Highly Reversible Conversion-Type FeOF Composite Electrode with Extended Lithium Insertion by Atomic Layer Deposition LiPON Protection

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ABSTRACT: High-energy conversion electrodes undergo successive Li insertion and conversion during lithiation. A primary scientific obstacle to harnessing the potentially high lithium storage capabilities of conversion electrode materials has been the formation of insulating new phases throughout the conversion reactions. These new phases are chemically stable, and electrochemically irreversible if formed in large amounts with coarsening. Herein, we synthesized FeOF conversion material as a model system and mechanistically demonstrate that a thin solid electrolyte [lithium phosphorus oxynitride (LiPON)] atomic layer deposition-deposited on the composite electrode extends the Li insertion process to higher concentrations, delaying the onset of a parasitic chemical conversion reaction and rendering the redox reaction of the protected conversion electrode electrochemically reversible. Reversibility is demonstrated to at least 100 cycles, with the LiPON protective coating increasing capacity retention from 29 to 89% at 100 cycles. Pursuing the chemical mechanism behind the boosted electrochemical reversibility, we conducted electron energy-loss spectroscopy, X-ray photoelectron spectroscopy, solid-state nuclear magnetic resonance, and electrochemical measurements that revealed the suppression of undesired phase formation and extended lithium insertion of the coated electrode. Support for the delayed consequences of the conversion reaction is also obtained by high-resolution transmission electron microscopy. Our findings strongly suggest that undesired new phase formation upon lithiation of electrode materials can be suppressed in the presence of a thin protection layer not only on the surface of the coated electrode but also in the bulk of the material through mechanical confinement that modulates the electrochemical reaction.

INTRODUCTION

Our understanding of fundamental degradation mechanisms in electrochemically active materials and their mitigation strategies are challenged by (1) constraints of the electrolyte environment, (2) the complexity of electrode-electrolyte interphase formation, namely the solid electrolyte interphase (SEI) layer, and (3) undesirable chemical and electrochemical reactions that lead to degradation of the electrode materials (EMs) themselves. Electrode degradation is a particular concern for “conversion electrode materials”, which typically undergo full chemical reactions with high Li content during lithiation, resulting in new phases with uncontrolled spatial distributions and relationships. Often these reactions generate insulating compounds that reduce electronic conductivity, increase overpotentials, and degrade electrochemical reversibility.

To mitigate these problems, efforts have been made to modify conversion electrode surfaces, forming layers of electrolyte additives or depositing layers on the electrodes. Here we report an atomic layer deposition (ALD) lithium phosphorus oxynitride (LiPON) protection layer on composite FeOF electrodes that substantially improves capacity retention upon cycling (~90% at 100 cycles), reduces overpotentials, and increases round-trip energy efficiency for the full electrode.
structure. Using results from a variety of characterization techniques [transmission electron microscopy (TEM), electron energy-loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), and solid-state nuclear magnetic resonance (NMR)] and from electrochemical measurements, we infer that these benefits result from delaying or suppressing spontaneous Li-induced conversion reactions of the FeOF so that the Li is accommodated mostly by insertion into the FeOF phase, rather than by reactive conversion of the material, accompanied by structural confinement of the material by the LiPON layer. Via the suppression of the conversion reaction, the levels of its insulating products (e.g., Li2O and LiF) are diminished and reversibility is enhanced. Our findings reveal new routes for diminishing undesirable phase changes in electrochemically active materials and are expected to impact various next-generation electrodes.

**Capacity Degradation in High-Performance Batteries.** The drive to increase battery energy and power encourages design characteristics that invite various degradation mechanisms. Electrode materials (EMs) with higher capacity and intrinsic energy density often go through a phase change upon lithiation/delithiation cycling that is too often partly irreversible. Increasing the Li capacity (higher Li/EM mass ratio) in selected EMs or higher-voltage cells provides a higher energy but invites degradation reactions.12–14 Parasitic chemical reactions with electrolytes at the EM surface produce surface layers, i.e., solid electrolyte interphases (SEIs), that consume Li and grow, degrading capacity.15,16 Larger surface areas achieved by nanostructure enhance such parasitic reactions. Finally, cell chemistries can introduce chemical impurities into the electrolyte, which may turn on new parasitic reaction channels associated with capacity degradation. Because capacity degradation is counterproductive in the context of increased power and energy in “better” batteries, some means of mitigating degradation in high-energy power performance batteries is a crucial need.

**Mitigating Capacity Degradation.** Most effort aimed at mitigating the reactivity of the electrode—electrolyte interface has been spent on introducing various additives into the electrolyte solution or delivering a specific surface treatment to the electrode of interest. The general idea is to form, during the electrochemical reaction, a solid electrolyte interphase (SEI) that stabilizes the surface of the EM without hindering the kinetics of electrochemical reaction pathways central to the energy storage function of the EM.17–20 Unfortunately, these reactions are not well controlled and typically not self-limiting, so their effect on the electrochemical cell changes with cycling.

An alternative strategy that is attracting a growing level of interest is to create an artificial SEI (A-SEI) layer before the performance of electrochemical cycling, such that the A-SEI layer is stable during subsequent cycling. Ideally, such a layer will serve as a solid electrolyte, allowing Li ion permeation but not electron transport, while repelling or neutralizing the effect of impurities from the electrolyte and preventing electrochemical decomposition of the electrolyte at the surface. Often such A-SEI layers are formed as well-controlled inorganic overlayers produced by ALD and exemplified by Al2O3 as an ideal ALD insulator.21–23 ALD exploits self-limiting adsorption and reaction of alternating chemical vapor precursors to produce films that are very uniform, even over challenging topography, including the nano/microscale particles of which composite electrodes are composed. ALD protection layer studies have been mostly focused on Li-ion battery cathode materials (e.g., LiCoO2)24 and more recently on a wider variety of EMs in nanostructured or particulate/composite form.15–17

Such ALD protection layers improve capacity retention with charge/discharge cycling. At the same time, density functional theory (DFT) calculations have shown how thin ALD insulating layers on the electrode suppress electron transfer, organic electrolyte decomposition, and uncontrolled formation of natural SEI.18,19

Once the cycling benefits of a protection layer are recognized, the question of how it stabilizes redox reactions of the underlying EMs’ “bulk” generally remains open. Here we demonstrate protection layer benefits for conversion EMs that undergo substantial chemical and structural change to form new products. This behavior and materials characterization results are suggestive of mechanisms by which the protection layer improves capacity retention and reversibility during charge/discharge cycling. The mechanism suggested herein proposes a new benefit from A-SEI, meaning control over the electrochemical changes of the electrode material itself rather than prevention of interfacial parasitic reaction or improvement of the EM’s structural and mechanical integrity.

**Conversion Electrode Materials.** Conversion EMs present a particular challenge for an A-SEI degradation mitigation strategy because of their extensive electrochemical reaction upon lithiation/delithiation. As this takes place, reaction products can become spatially isolated, electronically disconnected, and thus unable to re-form into original species for a reversible reaction, with a corresponding penalty for capacity retention. We have previously found that the ALD LiPON solid electrolyte coating as an A-SEI layer significantly enhances reversibility and capacity retention in RuO2 EM configured as an ALD RuO2 coating on multiwall carbon nanotubes as current collectors.22

As a follow-up to this work, we address here whether ALD LiPON can provide a similar benefit to capacity retention in a conversion material structurally configured as a composite electrode, mixing carbon black for electronic conduction with the binder and particulate conversion material, i.e., the kind of electrode structure that dominates in commercial Li-ion batteries. ALD processes can conformally coat particles with a uniform layer quite deep in such a composite electrode. We chose the FeOF composite electrode structure as the test case.

This oxyfluoride EM is attractive because it inherits both the relatively high output voltage of fluorides (FeF4)20–24 and the good kinetics of oxides (FeO).25,26 As a result, it is considered a potential next-generation electrode material with a theoretical high capacity, a promising electrochemical performance, and a low cost.27–29 Unfortunately, prior work demonstrated significant shortcomings.30 The first step of lithiation of FeOF (e.g., x = 1 in FeOF2−x) results in the formation of a metastable Li7FeOF2−x phase. As the number of Li ions (Li+, incorporated per FeOF formula unit increased beyond a certain point, this phase degraded spontaneously (even while being stored without bias) into the rock salt phase LiFeO2 and insolating LiF via the following reaction:

$$\text{Li}_x\text{FeOF} \rightarrow \text{Li}_{x-y}\text{FeO} + y\text{LiF}$$

Spontaneous formation of the highly insolating LiF phase electrically isolates the other components, which is catastrophic for the electrochemical reversibility of the EM. Furthermore, formation of this undesirable phase may form grains for nucleating more LiF upon further lithiation (during conversion) and facilitate phase separation between reaction
products, including LiFeO, FeO, fully reduced Fe, and LiF, leading to a significant loss of the active material after a limited number of cycles. In addition, the bare FeOF cathode is pulverized into nanoparticles upon lithiation (Figure S3). This is well-known behavior for conversion-type materials upon lithiation.31,32 Note that under the Li insertion conditions applied here, partial reaction by electrochemical conversion should occur, while uncontrolled spontaneous chemical conversion, as reported by Wiaderek, Chapman, and co-workers,30 is evidenced by the severe pulverization of FeOF at these stages of lithiation (and by analytical techniques to be discussed below).

**ALD Protection of Composite FeOF Conversion Electrodes.** Here we investigate the use of an ALD protection layer to suppress capacity degradation in a composite FeOF conversion electrode. We demonstrate success in controlling electrochemical and chemical degradation using an ALD lithium phosphorous oxynitride (LiPON) process to create a protection layer with high Li ion conductivity,33,34 evidenced as the stable electrochemical performance of the FeOF electrode and accomplished not only by suppressing the undesirable interfacial reaction but also by modulating the steps of lithiation of the EMs during discharge and mitigating the formation of irreversible conversion reaction byproducts. A mechanistic investigation of the electrochemical behavior of the EMs and the LiPON coating is conducted via both short- and long-term studies. The improvement in electrochemical performance, specifically in capacity retention with cycling, is profound in both thermodynamic and kinetic aspects, with a surprisingly large benefit for the long-term stability of the EM. These results strongly suggest that the electrochemical reduction pathway for conversion-type EMs can be modulated by carefully designing and implementing a protective confinement layer on the electrode surface. Note that we focus not only on the impressive electrochemical performances of the modified EM but also on the metrics used to demonstrate it (“how well it works”). Our primary focus is on the scientific reason behind the profound improvement of the performance (“why it

Figure 1. (a) FeOF composite electrodes as fabricated on Al foil. (b–d) SEM and TEM images of FeOF electrodes mixed with carbon black and binder PVDF. The FeOF particles are ~100 nm wide and ~800 nm long. (e–g) Cross-sectional STEM-HAADF images and EELS elemental mapping show the distribution of FeOF particles in the composite electrode with a film thickness of ~6 μm.
Figure 2. ALD solid electrolyte LiPON coating. (a) Schematic of ALD vapor phase coating on the composite electrode. (b) Four hundred cycles (~30 nm) of ALD LiPON conformal coating on FeOF particles. (c) ToF-SIMS analysis of the LiPON-coated composite FeOF electrode. Color bars show the elemental intensities of Li (red), Fe (blue), and Al (green) in the depth of the composite.

works”), trying to extract a rule of design, required for realization of next-generation EMs.

SYNTHESIS OF MATERIALS

Synthesis of FeOF Composite Electrodes. Composite electrodes of FeOF were synthesized using a previously reported procedure. Secondary electron microscopy (SEM) and (scanning) transmission electron microscopy [(S)TEM] show the structure and composition of the FeOF particles and the electrode in Figure 1, with additional details presented in Figure S1. The active material is composed of FeOF nanorod-like particles with a high aspect ratio [width of ~100 nm and length of ~800 nm (Figure 1b–d)]. Cross-sectional STEM high-angle annular dark field (STEM-HAADF) images and EELS elemental mapping of F and Fe results are shown in Figure 1e–g. The thickness of the composite electrode is ~6 μm, as shown in the STEM-HAADF image (Figure 1e), and the bright spots corresponding to FeOF (e.g., EELS Fe image in Figure 1g) are well distributed throughout the composite. The light gray and black contrast area in the STEM-HAADF images indicates the existence of the lighter compounds, which originated from the carbon black and the PVDF binder, as well as from porous regions in the composite electrode. EELS images in panels f and g of Figure 1 show that the F and Fe signals are spatially arranged in a very similar pattern, a clear indication of FeOF particles.

Solid Electrolyte Coating on the FeOF Composite by ALD LiPON. To coat the EMs with an ion-conductive protective layer, we deposited 400 cycles of plasma-assisted ALD LiPON. Figure 2a shows a schematic representation of FeOF particles conformally coated with ALD LiPON. XPS spectra for the as-deposited LiPON protection, measured in situ by direct transfer from the ALD chamber to the XPS system under ultrahigh vacuum without exposure to air, confirmed the chemical characteristics of the LiPON coating (Figure S2). We anticipated that the diffusivity of the vapor phase ALD precursors and nitrogen plasma in the depth of the composite electrode would not be complete, given the significant thickness (~6 μm) of the composite electrode, the high tortuosity of the porous composite, and the directional nature of plasma N2 exposure as part of the ALD LiPON process. To evaluate the depth of penetration of ALD LiPON into the composite, time-of-flight secondary ion mass spectroscopy (ToF-SIMS) was performed to measure the LiPON-coated composite FeOF electrode on the Al current collector, as shown in panels b and c of Figure 2. The elemental intensities of Li (red), Fe (blue), and Al (green) are shown as the color bars superimposed in the micrograph reflecting the presence of LiPON, FeOF particles, and the Al current collector, respectively, and indicating that the ALD LiPON penetrates ~2.5 μm into the FeOF composite layer. This is ~40% of its thickness and much deeper than what is possible with thin film coating by physical vapor deposition methods (e.g., evaporation or sputtering). We are currently developing alternative processes for LiPON that can achieve deeper penetration of the LiPON layer below the FeOF electrode surface, particularly by using a thermal (no plasma) step for the nitrogen component of LiPON.

Characterization and Electrochemical Results. Electrochemical tests were conducted using 1 M LiClO4 in a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with Li foil as the anode and the composite FeOF cathode either bare or protected by the LiPON A-SEI layer. The cell was discharged from the open circuit potential (OCV) to 1.2 V and charged to 4 V during cycling with a current density of 300 mA/g of FeOF. Charge/discharge cycling shown in Figure 7 shows the profound benefit of using the LiPON coating on the composite FeOF electrode, increasing capacity retention dramatically as measured at 100 cycles. We first analyze results from TEM, XPS, solid-state NMR, and EELS to provide a basis for interpreting the character of the lithiation/delithiation process before more closely examining electrochemical cycling and formulating a model.

Coating Stability. TEM. Panels a and b of Figure 3 show TEM images for LiPON/FeOF for as-prepared samples and samples after the first discharge to 1.2 V, respectively, both revealing a well-defined ~25–30 nm LiPON layer covering the FeOF cathode. Figure 3b shows that after discharge (confirmed by electrochemical measurements depicted in Figure S4), the thickness and structure of the deposited LiPON layer are retained despite the extensive ion motion associated with penetration of Li ions through the LiPON to the FeOF during lithiation. This demonstrates that the ALD LiPON has good ionic conductivity. More surprisingly, the presence of the LiPON protective layer seems to suppress pulverization of the FeOF, which is a typical consequence of the FeOF + nLi → Lix−yFeO + yLiF conversion reaction; i.e., the LiPON layer seems to stabilize the FeOF structure. Importantly, we
observed the preservation of the FeOF structure in the LiPON-coated electrode without Li storage capacity being sacrificed. The first discharge capacities of bare FeOF (red) and LiPON/FeOF (blue) both exhibited large amounts of lithium storage (Figure S4).

XPS. Using an integrated XPS system (Figure S5) that enables transfer of a sample from the ALD LiPON system through ultrahigh vacuum to the XPS instrument, we characterized the chemical identity of the resulting film. A full survey and high-resolution spectra of the P 2p peak (Figure 3c,d) confirmed that the chemical composition of the protection layer remained that of LiPON after the first discharge (the chemistry of as-prepared LiPON is shown in Figure S2). XPS spectra in panels c and d of Figure 3 reveal the presence of the LiPON protective layer through the presence of the phosphorus 2p core levels, persisting after transport of Li through the LiPON into the FeOF during discharge. To examine the long-term stability of the LiPON protection layer, we characterized structural and chemical changes after 100 cycles for the LiPON/FeOF-protected composite, as shown in panels e and f of Figure 3. Even after 100 discharge/charge cycles, the LiPON layer remained on the surface with a thickness of ∼28.5 nm, with the appearance of capped EMs with less pulverization due to repeated lithiation/delithiation. Figure 3f shows the high-resolution XPS P 2p spectrum that confirms the unchanged chemical property of the LiPON over
100 cycles of battery operation. The superior mechanical and chemical stabilities of LiPON under extensive electrochemical cycling enable the highly stable and reversible electrochemical performance of LiPON/FeOF electrodes. In contrast and as anticipated, the bare FeOF microparticle was converted into small nanoparticles through the conversion reaction at the first lithiation and over long-term cycling (shown in Figure S3).

**Solid-State NMR.** For solid-state NMR measurements, the PVDF binder was replaced with Na CMC (sodium carboxymethyl cellulose) to eliminate sources of 19F signals other than the FeOF. As shown in Figure 4, two 19F resonances at −170 and −190 ppm are observed in the spectrum of the pristine FeOF. Under the experimental conditions used here, it is unlikely that these resonances correspond to F sites within the FeOF phase (due to the presence of paramagnetic Fe ions, 19F resonances from this phase are likely to be shifted and significantly broadened by hyperfine interactions and fast spin−spin relaxation). Resonances around −190 ppm were observed in earlier studies of MgF2 and CuF2 and assigned to HF adsorbed on the surface of particles.36,37 Therefore, we tentatively assign these resonances to diamagnetic byproducts formed in the synthesis of the FeOF material. (19F resonances from this phase are likely to be shifted and significantly broadened by hyperfine interactions and fast spin−spin relaxation.) Resonances around −190 ppm were observed in earlier studies of MgF2 and CuF2 and assigned to HF adsorbed on the surface of particles.36,37 Therefore, we tentatively assign these resonances to diamagnetic byproducts formed in the synthesis of the FeOF material. Following the lithiation process, a prominent peak at −205 ppm appears in both the pristine/unprotected and LiPON-protected electrodes. This resonance can be assigned to LiF. The 19F environment in commercial LiF resonates at −204 ppm (see Figure S6); the slight shift and broadening of this resonance in the discharged electrodes can be caused by disorder and the proximity of the LiF phase to the paramagnetic electrode particles.37 The presence of this peak confirms earlier observations by Wiaderek et al.30 that chemical conversion results in the formation of a relatively large amount of LiF as a byproduct.

In the protected LiPON/FeOF, the same 19F resonances from FeOF particles before cycling are observed, but the intensity of the 19F resonance at −205 ppm is significantly lower for discharged LiPON/FeOF, i.e., a relatively small amount of FeOF went through the conversion reaction to form LiF. The 19F resonance at approximately −190 ppm from the synthesis byproduct (detected in both pristine and discharged electrodes) can be used to compare the amount of LiF formed in the bare versus coated electrodes, assuming it is not affected by the LiPON layer. Using DMFIT38 to fit the resonances at −190 and −205 ppm (including their spinning sideband manifold), we obtain a 1:0.89 ratio in the bare electrode compared with a 1:0.37 ratio in the LiPON/FeOF electrode between the byproduct and the LiF species. The decrease in the LiF resonance in the presence of LiPON protection provides clear evidence that the (spontaneous) conversion reaction is suppressed when the EM is capped with a stable solid electrolyte.

**EELS.** EELS was performed for EMs after the first lithiation to 1.2 V, and the results are presented in Figure 5. As shown in panels a and b of Figure 5, the cross-sectional STEM and high-angle annular dark-field imaging (STEM-HAADF) micrographs (the samples were prepared by focused ion beam (FIB)) show that the structure of bare EMs without the LiPON protection layer (red box) drastically changed, and no original FeOF morphology is preserved (compared with Figure 1c−e). In contrast, LiPON-protected EMs in panels c and d of Figure 5 (blue box) show the original elongated shape of structures of EMs remained after they had been lithiated to 1.2 V (∼1.3 Li insertion shown in Figure 6). The inset in Figure 5c confirms the elongated shape of EMs, contoured by yellow dashed lines, after lithiation. We further analyzed the chemical composition of lithiated EMs by STEM and EELS with high spatial resolutions. The spectra of bare lithiated EMs (red) and
LiPON-protected EMs (blue) are shown in Figure 5e. We observed that the bare FeOF decomposed into either FeO or Fe particles, both with loss of F. In contrast, EELS data for LiPON/FeOF clearly showed the existence of a F K-edge peak that confirmed the remains of F within FeOF particles after lithiation. In addition, in Figure 5e, the Fe peaks in EELS spectra show that the energy loss of Fe in bare EM is shifted to an energy lower than the energy loss of Fe in LiPON/FeOF, indicating the reduced state of Fe through the conversion reaction.

EELS elemental mappings of O, F, and Fe signals of the LiPON/FeOF electrode are shown as the insets of Figure 5d; the remaining structural integrity of FeOF after lithiation indicated the suppression of the formation of the new phase, LiF. This is in agreement with the solid-state NMR measurements given above that demonstrate that LiPON protection of FeOF (EMs) provides structural constraints, suppressing the formation of the LiF phase, causing the irreversibility of the lithiation reaction, and protecting the structural integrity of FeOF even with a large amount of Li insertion.

Both solid-state NMR (large-volume sampling) and EELS (local-region sampling) provide evidence of the suppression of conversion reaction and the formation of the insulating LiF compound.

**Electrochemical Performance: First Lithiation.** The electrochemical behavior in the first lithiation provides mechanistic clues about the role of the LiPON protection layer. Figure 6 presents voltages and their time derivatives as a function of the state of discharge of the cell and the number of Li ions transferred per FeOF molecular unit, at a low rate (∼22 mA/g). It has been shown in many previous works that the conversion-type electrodes displayed the sloped discharged curve as shown in Figure 6a. The results for the unprotected
FeOF electrode (red curve) show a phase transition (slope change) between two major plateaus in Figure 6a, at an ∼30–50% state of discharge as the conversion reaction proceeds: \( \text{Li}_x\text{FeOF} \) (insertion) \( + y\text{Li} \rightarrow \text{Li}_z\text{FeO} + (x+y-z)\text{LiF} \) (conversion). In contrast, no such phase transition (conversion reaction) is evident for the protected LiPON/FeOF electrode during the first lithiation, and the corresponding linear behavior in Figure 6a (blue curve) suggests the inserted Li is accommodated in the FeOF by maintaining the original FeOF phase. These distinctions between unprotected FeOF and LiPON-protected FeOF are further depicted in Figure 6b as time derivatives of data in Figure 6a. A major valley was observed in the derivative of the FeOF (red) profile that represents the occurrence of conversion reaction around 0.65 Li inserted into the FeOF formula unit, but an absence of that for the case of LiPON/FeOF (blue), which suggests that the EMs did not go through a major conversion reaction (only a small amount of conversion associated with the bump at 0.8 Li storage as indicated by the blue arrow, in Figure 6b, and the Li number is determined by the measured mass and transferred charges). Finally, the unprotected FeOF electrode shows (Figure 6a) a larger voltage drop (∼0.3 V) compared to the protected LiPON/FeOF electrode, suggesting an overpotential penalty associated with the conversion reaction.

Proposed Mechanism: Role of the LiPON Protection Layer. From these observations, we propose that the presence of the thin LiPON protection layer facilitates the morphological stability of the EMs (FeOF) by suppressing the spontaneous conversion reactions that normally lead to pulverization of the FeOF. This model is schematically illustrated as a phase diagram for Li storage in FeOF with and without LiPON protection in Figure 6c. Without protection, Li initially inserts into the FeOF as an insertion phase of \( \text{Li}_x\text{FeOF} \), up to 0.65 Li per FeOF. Further lithiation causes spontaneous degradation of the metastable \( \text{Li}_{0.65}\text{FeOF} \) phase into LiF and \( \text{Li}_y\text{FeO} \), i.e., initiating the conversion reaction. The LiPON protection layer structurally constrains the system, enabling lithiation to proceed by insertion rather than conversion, essentially to full discharge/lithiation state (1.3 Li per FeOF). If our hypothesis is valid, preventing or substantially delaying the onset of the conversion reaction should also prevent pulverization of the material and formation of insulating lithium compounds (e.g., LiF) that hinder the electrochemical performance and the reversibility of the redox reaction. This would explain the significant benefit to capacity retention we report below under extended charge/discharge cycling.

Electrochemical Performance: Extended Cycling and Round-Trip Efficiency. To further investigate the role of the LiPON protection layer, we cycled the FeOF and LiPON/FeOF at a 1C rate, finding a distinct difference in the electrochemical cycling behavior between the two (Figure 7). The contrast in behavior of bare versus LiPON-protected composite FeOF electrodes seen in the first lithiation correlates with a profound difference in cycling stability and capacity.
retention over 100 cycles, illustrating that the protection layer, intact through the first lithiation (see above), retains its capability to profoundly modify the character of lithiation-induced changes in the active FeOF material. The capacity of the bare FeOF electrode (Figure 7a) decays drastically upon cycling, while the LiPON/FeOF-protected electrode (Figure 7b) exhibits remarkably better cycling stability. The detailed capacity retention with cycling in panels c and d of Figure 7 shows that the bare FeOF electrode (red) without LiPON protection loses capacity rapidly, from \( \sim 250 \) to \( \sim 80 \text{ mAh/g} \) after 100 cycles, i.e., 29\% of the initial capacity. We attribute the associated low Coulombic efficiency (CE) of \( \sim 98\% \) to the formation of irreversible phases (e.g., LiF) formed by conversion. In contrast, the LiPON/FeOF composite electrode exhibits superior cycling stability for >100 cycles, achieving 89\% capacity retention after 100 cycles and 99.5\% CE. As postulated above, we attribute the \( \sim 3\)-fold benefit in capacity retention to the role of the LiPON in suppressing or delaying the onset of the conversion reaction, instead accommodating Li incorporation through an insertion mechanism. Note that the capacities we revealed in our experiments are lower than the theoretical capacity, which we attributed to the variations in kinetics, rates, and sample homogeneity. However, we observed a comparable initial capacity for both bare and LiPON-coated FeOF composite electrodes, indicating the consistency of the samples. The significance that we present here is not only a comparison of the absolute value of capacity but also a demonstration of the protective coating that showed a drastic improvement in long-term reversibility and prevented degradation.

Further evidence of the profound effect of the LiPON protection layer is shown in Figure 8. At the 20th cycle, LiPON protection reduces overpotentials asymmetrically (i.e., considerably more for charge than for discharge) in comparison to those of bare FeOF; this is as we reported elsewhere,\(^{32}\) namely that LiPON protection layer facilitates the reoxidation process by providing mechanical constraints of reaction byproducts and thus maintaining better electronic and ionic pathways for reoxidation. At the 100th cycle (Figure 8b), the overpotentials of the bare FeOF electrode increased prominently for both charge and discharge processes because of the significant degradation of materials that accompanies reaction and conversion of the FeOF material upon cycling. As shown in Figure 8c, LiPON protection provides the FeOF composite electrode with a notably improved round-trip energy efficiency.
through 100 cycles, resulting in efficiencies of 72% for protected versus 47% for unprotected composite FeOF, a >50% improvement as shown in Figure 8d. Taken together, these electrochemical measurements speak to the profound benefit offered by the 30 nm LiPON solid electrolyte protection layer in retaining capacity during cycling, reducing overpotentials, and improving round-trip energy efficiency.

**DISCUSSION**

Conversion-type materials typically possess the structures that allow a small amount of Li ion (∼0.5 Li) to initially intercalate into one formula unit of material with the preservation of the original structure of the compounds. When the amount of Li ion intercalation exceeded the threshold, the conversion reaction (phase transformation) takes over to form new compounds, reduced metal and lithium compounds (e.g., LiF and Li$_2$O). Chevrier, Cedar, and co-workers have reported the result of energetic thermodynamic calculation and found that conversion reactions are thermodynamically favorable from the very beginning of the Li ion insertion process; thus, the observed intercalated Li$_{1.3}$FeOF can be considered as an oversaturated solid solution phase. Therefore, the delay of the conversion reaction process must be dominated by kinetic effects (such as interfacial energy and nucleation barriers). We speculate that in addition to the original kinetic effects, the interfacial coating of LiPON further increases the kinetic barriers (by adding chemical inertness and/or mechanical strain effects) to conversion, so we observed further extension of the insertion phase (further retardation of the conversion reaction). Subsequent research through modeling and/or designed experiments to identify these kinetic factors associated with the conversion reaction pathway altered by thin, conformal coatings is crucially needed for both the fundamental materials science and practical application.

**CONCLUSIONS**

We have employed ALD to create a thin (∼30 nm) solid electrolyte layer on the surface(s) of a composite FeOF electrode, comprised of FeOF particles with carbon black and binder to replicate a typical battery electrode structure. The electrochemical results show profound benefits for capacity retention (∼3-fold) upon full discharge cycling to 100 cycles, a reduction in overpotentials, and a resulting improvement in round-trip energy efficiency, all of which are beneficial for application to high-energy batteries.

Characterization by TEM and XPS reveals that the LiPON layer remains intact through the electrochemical cycling protocols employed here, at least to 100 cycles.
TEM, EELS, and solid-state NMR further reveal the ability of the LiPON to preserve the FeOF structure, consistent with a primarily insertion-based lithiation process as opposed to reaction and conversion.

Taking these results together, we suggest a model in which the LiPON protection layer serves to constrain the electrode materials in such a way that insertion of Li into the FeOF is sustained while chemical reaction of Li with the (normally conversion-type) FeOF material is suppressed.

This work expands the body of evidence that shows that thin solid electrolyte protection layers afford substantial benefits for reversibility and capacity retention under cycling for conversion electrode materials. Because the extent of lithiation in these conversion EMs notably exceeds that available (∼0.5−1.0 Li per formula unit) from insertion-type EMs, such protection layers offer an attractive pathway to viable higher-energy electrode materials. Our findings strongly suggest that control over the electrochemical reaction upon lithiation of EMs can be achieved by coating the active material using carefully designed A-Sei. These findings can have a significant impact on the realization of conversion EMs and also the realization of EMs that goes through undesirable phase changes upon electrochemical reaction (e.g., high-voltage cathodes).

**REFERENCES**

16. Knoops, H. C. M.; Donders, M. E.; van de Sanden, M. C. M.; Notten, P. H. L.; Kessels, W. M. M. Atomic Layer Deposition for...


