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Nanoscale Protection Layers To Mitigate Degradation in High-Energy Electrochemical Energy Storage Systems

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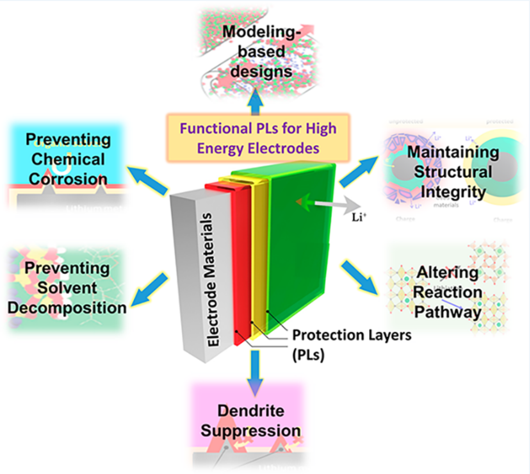

CONSPECTUS: In the pursuit of energy storage devices with higher energy and power, new ion storage materials and high-voltage battery chemistries are of paramount importance. However, they invite—and often enhance—degradation mechanisms, which are reflected in capacity loss with charge/discharge cycling and sometimes in safety problems. Degradation mechanisms are often driven by fundamentals such as chemical and electrochemical reactions at electrode−electrolyte interfaces, volume expansion and stress associated with ion insertion and extraction, and profound inhomogeneity of electrochemical behavior. While it is important to identify and understand these mechanisms at some reasonable level, it is even more critical to design strategies to mitigate these degradation pathways and to develop means to implement and validate the strategies.

A growing set of research highlights the mitigation benefits achievable by forming thin protection layers (PLs) intentionally created as artificial interphase regions at the electrode−electrolyte interface. These advances illustrate a promising—perhaps even generic—pathway for enabling higher-energy and higher-voltage battery configurations. In this Account, we summarize examples of such PLs that serve as mitigation strategies to avoid degradation in lithium metal anodes, conversion-type electrode materials, and alloy-type electrodes. Examples are chosen from a larger body of electrochemical degradation research carried out in Nanostructures for Electrical Energy Storage (NEES), our DOE Energy Frontier Research Center. Overall, we argue on the basis of experimental and theoretical evidence that PLs effectively stabilize the electrochemical interfaces to prevent parasitic chemical and electrochemical reactions and mitigate the structural, mechanical, and compositional degradation of the electrode materials at the electrode−electrolyte interfaces. The evidenced improvement in performance metrics is accomplished by (1) establishing a homogeneous interface for ion insertion and extraction, (2) providing mechanical constraints to maintain structural integrity and robust electronic and ionic conduction pathways, and (3) introducing spatial confinements on the electrode material matrix to alter the phase transformation (delaying the occurrence of the conversion reaction) upon Li insertion, which results in superior electrode performance, excellent capacity retention, and improved reversibility.

Taken together, these examples portray a valuable role for thin protection layers synthesized over electrode surfaces, both for their benefit to cycle stability and for revealing insights into degradation and mitigation mechanisms. Furthermore, they underscore the impact of complex electrochemical behavior at nanoscale materials and nanostructure interfaces in modulating the behavior of energy storage devices at the mesoscale and macroscale.

■ DEGRADATION MECHANISMS

Interfaces play a critical role in the behavior of electrochemical systems such as Li-ion batteries or "beyond Li-ion" versions proposed to enhance performance. In a simple electrical energy storage device—cathode, liquid organic electrolyte, and anode—the electrode−electrolyte interface is a center of attention, first because of the complex chemical and electrochemical reactions that occur there and second because the insertion/extraction of ions in the electrode creates mechanical changes that alter the reaction conditions. More specifically, these phenomena strongly affect (1) the efficiency of electron

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and ion transport,[1,2] (2) the stability of organic electrolytes,[3,4] and (3) the stability of the electrodes.[5,6]

Solid–Electrolyte Interphase Formation

In many cases electrode/electrolyte reactivity does not merely change the interface properties but rather forms an *interphase*, i.e., an extended region of material different from both the electrode and electrolyte. The *solid–electrolyte interphase* (SEI) is such a region, created by electrochemical reactions that decompose the electrolyte and leave a complex material on the electrode. The SEI was first discovered by Emanuel Peled and Doron Aurbach, is now recognized as a critical component, particularly in lithium-ion batteries (LIBs), and has been the subject of intense investigation.[7,8] The SEI is formed naturally by decomposition of the electrolyte, starting with the first lithiation/delithiation cycle, or even as soon as Li metal is exposed to electrolyte, and continuing through some subsequent cycles. On one hand, the SEI serves an important purpose in providing a protective interphase. On the other hand, it is heterogeneous and chemically complex, and while its growth ultimately slows, it is not reliably self-limiting. Furthermore, it is subject to cracking initiated by mechanical alterations of the underlying electrode during lithiation/delithiation, which exposes new regions of the electrode for regrowth of the SEI. This SEI growth consumes electrolyte, including solvent, anion, and more importantly Li ion, causing energy inefficiencies. Thus, the formation of a “natural SEI” layer offers both benefits and disadvantages.[9]

SEI formation affects both the anode and cathode. For example, the graphite anode and carbonate electrolytes (propylene carbonate (PC), ethylene carbonate (EC), etc.) react to form a non-self-limiting SEI through continuous decomposition of electrolyte at the Li-ion intercalation potential (<0.5 V vs Li/Li^+), leading to rapid consumption of the liquid electrolyte, a subsequent decrease in ion transport through the thick SEI,[7,9] and cell degradation. High-energy Li metal anodes (or analogous reactive metals, e.g., Na, Mg) experience more severe degradation in that Li is thermodynamically unstable with virtually all carbonate electrolytes, resulting in unlimited SEI formation at the Li–electrolyte interface.

Structural Reconfiguration

Other chemistries for high-energy density batteries incur significant degradation resulting from profound structural reorganization. In particular, conversion materials, including a significant representation of oxides, fluorides, and sulfides, react with Li to form Li compounds and metal particles (e.g., $4Li + RuO_2 \rightarrow 2Li_2O + Ru$). Such dramatic structural changes can readily impede reversibility of the reaction, as required for a secondary (rechargeable) battery, for example by electrical isolation of the metal particles within an insulating matrix of Li compounds, preventing them from participating in redox reactions, or by volume changes that generate fractures and disconnected particles.[10] Electrode materials that alloy upon lithiation (e.g., Si, Sn) can suffer large volume changes upon lithiation/delithiation, inviting stress as well as fracture. These volume changes and fracture—intrinsically accompanying nonuniform ion concentration during insertion/deinsertion in electrode materials—present a fundamental challenge in managing degradation across a wide range of battery chemistries.[11]

Dendrite Growth

Charge/discharge cycling of the battery involves moving Li ions back and forth between the cathode and anode, which risks the buildup of Li metal protrusions—dendrites—that occur as a result of the repeated nonuniform plating and stripping of Li. Once a dendrite has been initiated, electric field concentration at that point may cause runaway growth of the dendrite, followed by thermal runaway when the dendrite shorts the electrodes together. This is a serious safety problem: the resulting high current flow through a short-circuiting dendrite causes local heating that can ignite organic electrolytes, producing fire or explosion. The risk is greatest when recharging Li-ion batteries, as the plating of Li onto the anode can become highly localized from structural inhomogeneities that develop. Prior efforts to avoid the dendrite problem have included the addition of additives to electrolytes to alter the SEI properties,[12] applying selected overlayers as protection layers (PLs) on metal anode surfaces,[13,14] and using novel three-dimensional (3D) electrode architectures so that local current densities can be reduced.[15]

Chemical Species

Especially with highly reactive electrodes such as Li metal, mobile chemical species in the liquid electrolyte can attack the electrode, suppressing its redox activity and thus degrading the battery.[16] This can be a consequence of interaction between the cathode and anode chemistries. A well-known example is the dissolution of Mn ions from $Li_xMn_2O_4$ cathodes, making Mn ions available in electrolyte solution for interaction with reactive anodes.[17] Another is the formation of soluble polysulfides from sulfur cathodes, which travel to the Li anode in Li–S batteries and degrade the capacity. Besides these sources of unwanted chemical species intrinsic to the battery chemistry, extrinsic sources may play a role as well, the most notable being low levels of H_2O impurities in organic liquid electrolytes.

PROTECTION LAYER SYNTHESIS TO MITIGATE DEGRADATION

Degradation mechanisms are not just common but indeed are intrinsic to the electrochemistry of the battery materials across a wide variety of battery chemistries, posing a fundamental challenge: mitigation of the degradation in a generic way. Inspiration comes from the above recognition that the natural SEI layer that forms by electrode/electrolyte electrochemistry ultimately does mitigate degradation once it is formed on the electrode surface. However, natural SEI layers present multiple limitations: they are complex materials that are difficult to understand; they differ with battery chemistry and electrochemical operating range; they are not self-limiting and thus are ill-defined in thickness, with increasing SEI thickness typically increasing the impedance; and they are subject to fracture, rendering their growth even more uncontrolled.

Around a decade after the commercialization of Li-ion batteries, researchers began exploring whether intentional addition of material layers on particulate (composite) electrodes might serve to enhance capacity retention during charge/discharge cycling.[18] Beginning in 2010, atomic layer deposition (ALD) was employed to provide controllable nanoscale coatings of simple insulators (e.g., Al_2O_3) on typical electrode materials for Li-ion batteries to serve as thin effective PLs to accomplish this goal.[19] This gave credence to the notion of employing thin-film synthesis, e.g., ALD, to produce thin

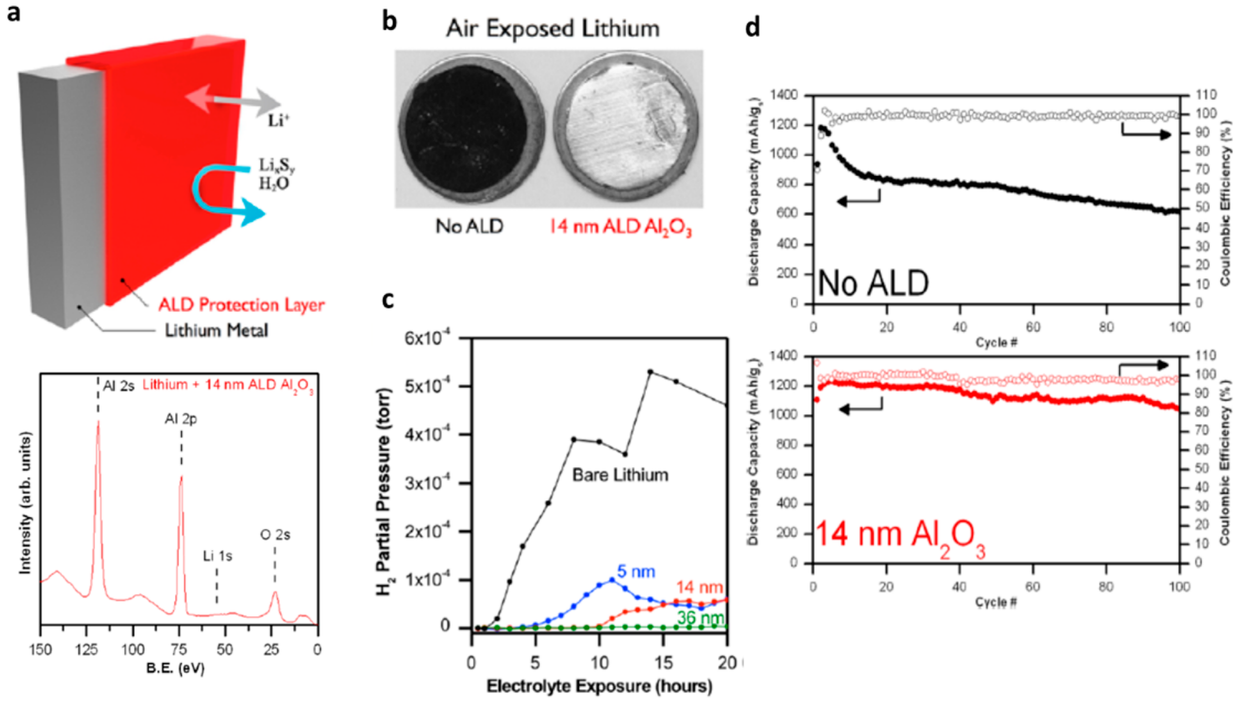

Figure 1. (a) Top: schematic of nanoscale thin ALD coatings. Bottom: in situ XPS of a 14 nm, pinhole-free Al_2O_3 coating on Li. (b−d) Corrosion tests under (b) ambient conditions, (c) organic solvent immersion, and (d) long-term cycling on protected Li metal and a control in full Li−S cells. Adapted from ref 21. Copyright 2015 American Chemical Society.

layers with suitable properties on an electrode as a kind of "artificial SEI", i.e., an *intentionally added electrode protection layer*. By separating the electrode and electrolyte by the additional PL, chemical and electrochemical interactions between them are suppressed, thus also diminishing the formation of the natural SEI. Generically speaking, an intentional PL should have relatively high ionic conductivity and low electronic conductivity, so that the PL can transport ions between the electrolyte and electrode, but not electrons. In addition, it is favorable to select or design the PL for the battery chemistry involved, from repelling unwanted chemical species from the electrode to managing the cycling-induced volume change and stress in that electrode. Together these properties present a significant challenge of interfacial engineering.

■ PROTECTION LAYERS IN NEES RESEARCH

Nanostructures for Electrical Energy Storage (NEES), a DOE Energy Frontier Research Center, has been pursuing the synthesis, properties, and functionality of such protection layers for several years, results from which comprise the primary focus of this Account. Many of these investigations have concentrated on model systems using thin-film synthesis methods to create planar or nanostructured electrode features, rather than particle composite electrodes, in order to elicit greater insight using a more powerful set of characterization techniques compatible with simpler model systems. This Account focuses on the use of ALD, as it provides highly conformal, vapor-deposited thin-film coatings that ensure uniformity over the model electrode systems, even those with high aspect ratio. Moreover, the large tunable parameter space (e.g., temperature, partial pressure, dose time, precursor choice, etc.) in ALD allows for sophisticated reaction chemistry that facilitates the development of functional materials in a highly precise and controlled manner.

This Account covers PL results for three high-capacity classes of electrodes. For (1) *metal anodes*, a well-designed PL effectively blocks reactions with the organic electrolyte and with H_2O impurities to extend cycle life. For (2) *conversion-type electrodes*, a thin solid-state electrolyte serves as a PL to drastically improve the structural integrity of the electrodes, so that the electrochemistry is largely reversible, not just for model electrode systems but for particle composite electrodes as well. Furthermore, a thin solid electrolyte protection layer delays the onset of the conversion reaction, so that a more favorable intercalation pathway can be followed to a higher lithiation state. Finally, for (3) *alloy-type electrodes*, a designed PL on a Si electrode mitigates degradation from mechanical stress associated with large volume expansion.

■ PROTECTION LAYERS TO STABILIZE REACTIVE LI METAL ANODES

Lithium metal has long been considered the "holy grail" of anode materials for next-generation energy storage devices (Li ion, Li−S, Li−O_2, etc.) because of its high specific capacity and high energy density.[20] However, its integration into commercially available secondary cells has been limited by several consequences of its high reactivity. Lithium's high reactivity and low equilibrium potential cause decomposition of most organic electrolytes used in batteries, resulting in SEI formation and corrosion of Li metal.[20] In addition, Li dendrite growth upon cycling can lead to electrical shorting between the electrodes, leading to fire and/or explosion.

A major challenge in producing a PL on reactive Li metal is to control the Li surface chemistry, recognizing that exposure to air or other reactive impurities will modify the Li surface. To address this, we utilized the unique configuration of our ALD

Nanostructures Laboratory (ANSLab), which enables "clean" Li foils to be transferred from a glovebox to ultrahigh vacuum (UHV) and then directly into the ALD reactor for PL deposition.

Li Anode Protection by Al_2O_3: Corrosion Prevention

The first experiments used Al_2O_3 for the PL as a well-known and well behaved ALD process that can be carried out at temperatures below the Li melting point (180.5 °C). The ALD process conditions were trimethylaluminum (TMA) and O_2 plasma at 150 °C, which realized a 14 nm Al_2O_3 coating on the Li surface.[21]

After deposition, samples can be transferred through UHV to a Kratos surface analysis system without exposure to contaminants. XPS results for this surface are shown in Figure 1a, revealing the Al and O species from the PL as well as Li presumably underneath the Al_2O_3. Corrosion of the Li metal is expected upon exposure to air, leading to a black tarnish. Such tarnish is evident in Figure 1b ("No ALD") but absent for the 14 nm ALD Al_2O_3 PL after 20 h of air exposure.[24] Since one expects tarnishing to decorate defects/pinholes in the PL, the result suggests that the PL is pinhole-free.

Corrosion inhibition by the PL was also tested by immersing electrodes in propylene carbonate electrolyte and measuring the H_2 evolution that results from electrolyte decomposition. These measurements, carried out by mass spectrometry on the headspace of a sealed cell containing the sample, show significant H_2 without the PL, compared with much-reduced H_2 (after a 10 h delay) for 5, 14, and 36 nm Al_2O_3 PLs (Figure 1c). Corrosion of Li by a 1 M sulfur/dimethoxyethane electrolyte (commonly used in Li−S batteries) forms soluble polysulfides, but this was also retarded by the Al_2O_3 PL.[21]

The Al_2O_3 PL provides a substantial benefit to the Li anode when employed in a Li−S battery cell, as shown in Figure 1d. Sulfur cathodes were fabricated as composites of activated carbon cloth and sulfur and then combined with bare or protected Li anodes in coin cells for testing capacity degradation with cycling. The presence of the 14 nm Al_2O_3 PL caused a profound improvement in capacity retention to ∼90% over 100 cycles—which is attributed to the PL shielding the Li anode from access by polysulfides originating in the cathode.

Constrained density functional theory calculations by Leung et al.[22] provide insight into the role of the PL. For ethylene carbonate electrolyte, the results predict that the PL (Figure 2c,d shows results for $LiAlO_2$ and Al_2O_3 PLs, respectively) causes a significant decrease in the kinetics of the electron transfer and thus electrolyte decomposition, so that natural SEI formation is suppressed. This implies that the PL serves as an "artificial SEI" layer as expected.

Li Anode Protection by Hybrid LiPON: Dendrite Suppression

While the above example of a thin Al_2O_3 PL demonstrates the benefit of an intentionally added electrode protection layer, it does not directly address other properties and functionality that would better serve the purpose. An ideal PL would be ion-conducting, essentially functioning as a solid electrolyte as synthesized. While Al_2O_3 will gradually incorporate Li upon sufficient lithiation cycling, in the form of Li aluminate ($LiAlO_2$), its ionic conductivity is low (∼10^{-10} S/cm).[31] In contrast, the preponderance of solid-state batteries—where a solid electrolyte is required—employ LiPON, a nitrogen-doped Li phosphate material with ionic conductivity in the range of ∼10^{-6} S/cm. LiPON is often synthesized by thin-film deposition, specifically sputtering, but nanoscale thickness control and conformal coverage over topography are limited. Therefore, we developed a low-temperature (150 °C) ALD process for LiPON,[23] i.e., below the Li melting point (180.5 °C), enabling its deposition onto Li metal foils or films.

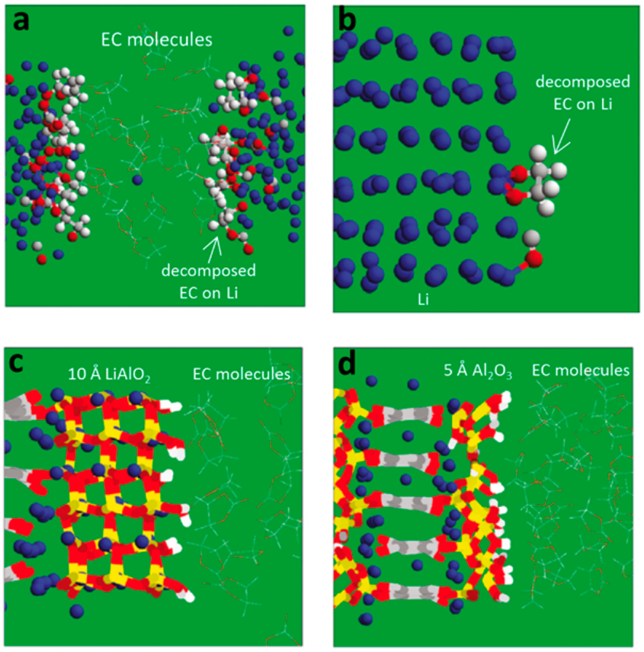

Figure 2. (a, b) EC molecules decomposed on the Li surface. (c, d) No decomposition of EC on (c) a 10 Å $LiAlO_2$ coating or (d) a 5 Å Al_2O_3 coating because of the slow kinetics of electron transfer. Adapted from ref 22. Copyright 2011 American Chemical Society.

Another PL concern is the structural integrity of the interface between the PL and the underlying electrode. In the case of Li metal anode protection, and particularly at high power, the Li metal may not readily accommodate the high Li insertion or deinsertion flux, leading to volume changes and mechanical stresses in the Li and/or at the interface. It seems advisible to incorporate a mechanical flexibility function into the PL design strategy. We pursued this by incorporating an elastomer component into the PL to add mechanical flexibility.[24] An elastomer layer was first synthesized by electrochemically pretreating the Li surface in 1,3-dioxolane (DOL) at a low current density (30 $\mu A/cm^2$) to polymerize the DOL molecules, forming an ∼800 nm layer to accommodate Li plating and stripping. Then a thin (∼20 nm) ALD LiPON layer was deposited over the elastomer at 150 °C. The resulting hybrid PL was then evaluated for its resistance to electrochemical degradation (measured as capacity retention upon cycling) at high current densities normally sufficient to initiate dendrite formation.

In-operando optical imaging was performed to investigate the effects of the elastomer-only protection layer, i.e., without LiPON component, as shown in Figure 3a. The current density applied to the Li metal was 2 mA/cm^2, which is beyond the reported 1 mA/cm^2 threshold for dendrite formation.[25] The edges of the Li metal without elastomer (Figure 3a, top row) display dendrite growth in a short period of time, but the elastomer-protected Li metal (Figure 3a, bottom row) exhibits stable Li−electrolyte interfaces without evidence of dendrite growth. However, the elastomer-only PL alone is inadequate,

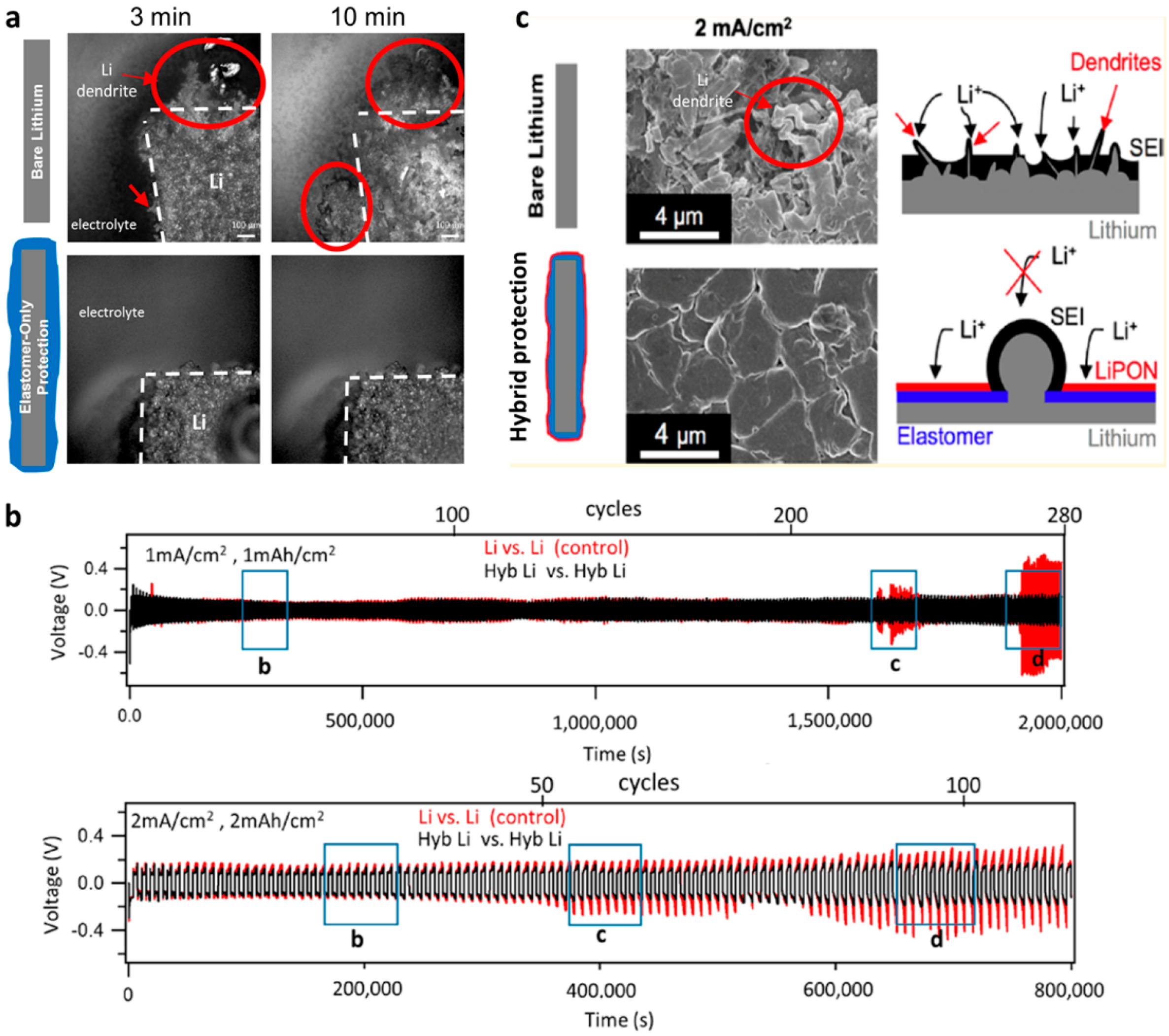

Figure 3. (a) In-operando imaging of bare Li vs elastomer-only protected Li at 2 mA/cm^2. (b) Long-term cycling on symmetric cells at 1 and 2 mA/cm^2 without and with the hybrid PL. (c) Post-mortem morphology characterization after 100 cycles and the proposed mechanisms. Adapted from ref 24. Copyright 2017 American Chemical Society.

in that it degraded in common carbonate-based electrolyte over time.[24]

The hybrid elastomer/LiPON PL displayed cycling stability as well as dendrite suppression. As shown in Figure 3b, cycling of symmetric Li−Li cells remains stable for over 280 cycles when hybrid elastomer/LiPON PLs are present, but instabilities (overpotentials) occur on bare Li electrode surfaces without the hybrid PL. The stability of hybrid-protected Li electrodes at 1−2 mA/cm^2 suggested dendrite resistance as well. This is confirmed in Figure 3c, where SEM images show dendrite formation after 100 cycles at 2 mA/cm^2 on bare Li but not on hybrid-PL-covered Li.

A possible explanation for this behavior is suggested by the schematic in Figure 3c. Reaction of the organic electrolyte with the bare Li anode forms a natural SEI but does not prevent dendrite formation. When the hybrid PL (elastomer + LiPON) is present over the Li surface, it enables Li transport between the Li metal electrode and the electrolyte. If cracks or pinholes are present in the hybrid PL, as is likely, the exposed Li contacting the electrolyte will form an SEI layer that suppresses Li plating/stripping at that location. Nevertheless, plating/stripping current is sustained through the Li-permeable hybrid PL. Thus, Li plating/stripping current will not be concentrated at the crack/pinhole location, and indeed, the current density there will decrease as the natural SEI grows there.

PROTECTION LAYERS TO PROMOTE REVERSIBILITY OF CONVERSION-TYPE ELECTRODES

Maintaining Structural Integrity

Given the chemical and structural complexity of lithiation/delithiation reactions in conversion materials, we investigated the potential for PLs to stabilize lithiation products. The results demonstrated that the reversibility of the reaction could indeed be enhanced. As a 3D model system, multiwalled carbon nanotubes (MWCNTs) in a sponge-like architecture were employed as an integrated current collector for an active RuO_2 electrode material as a core−shell MWCNT@RuO_2 structure.[26] Upon lithiation, RuO_2 undergoes the conversion reaction $RuO_2 + 4Li \rightarrow Ru + 2Li_2O$, with four Li stored per formula unit of RuO_2.

The transmission electron microscopy (TEM) images shown in Figure 4a reveal structural deterioration and thick SEI formation (~30 nm) for the MWCNT@RuO_2 electrodes, which is typical behavior for conversion-type electrodes.

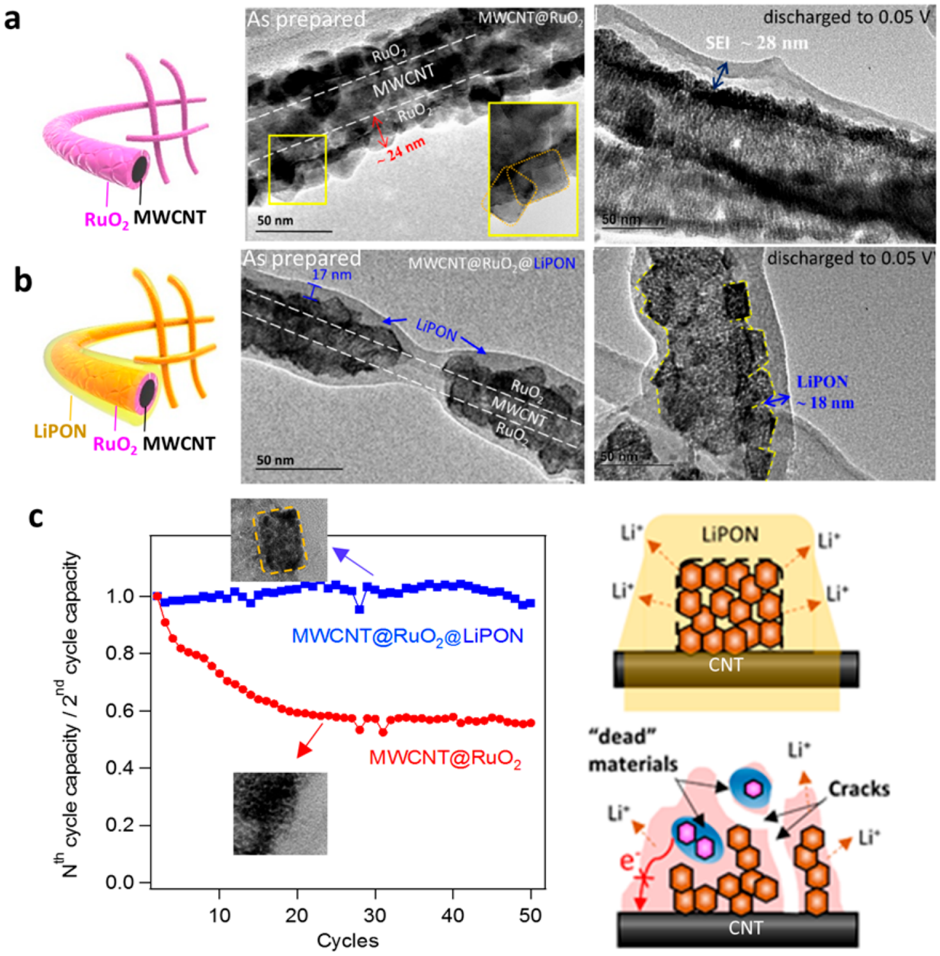

Figure 4. TEM images of (a) unprotected MWCNT@RuO$_2$ and (b) LiPON-protected MWCNT@RuO$_2$@LiPON before (left) and after (right) lithiation. (c) Cycling performance on LiPON-protected (blue) vs unprotected (red) electrodes and schematics of possible mechanisms. Adapted from ref 26. Copyright 2016 American Chemical Society.

However, for LiPON-coated MWCNT@RuO$_2$, no SEI is observed. Instead, the LiPON remains intact as a nanocladding layer to maintain the original tetragonal crystal shape of RuO$_2$, as is evident in Figure 4b. Capacity retention with cycling is depicted in Figure 4c. Clearly, the addition of a LiPON PL to create a protected MWCNT@RuO$_2$@LiPON structure significantly improves the capacity retention, providing near-ideal cycling stability after the first cycle, while without the LiPON PL, half the capacity is lost within ~20 cycles.[26]

This is a quite striking result, given that the chemical and structural changes accompanying the conversion reaction are very substantial. The schematics in Figure 4c present a possible explanation. For the unprotected case (Figure 4c, lower-right), lithiation forms Ru metal particles immersed in a Li$_2$O matrix, with some of the Ru particles electrically disconnected from the CNT current-collecting material and hence electrochemically "dead". For the LiPON-protected case (Figure 4c, upper-right), the LiPON confines the materials to largely prevent disconnection of the Ru particles.

These phenomena are expected to be rather general, in that the materials chemistry of lithiation of many oxides, sulfides, and fluorides involves a conversion reaction, leading to SEI formation by parasitic decomposition of electrolyte in contact with the electrode, accompanied by reaction to form (typically insulating) Li compounds surrounding metal particles, some of which may be electrically disconnected. Spatial confinement of the reaction products by the LiPON PL, as suggested above, seems plausible but is by no means proven. Further theoretical and experimental research is underway to seek fundamental explanations for this behavior.

Delaying Irreversible Conversion Reactions

To assess the broader applicability of the LiPON PL, conversion materials were used to fabricate composite electrodes typical for commercial batteries. Nanoparticles of FeOF were mixed with carbon black and poly(vinylidene difluoride) (PVDF) binder to form composite electrodes on Al foils. For the LiPON PL process, the vapor-phase ALD precursors diffuse ~40% into the thickness of the tortuous composite, as shown in Figure 5a,b. Lithiation/delithiation cycling of bare (no ALD LiPON) FeOF and 30 nm LiPON-coated electrodes were tested in a half-cell configuration, and the results are shown in Figure 5c. The LiPON PL produces an excellent Coulombic efficiency (C.E.) of >99.5%, retaining ~90% capacity after 100 cycles at a cycling rate of 1C. In contrast, the bare FeOF electrode shows only ~30% capacity retention after 100 cycles.[27]

As in the case of RuO$_2$ above, the significantly enhanced capacity retention upon cycling suggests that the LiPON PL enhances the structural stability of the electrode. Other evidence suggests that the PL may in fact alter the Li ion storage mechanism, delaying the onset of the conversion in

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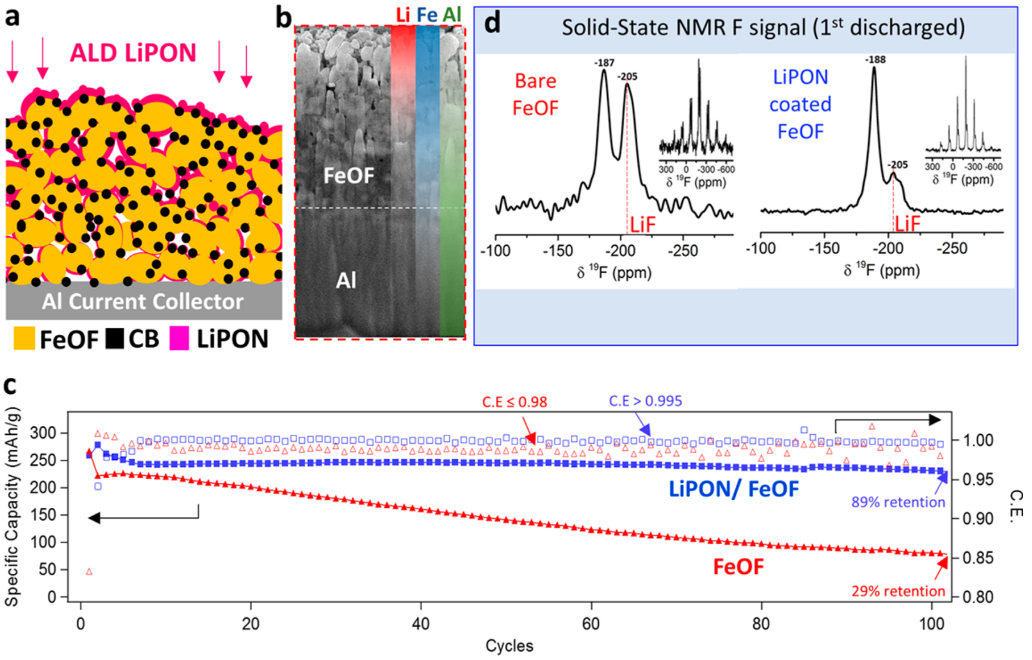

Figure 5. (a) Illustration of ALD penetration in a composite electrode. (b) Time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis of ALD-LiPON-coated FeOF. (c) Comparison of cycling performance. (d) Solid-state NMR analysis of bare FeOF vs LiPON/FeOF after the first lithiation, showing a reduction in the intensity of the LiF peak (−205 ppm) for protected FeOF. Adapted from ref 27. Copyright 2017 American Chemical Society.

favor of extending the range of ion insertion. Conversion materials will typically allow a small amount of Li ions (∼0.5 Li) to initially insert into one formula unit while preserving the original structure. When insertion continues past this threshold, the conversion reaction (phase transformation) takes over and forms new compounds—LiX + M (M = reduced metal; LiX = LiF, Li_2O). While the conversion process offers larger Li storage capacity, it sacrifices materials integrity and reaction reversibility. Prior evidence suggests the possibility that the PL can modify Li ion storage by delaying the onset of conversion to occur at a higher lithiation level.

The solid-state NMR spectra shown in Figure 5d reveal a major reduction in the formation of LiF (peak at −205 ppm) in the LiPON-protected FeOF electrode after first lithiation beyond the onset threshold of the conversion reaction (∼0.65 Li per FeOF). The reduced formation of LiF indicates that a large amount of Li is stored in LiPON-protected FeOF without undergoing irreversible phase transformation (conversion reaction). We hypothesize that the delayed onset of the conversion reaction may account for the superior reversibility observed in long-term cycling tests.[30] Furthermore, electron energy loss spectroscopy (EELS) studies of individual lithiated FeOF particles provide insight into the chemical reactions taking place with and without the LiPON PL. The FeOF composition is retained when the LiPON PL is present (Figure 6b, blue curve), as evidenced by the presence of both O and F K-edges. In contrast, without the LiPON PL (Figure 6b, red curves), the particle compositions are notably altered: for one particle, Fe remains but without O or F, i.e., as Fe metal; for another particle, O is present without F, suggesting FeO_x composition and release of F.[27,28] With such spectroscopic information as a function of Li inserted, we could estimate that the LiPON PL enables insertion of over 1.3 Li per FeOF formula unit with only a small amount of conversion reaction. In contrast, without the LiPON PL, the bare FeOF composite electrode undergoes conversion at ∼0.65 Li per FeOF formula unit. These inferences are depicted schematically in Figure 6c. For bare FeOF, initial Li insertion switches over to the conversion reaction at ∼0.65 Li, producing new phases and degrading the reversibility. With the LiPON PL, insertion is extended to 2 times higher Li content with little conversion taking place, and hence, the reversibility of the reaction is much improved. If such a delayed conversion is correct and a general phenomenon, it could significantly benefit energy storage by opening the door to high-energy conversion materials.[27]

DESIGN OF PROTECTION LAYERS FOR HIGH-CAPACITY ELECTRODE SYSTEMS

The examples above illustrate growing success in utilizing PLs to stabilize electrochemical storage systems against capacity degradation during cycling. As only a limited set of PL materials and structures have been demonstrated, the question arises whether there are quantitative criteria that can be used to choose materials, define design rules, and understand their consequences. This is especially important for high-capacity electrodes, such as PL-coated Si-based nanostructures. A PL will act as a buffer layer to the large volume changes of the electrode during lithiation. However, a thick PL can cause higher compressive stress in the Si-based nanostructure that prevents its lithiation, leading to a lower Li capacity. Thus, there is a critical thickness of the PL that balances the maximum tensile stress that the shell can tolerate without cracking and the maximum compressive stress that the Si can tolerate without stopping lithiation. This design criterion was exemplified in reactive molecular dynamics (MD) simulations by Kim et al.,[29] who tracked the chemical, structural, and mechanical evolution during lithiation of a Si nanowire core coated with an Al_2O_3 or SiO_2 shell. Various coating thicknesses (2.5, 4.5, and 7.5 Å) of Al_2O_3 or SiO_2 were simulated on Si

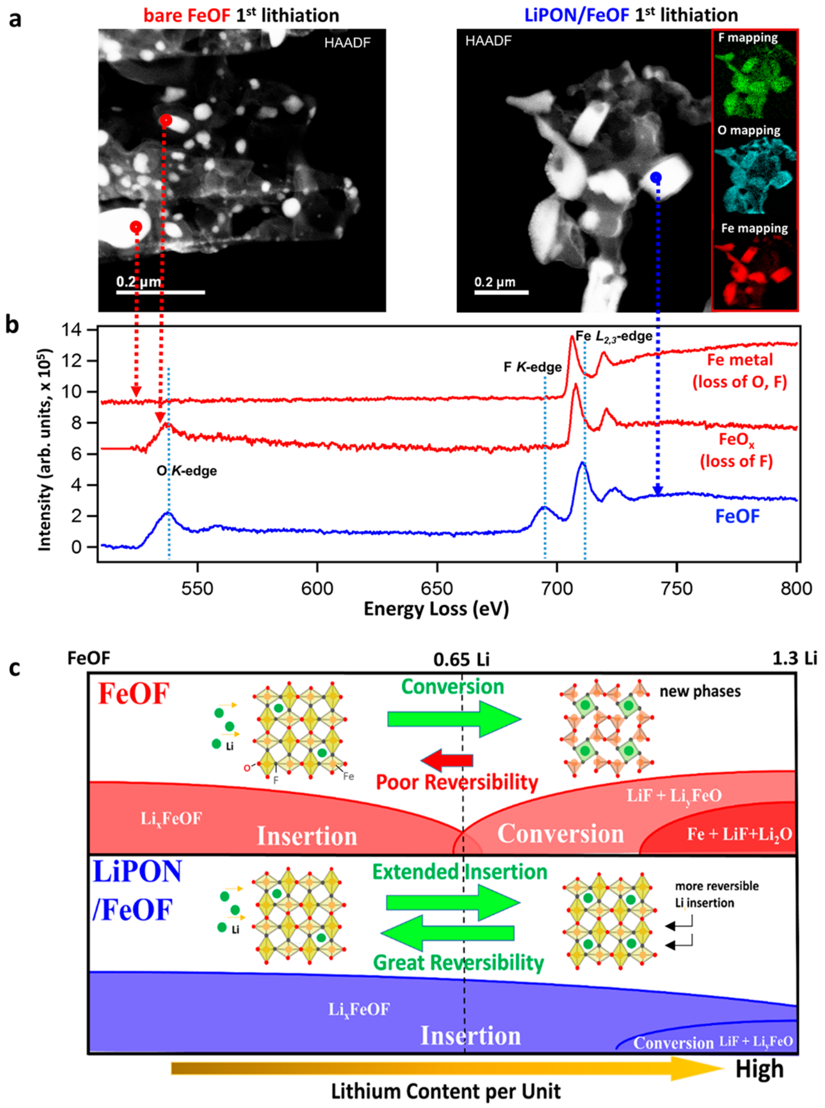

Figure 6. (a, b) STEM and EELS spectra of FeOF particles with and without the LiPON PL. Some bare FeOF particles (red) show loss of F (suggesting FeO_x composition), while others show loss of both F and O (suggesting Fe metal). With the LiPON PL present on the FeOF particle, both O and F are present, suggesting Li insertion without decomposition/reaction of the particle. (c) Schematic phase diagram illustrating the role of the LiPON PL, namely, to extend the Li insertion regime and diminish the extent of conversion in the FeOF particles.

nanowires, as shown in Figure 7a. Li diffused through and lithiated the Al_2O_3 or SiO_2 PL before the Si core was lithiated. With the assumption that the PL is a uniform layer under elastic deformation, a simple criterion to avoid PL cracking during lithiation was developed:

(1)

where h is the PL thickness, R (SOC) is the radius of the Si wire at a given state of change (SOC), σ_f^{coat} is the PL fracture stress, ΔG is the chemical potential for lithiation, and Ω is the atomic volume of lithium. These material properties can be obtained from experiments or predictive modeling. For example, with a DFT-predicted ΔG of ~0.5 eV, an experimentally measured Ω of ~9 cm^3/mol for lithiated Si, and an MD-predicted Young's modulus (E) of 45 GPa for lithiated Al_2O_3 coating,[29] with the assumption that $\sigma_f^{coat} = 0.3E$, it was estimated that the critical coating thickness is ~6.0 Å for an Al_2O_3 coating on a lithiated Si nanowire with a radius of 1.5 nm.[32,33] It is important to realize that lithiation can alter the transport and mechanical properties of the PL materials. As long as the PL properties after lithiation were used, the size ratio agreed well with the MD simulation results, as shown in Figure 7b. Ultimately, with a 7.5 Å Al_2O_3 PL, the PL remains mechanically and structurally intact while imposing a 13% compression of the volume of the Si core.

This simple analytical model, however, could not explain why Al_2O_3 was more resistant to cracking than SiO_2 at the same thickness. The MD simulations revealed an additional mechanism. The energy barrier for Li diffusion in SiO_2 is lower than that in Al_2O_3,[30] so the SiO_2 shells were immediately lithiated, followed by lithiation of the Si core. Therefore, there is a negligible lithium concentration gradient in SiO_2 PLs, which can be treated as uniform coatings. In contrast, because of the high diffusion barrier of Al_2O_3, the thicker Al_2O_3 layers (4.5 and 7.5 Å) exhibit a lithium concentration gradient with a high Li concentration at the outer shell and a low lithium concentration at the inner shell. The concentration gradient builds up gradually as the thickness of the Al_2O_3 coating increases from a certain threshold. At the same time, the

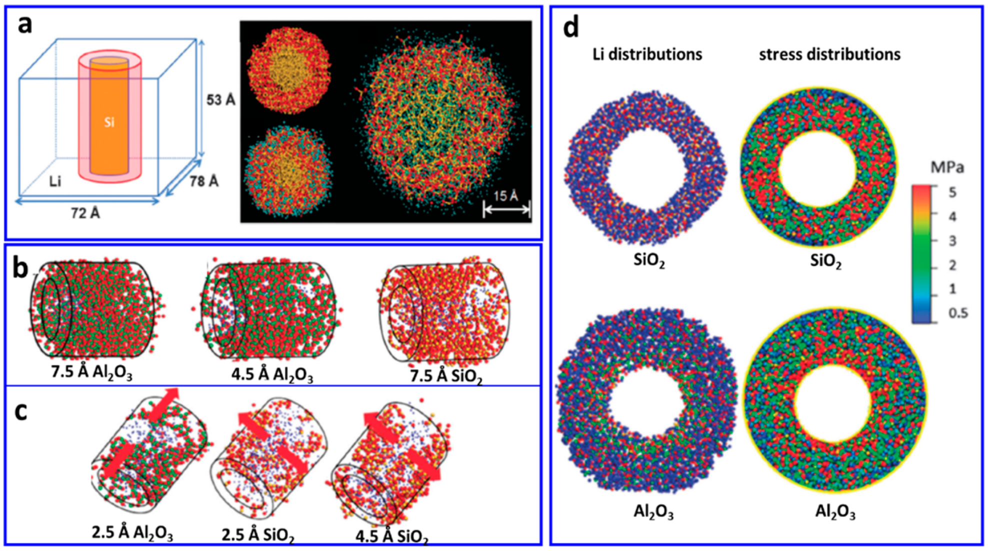

Figure 7. (a) Illustration of the reactive MD simulation of the lithiation process of oxide-shell-covered Si cores. (b, c) Shell failure mechanisms with various coatings. (d) Li and stress distributions of various coatings. Adapted with permission from ref 29. Copyright 2016 the PCCP Owner Societies.

lithiation process softens the oxide coating material. Thus, the lithium concentration gradient in the Al_2O_3 shell results in a modulus gradient of the shell in which the inner shell (less lithiated) is stiffer and the outer shell (more lithiated) is softer. The stiffer-inside and softer-outside modulus gradient causes a stress gradient that stops crack propagation and maintains the mechanical integrity of the PL until full lithiation of the Si core. These stress gradients are illustrated in Figure 7d, right. For the SiO_2 shell, the stress is distributed uniformly inside the coating, so a crack nucleated at the Si-core−PL interface will propagate through the shell. Interestingly, the naturally formed SEI also has a similar modulus gradient, with a stiffer-inside inorganic layer and softer-outside organic layer. The merit of this theoretical framework accelerated the optimization of surface coatings and contributed to strategies aimed at mitigating degradation.

■ CONCLUSIONS

Degradation mechanisms are common and influential in the performance of secondary (rechargeable) batteries, particularly those sought in order to achieve considerably higher energy and power. Recent results have shown that thin protection layers offer a pathway to mitigate degradation, retaining capacity as charge/discharge operations are carried out over extended cycles and also suppressing failure modes that pose serious safety risks.

Here we have briefly conveyed selected examples of the use of nanoscale coatings to mitigate degradation of high-energy electrodes, particularly for reactive metal anodes and high-energy conversion electrode chemistries. Thin-film synthesis, especially atomic layer deposition, provides a means to create such thin protection layers on various materials even when their structure and topography are complex and challenging.

In addition, we have conveyed experimental evidence suggesting the possibility that protective layers may be used to alter lithiation pathways. In the case of conversion materials, it appears that such protective layers may enable higher levels of lithiation by insertion, deferring the onset of conversion reactions and thus increasing the reversible capacity of these electrode systems.

Finally, we have summarized and recognized new avenues of theoretical pursuit that employ continuum mechanics and molecular dynamics to understand the lithiation-induced changes in composition, mechanical properties, and other factors pertaining to multicomponent electrode nanostructures. This avenue is promising and critical to inform the codesign of electrode and protection layer materials and structures.

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