractive anode for the next generation of high energy density lithium-ion batteries due to its high specific capacity  $(3,860 \text{ mAh g}^{-1})$  and lowest overall anode potential. However, the key issue is that the static solid electrolyte interphase cannot match the dynamic volume changes of the Li anode, resulting in side reactions, dendrite



growth, and poor electrodeposition behavior, which prevent its practical applications. Here, we show that the "solid-liquid" hybrid behavior of a dynamically cross-linked polymer enables its use as an excellent adaptive interfacial layer for Li metal anodes. The dynamic polymer can reversibly switch between its "liquid" and "solid" properties in response to the rate of lithium growth to provide uniform surface coverage and dendrite suppression, respectively, thereby enabling the stable operation of lithium metal electrodes. We believe that this example of engineering an adaptive Li/electrolyte interface brings about a new and promising way to address the intrinsic problems of lithium metal anodes.

#### INTRODUCTION

Silly Putty (SP) is a popular children's toy that exhibits unique and intriguing properties. If touched gently, it is soft and can be easily kneaded into various shapes due to its flowability. However, if SP is stretched or impacted quickly, its stiffness increases sharply, and it bounces while maintaining its shape. The secret to the seemingly magical viscoelastic behavior of SP lies in its dynamic cross-linking. SP is primarily comprised of polydimethylsiloxane (PDMS) cross-linked by transient boronmediated cross-links<sup>1,2</sup> (Figure 1a). These dynamic bonds can bind the PDMS chains together to temporarily lock the shape of the material. If the deformation rate is fast enough such that the dynamic cross-links do not have enough time to transiently break and reconnect, SP can temporarily act as an elastic solid and drastically increase in stiffness. However, as the polymer chains are mobile, the dynamic connections can break and reform at a different location. This "break-reconnect" behavior of the dynamic cross-link happens constantly and has been used to explain why the shape of SP is not permanently locked in place but instead can gradually spread and flow like a liquid over time.<sup>2–4</sup> With its diametric behavior, SP is technically termed as a "shear-thickening material",<sup>3-5</sup> and it can be considered as a dynamic smart material<sup>6</sup> with "solid-liquid"-like properties.<sup>4,5</sup> Such "solid-liquid"-like properties also make SP different from self-healing polymers recently demonstrated for artificial electronic skin and battery electrode binders.<sup>7,7</sup>

Here, we propose that the "solid-liquid" hybrid behavior of this dynamically cross-linked polymer makes it an attractive interfacial layer for "smart" Li metal anodes. Lithium metal is



Figure 1. Schematic diagrams showing the design of the SP-modified Li anode. (a) Molecular structure of SP. (b) Growth of Li dendrites for unprotected Li metal anodes. (c) The covered dynamically crosslinked polymer (SP) can eliminate SEI cracking and potential catastrophic dendritic growth.

considered to be the optimal choice of anode material for lithium-ion batteries due to its high specific capacity (3,860 mAh  $g^{-1}$ ) and the lowest potential of all possible anode

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materials.<sup>9-15</sup> However, for Li metal anodes to be viable for practical batteries, two fundamental challenges need to be resolved: (1) Li is one of the most electropositive elements; thus, controlling the reactivity between Li and the electrolyte is particularly important. Fresh Li metal surfaces exposed during cycling increase side reactions between lithium and electrolyte, lowering the Columbic efficiency of Li deposition and stripping through the formation of electrochemically irreversible compounds.<sup>13-17</sup> (2) The lithium deposition/stripping process is intrinsically nonuniform.  $^{18-20}$  During cycling, the Li metal electrode can develop occasional "hot-spots" where the rate for Li stripping/deposition is faster (Figure 1b), resulting in localized regions of much higher relative volumetric change. This uneven expansion of the Li metal anode leads to straining and cracking of the intrinsically brittle<sup>21,22</sup> solid electrolyte interphase (SEI) on the Li surface. These regions of low impedance for Li deposition/stripping<sup>23</sup> further exacerbate the problem and lead to rapid growth of high surface area Li filaments and dendrites from the cracks. Moreover, the dendrites can possibly penetrate through the polymer separator to form a short circuit between the positive and negative electrodes, inducing fire and even explosions and causing serious safety issues.

In recent years, much effort has been devoted to addressing these problems. One promising strategy involves using additives in liquid electrolytes to chemically passivate the Li metal surface to improve the stability of the SEI layer and reduce electrolyte decomposition.<sup>25–32</sup> However, the resulting SEI layers are still brittle and unable to adapt their shape to lithium electrode volume changes. Therefore, cracks in the SEI can still form, and lithium dendrite growth is unavoidable. On the other hand, rigid solid electrolytes or interfacial coatings have been used for their ability to mechanically mitigate dendrite growth.<sup>33-45</sup> However, most solid electrolytes suffer from low ionic conductivity, resulting in low power output and high polarization. Moreover, because of their rigidity, the solid electrolytes or coatings cannot contact the lithium metal anode conformally on a microscopic scale during the charge/discharge process. As such, interfacial issues remain largely unresolved. Most recently, examples of creating host materials for Li metal deposition show exciting progress for Li metal anodes, although the interface between the host materials and Li metal still needs to be engineered.46-49

Here, we demonstrate improvement of the cycling lifetime and morphology of lithium metal anodes by coating a thin layer of SP onto the electrode as the interfacial layer facing the organic liquid electrolyte. On the basis of the known properties of SP, we hypothesize that it offers several advantages for improving the performance of the Li anode (Figure 1c). (1) SP flows on the time scale of each charging and discharging cycle of the lithium anode. It uniformly covers the electrode even at the microscopic scale and constantly changes its shape, adapting to the morphology and volumetric evolution of the electrode during continuous deposition and stripping of lithium metal. Thus, SP acts as a stable, conformal interface between the Li metal and the electrolyte to reduce side reactions between lithium and electrolyte. (2) If occasionally there are some "hot-spots" where the deposition and expansion of lithium is faster than at other places on the electrode, the SP coating on the protruding Li locally increases in stiffness. Here, SP acts as a clamping layer to help eliminate fast local overgrowth or expansion of Li metal and SEI breakage, effectively suppressing Li dendrite and filament growth. (3)

The properties of flowability and stiffness of SP can reversibly switch depending on the rate of lithium growth. When a local inhomogeneity in Li deposition rate occurs on the electrode, SP will respond and stiffen to constrain the localized increase in Li growth. However, once the aberrant growth rate is suppressed by SP, the coating recovers its fluidlike property and conformally adapts its shape according to the structure of the lithium metal electrode. Thus, the SP acts as a smart dynamic protection layer for the stable operation and uniform deposition/stripping of lithium metal electrodes.

#### RESULTS AND DISCUSSIONS

**Characterization of the "Solid-Liquid" Properties of SP.** The viscoelastic behavior of the SP was studied first. The loss modulus (G'') and the storage modulus (G'), which represent the viscous and elastic properties of SP, respectively, were measured by rheometer at room temperature. When the strain rate is low ( $<10^{-2} \text{ s}^{-1}$ ), G'' is significantly larger than G', indicating that the viscous property dominates the behavior of SP, and the SP behaves more like a flowable liquid (Figure 2a).



**Figure 2.** Characterization of the "solid-liquid" property of SP. (a) Rheological study of SP. (b) Rheological study of PDMS with static cross-links using siloxane cross-linking (static cross-linking) reagents. (c) Digital pictures of SP mounted over a hole punched on a Petri dish. At each time point, both front (left) and side (right) view are shown. The scale bar is 5 mm. (d) SP was stretched at different rates to show the dynamic stiffening property. (e) If the stretching rate is fast (~50 cm/s), the SP stiffens upon stretching and eventually breaks. The sharp and smooth cross-sections (marked by dotted circles) after breakage indicate the rigidity of SP at high stretching rate. (f) If stretched slowly (~1 cm/s), the SP can be stretched into very long strings.

As the strain rate increases, G' increases significantly, indicating that the SP becomes stiffer. G' even exceeds G'' by almost an order of magnitude at high strain rates (>10<sup>-2</sup> s<sup>-1</sup>), at which point SP exhibits more elastic solidlike behaviors. This interesting viscoelastic behavior of the SP is a reflection of its "solid-liquid" property, where the dynamic cross-links inside the material are crucial for determining its behavior.<sup>2</sup> In contrast to SP, PDMS with static siloxane cross-links shows no significant increase in G' and G'' as the strain rate increases (Figure 2b).

For the "solid-liquid" property to be visualized directly, a piece of SP was mounted over a hole punched into a transparent Petri dish (Figure 2c). Over time, the SP gradually flows and spreads on the Petri dish, eventually sinking into the hole just like a fluid, clearly indicating its liquidlike flowability. The dynamic stiffening property of SP is also qualitatively shown by manually stretching SP at different rates in Figures 2d–f. As shown in Figure 2e, if the stretching rate is fast (e.g.,  $\sim$ 50 cm/s), the SP stiffens upon stretching and eventually breaks with a sharp and smooth cross-section, reflecting its rigidity at high strain rates. However, if stretched slowly (e.g.,  $\sim$ 1 cm/s), SP is highly mechanically stretchable and can be slowly pulled into thin filaments (Figure 2f) with a diameter of tens of micrometers, reflecting the excellent adaptability and flowability of SP at low deformation rates.

Battery Testing. Next, we coated a thin layer of SP onto battery electrodes and tested the electrochemical performance in coin-type cells. During each test cycle, Li is deposited from the Li metal foil counter electrode onto the SP-coated Cu working electrode to an areal capacity of 1 mAh cm<sup>-2</sup> in etherbased electrolyte. After complete stripping of the Li from the Cu foil, the Coulombic efficiency (CE), defined as the ratio of the amount of Li stripped to the amount plated onto the working electrode, was calculated for each cycle. The SP-coated electrode shows good cycling performance, maintaining an average CE of 97.6% in DOL/DME electrolyte for over 120 cycles at 0.5 mA cm<sup>-2</sup>, whereas the CE of the bare Cu electrode drops below 90% after only 75 cycles (Figure 3a). At a higher current density of 1 mA cm<sup>-2</sup>, the SP-modified electrode achieves an average CE of 97.0% over 120 cycles, whereas the control electrode without SP coating maintains CEs over 90% for only 65 cycles. Even for a high Li deposition capacity of 2.5 mAh cm<sup>-2</sup>, the SP-coated electrode maintains an average CE of 97.5% over 40 cycles, whereas the CE for the control electrode drops below 97.0% after 24 cycles (Figure S1a). Similarly, SPcoated electrodes can stably cycle at a high current density of 3 mA cm<sup>-2</sup> with CE above 90% for over 70 cycles, whereas control electrodes exhibit poor cycling stability and CE decays rapidly after 30 cycles (Figure S1b).

The improvement in electrode cycling performance is attributed to the SP-mediated lithium-electrolyte interface, as indicated by the stable Li deposition/stripping polarization in the voltage profile. The Li deposition voltage plateau on the bare Cu electrode is seen to increase by nearly 50% from 20 to 29 mV from cycle 10 to 80 (Figure 3b). The continuous mechanical breaking, reformation, and accumulation of electrochemically irreversible SEI resulting from uneven Li deposition leads to increased electrode resistance.<sup>26</sup> However, upon modification with SP, the Li deposition overpotential decreases from 25 to 22 mV (Figure 3c). This reduced polarization is an indication of the stable SEI resulting from the SP protective layer coated on the Li electrode. Moreover, the voltage hysteresis of Li deposition/stripping continuously increases for bare Cu as the electrodes are cycled (Figure 3d), indicating the unstable SEI interface between the electrode and electrolyte. However, with the SP coating layer, the hysteresis decreases and remains stable after initial cycles, which may be due to improved SEI stability and the higher lithium ion conductivity of the SP after it is swelled and cycled (see Note S1 in the Supporting Information).



**Figure 3.** Electrochemical properties of the electrodes for Li cycling. (a) Comparison of the Coulombic efficiency (CE) of Li deposition/ stripping (1 mAh cm<sup>-2</sup>) on SP-modified electrodes (solid symbols) and control Cu electrodes (empty symbols) at current rates of 0.5 and 1.0 mA cm<sup>-2</sup>. (b, c) Voltage profiles of a (b) control Cu electrode and (c) SP-modified electrode at the 10th (black) and 80th (red) cycles. (d) Comparison of the hysteresis of Li deposition/stripping for the bare copper electrode (black) and SP-modified electrode (red).

**Mechanism Studies.** The improved cycling stability of the lithium metal electrode can be attributed to the dynamic "solid-liquid" features associated with the SP coating:

1. SP can flow freely at the time scales of normal charge and discharge, so it uniformly covers the lithium metal electrode and constantly changes its shape according to interface and volume changes of the electrode. If the lithium is deposited/ stripped uniformly, the average strain rate exerted on SP by the growing lithium metal electrode was estimated to be on the order of  $10^{-3}$  s<sup>-1</sup> (for details, see Note S2 in the Supporting Information), at which G'' exceeds G' by nearly one order of magnitude (see Figure 2a). Thus, in this viscous regime, SP is able to act as a conformal stable interface facing the electrolyte to reduce the side reactions between lithium and electrolyte. For the high coverage of Li metal by SP to be shown, the morphology of the as-deposited Li metal on an SP-coated electrode was observed by ex-situ SEM. After lithium metal deposition, the SP is able to completely and conformably coat the deposited Li metal, as seen from cross-sectional SEM (Figure 4a). Even the sides of the Li metal newly exposed from breaking the electrode for SEM imaging and deep ridges and fissures (inset, Figure 4a and Figure S3) are well coated with SP, demonstrating the ability of the polymer to flow. After stripping of lithium, SP still shows good coverage of the electrodes including any small inhomogeneities present (see Figure S4a). SP can also gradually flow into any deep cracks formed in the SEI and seal it, removing hotspots for Li dendrite growth, as indicated by the in situ optical microscope



Figure 4. Mechanism for improved cycling of the SP-modified electrode. (a) Cross-sectional SEM of SP-coated Li metal deposited onto a Cu-coated glass slide electrode. (inset) Cross-sectional SEM showing the conformal coating of SP even on big fissures. The white arrow points to a naturally occurring defect in the deposited Li metal. The SP fully coats the surface, even penetrating into the fissure itself. (b) Top-view SEM images of Li metal (1 mA cm<sup>-2</sup>) deposited on a control Cu electrode after 75 cycles of Li deposition and stripping. (c) Magnified image of the Li metal on bare Cu, clearly showing Li metal filaments growing from cracks between granular Li metal deposits (some indicated by white arrows). (d) Top-view SEM image (2 keV) of Li deposited on an SP-modified electrode. (inset) Higher accelerating voltage (5 keV) SEM image of the highlighted area showing the morphology of Li underneath the SP coating. (e) Uniform and tightly packed Li deposits are visible after the SP coating was removed during sample preparation by rinsing with fresh 1,3dioxolane (DOL). (f) Series of optical microscope images depicting the Li metal deposition process on bare Cu. Scale bar: 20  $\mu$ m. (bottom) Schematic of Li deposited on bare Cu. (g) Series of optical microscope images depicting the Li metal deposition process on SPcoated Cu. Scale bar: 20  $\mu$ m. (bottom) Schematic of Li deposited on SP-coated Cu. The red color in the SP coating represents the local dynamic stiffening.

observation (Figure S4b and c). Moreover, the SP protective layer did not change its properties upon coating onto the lithium metal anode, as indicated by the unchanged Fourier transform infrared (FTIR) spectra (Figure S5). Thus, the flowability of SP allows it to uniformly cover and protect the surface of lithium metal no matter how its volume and morphology changes.

2. The dynamic stiffening SP acts as a clamping layer; the constraining force of the rigid layer dissuades crack formation and suppresses dendrite growth.<sup>23,33–39</sup> For this mechanism to be investigated, electrodes were studied by SEM after 75 deposition/stripping cycles. Li metal deposited onto a bare Cu electrode results in uneven granular Li with obvious cracks and voids (Figure 4b). Li filaments and extrusions can be clearly

observed growing out of these cracks and spaces, indicating cracking or breaking of the Li metal SEI (Figure 4c). Moreover, these large spaces between deposits increase the electrode surface area and may aggravate detrimental electrolyte decomposition. With the addition of the protective SP coating, the electrode surface and underlying Li metal maintains a smooth and conformal morphology with no protruding growths (Figure 4d and inset). For the morphology of the asdeposited Li to be seen clearly, the SP coatings were removed by thoroughly rinsing with DOL, exposing the bare Li metal for SEM observation. In contrast to the rough, high-surface area structures seen on bare Cu electrodes, Li metal grown on SPmodified electrodes exhibits clearly improved morphology and appears as a smooth and flat surface with closely packed individual grains of Li metal without any significant cracks or dendrites (Figure 4e). The protective benefits of the uniform and flowable coating of dynamic stiffening SP are apparent over large areas of the electrode (Figure S6). Additional SEI and impedance studies (Figure S7) highlight the ability of the SP coating to stabilize the Li SEI over extended cycling. Thus, the dynamic "solid-liquid" behavior of SP greatly improves Li morphology and improves cycle stability by enabling SP to act as a conformal interfacial layer and suppress the heterogeneities in Li deposition and the overgrowth of lithium dendrites.

To confirm the proposed mechanism of SP, we observed the initial stages of Li deposition in homemade optical cells in realtime (details in Figure S8). Using LiFePO<sub>4</sub> as a lithium source, Li was first electrodeposited onto a Cu working electrode, and the temporospatial evolution of the Li metal growths was observed by optical microscope (Figure 4f and Video S1). It can be clearly seen that Li grown on bare Cu nucleates as discrete particles spaced apart from each other. As more Li is deposited, the existing particles act as "hotspots" and begin growing larger and can develop into individual filaments or dendrites if nonuniform Li<sup>+</sup> flux develops. On the other hand, note that Li deposited on SP-coated Cu immediately begins expanding outward and avoids the formation of many individual Li nonuniformities (Figure 4g and Video S1). The SP coating acts as a dynamic constraining layer, reacting to and suppressing any central Li overgrowth while promoting additional Li deposition on the sides of the initial Li protrusion. As such, any locally enhanced Li<sup>+</sup> flux is remediated and effectively redirected to form more uniform flat Li domains while avoiding filamentary Li growth.

To emphasize the unique role of the "solid-liquid" dynamic property of the SP coating in improving cycling stability and Li deposition uniformity, we tested two other control polymer coatings: (1) Electrodes coated with siloxane cross-linked PDMS, which exhibits solidlike properties without liquidlike flowability due to static cross-linking (rheological study shown in Figure 2b), had significantly poorer cycle stability than that of SP (Figure 5a), and many Li filaments were observed on the Li electrode after 75 cycles of deposition/stripping (Figure S9). (2) Electrodes coated with uncross-linked PDMS-free polymer chains, which have liquidlike flowability without the dynamic stiffening property, similarly showed lower CE and lower cycle life compared to that of the SP-coated electrodes (Figure 5a and inset). These control experiments clearly indicate that the "solid-liquid" property of SP, which arises from the internal dynamic cross-linking, is crucial for improving the cycling stability of SP-coated lithium metal anodes.

We further simulated in COMSOL the deposition of Li on electrodes coated with various classes of polymers: (1) rigid,



Figure 5. Optical microscopy and simulations of Li metal deposition on various electrodes. (a) Side-by-side comparison of the Coulombic efficiency of Li deposition/stripping using Cu electrodes modified with different cross-linked polymers: statically cross-linked PDMS (blue), uncross-linked linear PDMS (black), and dynamically cross-linked PDMS, i.e., SP (red). (inset) Higher magnification plot for more detail. The batteries were cycled at 1 mA cm<sup>-2</sup> to an areal capacity of 1 mAh cm<sup>-2</sup>. (b–d) Simulations of Li metal deposition with (b) rigid, nondynamic, (c) flowable, nondynamic, and (d) flowable, dynamic stiffening polymer coatings. The color in each simulation snapshot indicates the magnitude of spatial Li<sup>+</sup> flux, and the streamlines show the direction of the Li<sup>+</sup> flux. Scale bar: 400 nm.

nondynamic; (2) flowable, nondynamic stiffening; and (3) flowable, dynamic stiffening (details in Note S3 and Figure S10 in the Supporting Information) to represent (1) static crosslinked PDMS (solidlike), (2) uncross-linked PDMS (liquidlike), and (3) flowable, dynamic stiffening SP (solid-liquid hybrid property). For the rigid nondynamic polymer, we generated a pinhole 0.5  $\mu$ m in diameter, representing its inability to flow and repair cracks. Upon Li deposition, a large pillarlike Li whisker grew out of the pinhole (Figure 5b and Video S2). For the flowable but nondynamic stiffening polymer coating, a smaller but still significant Li filament appeared upon deposition (Figure 5c). However, with a flowable and dynamic stiffening polymer, such as SP, a small Li protrusion appeared at the induced defect, but it was immediately remediated when the polymer coating stiffened and Li deposition proceeded uniformly over the entire electrode surface (Figure 5d). Note that the SP-coated electrode has very uniform Li<sup>+</sup> flux without any hotspots, whereas for the control cases, the regions of enhanced Li<sup>+</sup> flux (hotspots) at the tips of the Li filaments are very obvious. By comparing the growth rates of the Li at the defect and in the bulk regions (Figures S10e-g), it is apparent that the dynamic "solid-liquid" behavior of the SP coating rapidly suppressed the aberrant growth, preventing the deposition of an amplified Li filament.

Furthermore, we did a full cell test of SP-coated Li metal anode paired with a typical cathode, LiFePO<sub>4</sub> (LFP). The cell maintained a high average CE of 99.5% and a stable capacity of 142.1 mAh/g for over 50 cycles (Figure S11), indicating that the strategy of SP coating is promising for practical battery system applications.

#### CONCLUSIONS

In conclusion, a kind of dynamically cross-linked polymer (Silly Putty) has been successfully employed as a "smart" interfacial coating between Li metal anodes and electrolyte. The adaptive "solid-liquid" property arising from the dynamic covalent bonds makes the SP an excellent interfacial layer for dendrite-free uniform Li metal deposition and significantly improves cycling stability for Li metal electrodes. The dynamic stiffening of SP introduces a new concept of "smart" Li anode for solving the notorious problem of nonuniform deposition of Li metal. The coating of SP onto the electrode is quite facile and straightforward and can be easily scaled up. In addition, no complex equipment or synthesis processes are involved to be entirely compatible with the conventional process for manufacturing lithium batteries. For the performance to be improved further, additional polymer chemistry design is needed in terms of molecular chain length, chemical structure, dynamic cross-linking density, and so forth to tune the storage and loss modulus of the polymer coatings. Moreover, increasing the Li ion conductivity of the polymer coating by incorporating a proper polymer molecular structure, e.g., poly(ethylene oxide) chains copolymerized with PDMS, is highly promising for future work. In addition, although we have not tested the performance of SP-coated electrodes with "next-generation" Li-air or Li-sulfur batteries, we believe that the SP coating on the anode could protect the Li metal from problems with crossover molecules (O and S species) present in the Li-air or Li-S systems, such as polysulfide shuttling. It is anticipated that the concept of a dynamic stiffening polymer like Silly Putty can also be used as a smart clamping layer for other electrode materials with heterogeneous deposition issues, such as Zn and Cu.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b13314.

Experimental section, calculations of diffusion coefficient and strain rate, SEM images, FTIR spectra, impedance spectroscopy, Li deposition cell details, simulation details, and Coulombic efficiency plots (PDF)

Optical microscope videos of optical cell of the bare Cu and SP-coated anode (AVI)

Compiled simulation results of the Li metal deposition with rigid and nondynamic, flowable and nondynamic, and flowable and dynamic stiffening polymer coatings (AVI)

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#### Notes

The authors declare no competing financial interest.

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