Stabilizing Lithium Plating by a Biphasic Surface Layer Formed In Situ
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Abstract: The dendritic growth of Li metal leads to electrode degradation and safety concerns, impeding its application in building high energy density batteries. Forming a protective layer on the Li surface that is electron-insulating, ion-conducting, and maintains an intimate interface is critical. We herein demonstrate that Li plating is stabilized by a biphasic surface layer composed of a lithium-indium alloy and a lithium halide, formed in situ by the reaction of an electrolyte additive with Li metal. This stabilization is attributed to the fast lithium migration through the alloy bulk and lithium halide surface, which is enabled by the electric field across the layer that is established owing to the electron-insulating halide phase. A greatly stabilized Li-electrolyte interface and dendrite-free plating over 400 hours in Li symmetric cells using an alkyl carbonate electrolyte is demonstrated. High energy efficiency operation of the Li$_x$T$_{12}$O$_{12}$ (LTO) | Li cell over 1000 cycles is achieved.

The development of electric vehicles places great emphasis on rechargeable batteries. Beyond lithium-ion technologies, potential candidates that can offer high energy density are Li metal batteries, that include Li–S and Li–O$_2$ chemistries, in which a Li metal anode is the pivotal element.[1–5] However, the structural degradation and safety concerns of Li metal over continuous plating/stripping cycles hinders its application.[6–8] This originates from the interplay of the inherent dendritic growth of Li and its reactivity with the electrolytes. Based on Chazalviel’s model, anion depletion in low transference number electrolytes intrinsically causes spatial charge accumulation. It incurs a large electric field that drives dendritic growth at high currents.[9,10] On the other hand, parasitic reactions of Li with the electrolyte lead to a non-uniform and ion-impeding solid electrolyte interphase (SEI) that causes localized heterogeneous current at high flux and aggravates dendrite growth (Figure 1a) [11,12].

Much effort has been devoted to tackle the dendrite growth problem from different perspectives. Accommodating Li in a 3D host framework lowers the effective current density and alleviates volume expansion.[13–15] Artificial SEIs that are mechanically robust have been shown to effectively block the vertical growth of Li dendrites.[16–18] Modifying the SEI compositions via concentrated electrolytes[19,20] and electrolyte additives[21]—mostly via increasing the fraction of LiF—show promise in stabilizing the Li metal anode performance. Relying on the reaction of Li with additives of polysulfides, LiNO$_3$, organosulfides, fluoroethylene carbonate or a combination of them, a chemically stable SEI forms and increases the plating efficiency.[22–27] However, formation of an ion-conducting but electronically insulating SEI that is stable in alkyl carbonate electrolytes—and which also maintains intimate contact with Li metal—remains an ongoing challenge.

We and others have recently reported that Li-In alloy composite coated Li electrodes prepared by solution pre-treatment can sustain long-term dendrite-free plating.[28,29] Herein, instead of relying on ex situ pre-treatment, we demonstrate a simple approach to realize a biphasic protective layer in situ (that is, in the assembled cell), by reaction of Li with indium halides (InX$_y$, X = F, Cl, Br, I) that are added to the electrolyte. An immediate advantage is the locally intimate contact of the biphasic layer with Li, irrespective of the rough Li foil surface, which also helps prevent layer delamination during cell operation. Furthermore, the InX$_3$ excess in the EC/DMC electrolyte allows self-healing of the protection layer during cycling. While the alloy phase Li$_x$In$_y$ exhibits a high bulk diffusion coefficient ($D_L$ = 10$^{-3}$– 10$^{-5}$ cm$^2$s$^{-1}$)[30,31] compared to 5.69 × 10$^{-13}$ cm$^2$s$^{-1}$ in bulk lithium metal[32]) and the LiX halides enable fast surface lithium migration,[21] the electron-insulating LiX phase is necessary to establish an electric field to drive lithium ions across the layer (Figure 1b). We show that with a low...
concentration of 60 mM InF₃ in a conventional alkyl carbonate electrolyte, Li plates in a non-dendritic and compact morphology. A stabilized Li-electrolyte interface and high plating/stripping reversibility is obtained in Li|Li symmetric cells with InF₃ added to the electrolyte, which is superior to control cells using blank or LiF-added electrolytes.

The formation of the two phases—Li, In, and LiF—at the Li-electrolyte interface occurs via the following reactions [Eq. (1),(2)]:

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\begin{align*}
3 \text{Li} + \text{InX}_3 & \rightarrow \text{In} + 3 \text{LiX} \quad (X = \text{F}, \text{Cl}, \text{Br}, \text{I}) \\
x \text{Li} + y \text{In} & \rightarrow \text{Li}_x\text{In}_y
\end{align*}
\]

To examine the surface composition and morphology upon cell operation, polished Li foil was treated in 60 mM InF₃ carbonate electrolyte for 48 hours at 25°C. With the InF₃ treatment, the Li shows a dense particulate surface with a layer thickness of approximately 1 μm (Figure S1 in the Supporting Information). The Li-In alloy phase, which appears bright in the back-scattered scanning electron microscopy (SEM) images, is distributed homogeneously within the LiF phase, which makes the allyl-halide composite layer electronically insulating as previously reported. The observed fine thickness indicates that film growth becomes limited by both mass transport and by its insulating nature. X-ray photoelectron spectroscopy (XPS) confirms the formation of the two targeted phases. The In 3d spectrum of InF₃ treated Li shows one major component corresponding to In⁺ characteristic of Li-rich alloys (3d₃/₂: 442.5 eV, Figure S2a), along with a small fraction of In metal (3d₃/₂: 443.1 eV). The F 1s spectrum confirms a majority fraction of LiF along with a marginal component of LiPF₆, as a result of LiPF₆ decomposition (Figure S2c). The X-ray diffraction pattern of the InF₃ treated Li shows the presence of crystalline Li₁₀In₄, LiF and In metal (Figure S3). Un-alloyed In metal was absent after Li plating (2 mA cm⁻²), indicating that further alloying of In occurs over initial conditioning (Figure S2b and S3). The lower reactivity of InF₃ than InCl₃ yields a much thinner layer than that previously demonstrated with InCl₃. As we will later show, the biphasic layer of this composition is effective in suppressing dendrite growth over long-term cycling, as it can self-repair owing to the excess additive present in the electrolyte (see Note S1 in the Supporting Information).

The Li plating behavior in a classic battery electrolyte (1 M LiPF₆ in ethylene carbonate/dimethyl carbonate, EC/DMC) with added InF₃ is revealed by SEM imaging. Li electrodes were retrieved after plating 2 mA cm⁻² Li at a current of 0.5 mA cm⁻² in Li|Li symmetric cells. The Li plated in the blank electrolyte shows a typical needle-shaped morphology across the thickness and exhibits high porosity (Figure 2a,d). The Li plated in the LiF-only electrolyte shows a similar morphology, albeit with reduced porosity (Figure 2b,e). In contrast, the plated Li in the InF₃-added electrolyte shows a compact and relatively smooth surface, indicating film-like growth behavior (Figure 2c,f). Confirmation of plating of Li under the protective layer is afforded by SEM imaging, which easily discriminates between the underplated Li and the protective layer (which is brighter due to its heavier In component; Figure 2f). This is further supported by the observation of Li, In, alloy and LiF on the surface after plating (XPS, Figure S2b,d). The Li surface morphology and SEI thickness after 50 cycles confirms the long-term effectiveness of the biphasic layer in isolating Li metal and suppressing parasitic reactions (Figure S4).

The evolution of electrochemical impedance spectra (EIS) upon open-circuit rest of the Li|Li symmetric cells reveals the chemical stability of the Li-electrolyte interface. Upon a 30 minute rest, the InF₃ cell shows a 10-fold lower interfacial charge transfer resistance (Rct) compared to the blank cell (25 vs. 300 Ω cm²), as determined by the intercept of the semicircle with the abscissa (Figure 3a,b, Figure S5a,b). This demonstrates that the spontaneous formation of the biphasic layer suppresses electrolyte decomposition while serving as a Li-ion migration conduit. The Rct of the blank cell exhibited a continuous increase over 24 hours, whereas that of the cell with added InF₃ remains almost constant, indicating high chemical stability of the interphase.

It has been demonstrated that highly evolving potential profiles of a Li|Li symmetric cell signify microstructure formation/consumption upon plating/stripping. As shown in Figure 3c, the Li plating in the blank electrolyte experiences a large overpotential for Li nucleation. Upon Li stripping, the voltage of the blank cell clearly evolves in a volcano curve, where the potential first increases and then decreases, corresponding to the dissolution of plated dendrites and of the bulk Li forming surface pits, respectively. The voltage of the cell with the LiF-added electrolyte also evolves in a volcano-like curve, albeit with less potential variation (Figure 3c). In contrast, the cell in the InF₃-added
electrolyte shows a rather flat potential profile, indicating suppressed surface area variation and dendrite formation.

The plating/stripping cycling stability on Cu foil was evaluated by cyclic voltammetry (CV; Figure 3d, S5c). On the 1st cycle, the cell using the blank electrolyte shows almost zero current. On the 5th cycle, the LiF and InF$_3$ cells show much higher current than the blank cell (stripping: 12.5, 12.0 and 5.0 mA cm$^{-2}$, respectively), indicating that both the LiF and InF$_3$ derived SEIs exhibit more favorable interfacial kinetics. However, on the 10th cycle, in contrast to the stabilized current presented for the InF$_3$ cell, the current of the LiF cell declines to about 9 mA cm$^{-2}$ (Figure S5c). This indicates inferior lithium conductivity and structural stability for the LiF derived SEI, which likely degrades over continuous plating/stripping.

Figure 4a shows the evolution of the voltage profile with plating/stripping in Li|Li symmetric cells at a current of 1 mA cm$^{-2}$. The cell using a 60 mM InF$_3$ carbonate electrolyte (denoted as InF$_3$-60 mM) shows stable voltage profiles over 400 hours of cycling, whereas the blank cell experiences fluctuating and increasing overpotential, indicating accumulation of an impeding SEI and ubiquitous local short-circuits. The cell with the LiF-60 mM electrolyte also shows a voltage increase after cycling for 200 hours (Figure S6). Electrolytes with a lower concentration of InF$_3$ additive were also examined. The InF$_3$-15 mM cell shows a stable evolution of the voltage profile, but the InF$_3$-7.5 mM cell experiences a potential increase after 150 cycles (Figure S7a). Furthermore, even at a higher current density of 4 mA cm$^{-2}$, the InF$_3$-added cell also exhibits stable voltage profiles over 100 cycles, in contrast to the fluctuating voltage of the blank cell (Figure S8). In a glyme electrolyte (which presents better chemical stability with Li) the InF$_3$ added cell maintains exceptional plating/stripping over 1000 hours (Figure 4b).

We expanded the study to other indium halide additives (15 mm), and further elucidated the respective roles played by the Li-In alloy and LiF. The cell using InCl$_3$-added electrolyte exhibits stable evolution of the voltage profile as that of the InF$_3$ added cell (Figure S7b), implying that both LiF and LiCl are effective in enabling lithium migration and maintaining structural stability. However, cells with InBr$_3$ and InI$_3$ added electrolytes underwent a dramatic voltage increase after 70 and 40 cycles, respectively (Figure S7c). We observed that these electrolytes turned dark in color and gelled on the Li surface after cycling; thus we propose the occurrence of unexpected electrolyte decomposition/polymerization initiated by the strong Lewis acids I$^-$/Br$^-$ and the heat generated by the reaction shown in Equation (1).

To further demonstrate the practical significance of the in situ formed biphasic protective layer, Li metal cells were assembled using zero-strain Li$_2$Ti$_3$O$_7$ (LTO) as the working electrodes. The LTO/Li cells were cycled at 5C (ca. 1.9 mA cm$^{-2}$) in EC/DMC-based electrolytes. The cell using a blank alkyl carbonate electrolyte experienced sudden death at 320 cycles, whereas the InF$_3$-added cell exhibits stable cycling with a capacity retention of 67% over 1000 cycles (Figure 4c). Energy efficiency (EE) of the LTO/Li cell—defined as the discharge energy over charge energy—is an important metric to monitor the cell polarization (note the LTO cells exhibit nearly 100% coulombic efficiency over cycling (Figure S9)). The EE of the InF$_3$-added cell reaches a maximum of 82.5% after a few conditioning cycles, followed by slow fading to 73.8% over 1000 cycles, in contrast to the...
rapid fading from 79.5% to 64.7% over 320 cycles for the blank cell (Figure 4c). The voltage profiles for the 250th cycle in Figure 4d confirms the difference in polarization, indicating favorable ion transfer in the alloy-LiF based SEI. We have also coupled a LiFPEO electrode with the protected Li metal anode using a EC/DMC based electrolyte in the window of 2.2–4.2 V (Figure S10). While long-term cycling (as for LTO) has not yet been conducted at this preliminary stage, the positive effect of the layer is still apparent. We observed both higher capacity retention and lower voltage polarization for the cell using the InF3-added electrolyte versus the blank cell, confirming the validity of this approach to higher voltage batteries.

In conclusion, we show that the in situ formation of an lithium-conducting, electron-insulating, and chemically stable biphasic layer on the Li metal surface leads to dendrite-free and stabilized Li plating in alkyl carbonate electrolytes. The function of the biphasic layer is two-fold. The physical isolation of Li leads to significantly reduced parasitic reactions with the electrolyte, thus creating a uniform SEI and alleviating current/nucleation heterogeneity. The Li-In alloy provides efficient lithium-migration channels, allowing Li plating under the protecting layer, while the insulating LiF phase prevents electron transfer across the layer. Stable long-term plating/stripping of symmetric cells over 400 hours in carbonate electrolytes was demonstrated. This concept represents a viable and scalable avenue for generating an SEI with desired properties in situ using rationally designed electrolyte additives.

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Conflict of interest

The authors declare no conflict of interest.

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