Advanced energy storage systems are urgently needed to satisfy the continuously surging demand in consumer electronics, electric vehicles, and grid storage.\(^1\) Rechargeable Li metal batteries are considered the “Holy Grail” of energy storage systems because Li metal has an extremely high theoretical specific capacity (3860 mAh g\(^{-1}\)) and the lowest negative electrochemical potential (\(-3.04\) V versus the standard hydrogen electrode).\(^2\) However, rechargeable Li metal batteries have not yet been commercialized because of the uneven deposition/dissolution of Li metal and the side reaction between Li metal and electrolytes.\(^3\) Because of its highly reactive nature, Li metal reacts spontaneously with most organic electrolyte solvents and Li salts to instantly form a solid electrolyte interphase (SEI) layer on the Li surface. During the Li deposition process, the SEI layer is broken, and Li dendrites are generated at the sites where the current density is locally enhanced.\(^{2d}\) Therefore, a large amount of fresh Li metal is exposed to the organic electrolyte during the formation and growth of the Li dendrite, continuously generating new SEI layers during cycling. The repeated breakage and repair of the SEI layer consumes both Li metal and electrolyte, leading to the drying up of electrolyte and serious corrosion of the bulk Li,\(^4\) which further results in low Coulombic efficiency of the batteries.\(^{2c}\) Furthermore, the uncontrolled Li dendrite growth during long-term cycling often leads to short circuits and sometimes catastrophic failure.\(^{3f}\)

There are numerous reports in the literature which attempt to solve these problems. Various strategies have been developed to control the Li deposition morphology, including the use of modified separators,\(^6\) physical protective layers,\(^7\) nanostructured anodes,\(^8\) and electrolyte additives.\(^9\) These strategies can reduce the dendrite structure or block dendrite penetration. However, these strategies do not change the breakage/repair mechanism of SEI layer. Numerous approaches have been developed to enhance the stability of the SEI layer through optimization of electrolytes.\(^{10}\) These approaches can improve the stability of the SEI layer; however, because Li is thermodynamically unstable in organic solvents, achieving sufficient passivation of the Li surface in liquid solutions is difficult.

Recently, solid-state electrolyte protection film,\(^{11}\) carbon-based interlayers\(^{12}\) have been used as stable interface layers in the Li metal anode or silicon anode. However, as indicated by Aurbach and co-workers,\(^{13b}\) in a practical Li metal battery, the partial dissolution of the native film (Li\(_2\)CO\(_3\), LiOH, and Li\(_2\)O) and formation of the SEI layer lead to a porous structure where the Li ionic flux is locally enhanced, thereby promoting Li dendrite formation and growth.\(^{6a,b,c,11b}\) Removing the unstable composition of the native film while simultaneously forming a stable SEI layer is difficult. To address these issues, we designed an artificial Li\(_3\)PO\(_4\) SEI layer (Scheme 1) by in situ reaction of polyphosphoric acid (PPA) with Li metal and its native film. The uniform Li\(_3\)PO\(_4\) SEI layer was demonstrated to be stable in the electrolyte and during cycling in Li|LiFePO\(_4\) battery systems without a breakage/repair mechanism. Thus, the uniform Li\(_3\)PO\(_4\) SEI layer can restrain the unfavorable reaction between the Li metal and the electrolyte. Furthermore, the Li\(_3\)PO\(_4\) layer can enhance Li-ion transport between the Li metal interface and the electrolyte. Thus, Li dendrite growth can be restrained in Li|LiFePO\(_4\) battery systems.

To obtain a uniform artificial SEI layer, low moisture and reaction time control are necessary. A small amount of moisture, including the moisture in the dimethylsulfoxide (DMSO) solution, and using the 85 wt% H\(_3\)PO\(_4\) as the solute (Figure S1a–d, Supporting Information), can lead to a rough surface. Although PPA can adsorb the moisture in the DMSO solution and generate H\(_3\)PO\(_4\), high-purity DMSO (>99.9%) is necessary. A long reaction time can also lead to a porous and rough interface (Figure S1e,f, Supporting Information). As shown in the scanning electron microscopy (SEM) images (Figure 1a,b), the surface of the Li metal is smooth. Although the oxygen is uniformly distributed on the surface of the Li metal (Figure 1d), the carbon is nonuniformly distributed (Figure 1c), indicating that Li\(_2\)CO\(_3\) has a nonuniform distribution on the surface of the Li metal. After treatment of the Li metal with PPA solution, the resulting PPA-Li has a smooth and uniform surface (Figure 1e,f) on which phosphorus and oxygen are uniformly distributed (Figure 1g,h). The X-ray photoelectron spectroscopy (XPS) with argon-ion sputtering technology was employed to detect the depth profile information of the PPA-Li anode (Figure 1i). Although the artificial SEI layer can be up to \(\approx 200\) nm detected by SEM (Figure S2, Supporting Information), the dominant composition of artificial SEI layer at depth of 100, 150, 200 nm is Li metal. Thus, the effective thickness of the artificial SEI layer is \(\approx 50\) nm. The peak force tapping (PFT) mode\(^{14}\) of the atomic force microscopy (AFM) was employed to measure the morphology and the Young’s modulus of PPA-Li anode (Figure 1k).

Dr. N.-W. Li, Dr. Y.-X. Yin, C.-P. Yang, Prof. Y.-G. Guo
CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, and Beijing National Laboratory for Molecular Sciences
Institute of Chemistry, Chinese Academy of Sciences (CAS)
Beijing 100190, P. R. China
E-mail: ygguo@iccas.ac.cn
C.-P. Yang, Prof. Y.-G. Guo
University of Chinese Academy of Sciences
Beijing 100049, P. R. China

DOI: 10.1002/adma.201504526
The PPA-Li anode exhibits a smooth surface and the value of Young’s modulus is \( \approx 10^{-11} \) GPa. According to Newman’s and Balsara’s reports,[15] the solid film with a Young’s modulus higher than 6 GPa should be sufficient to suppress the lithium dendrite growth. The PPA-Li anode with thin artificial layer (PPA-Li-T) was also obtained using low-concentration treatment solution (Figures S3 and S4, Supporting Information). In local region of the PPA-Li-T anode, the Young’s modulus is lower than 6 GPa, which is adverse to restraining the lithium dendrite. To effectively evaluate the morphology of the Li anodes in the Li metal batteries, commercial LiFePO₄ cathodes were used as the counter electrodes. After 12 h of storage at open-circuit potential, the Li metal has a porous morphology (Figure 2a) because of the native film dissolution and the reaction between the Li metal and the electrolyte during SEI layer formation.[13b,c] Furthermore, the diethyl carbonate (DEC) in the electrolyte

![Scheme 1. Schematics of the different Li anode structures. a) The general Li metal and b) Li₃PO₄-modified Li metal anodes during SEI formation and cycling.](image)

![Figure 1. a) Low-magnification SEM image of Li metal, b) high-magnification SEM image of Li metal, and corresponding elemental mapping images of c) C and d) O. e) Low-magnification SEM image of PPA-Li, f) high-magnification SEM image of PPA-Li, and corresponding elemental mapping images of g) P and h) O. i) Depth profile for the PPA-Li anode. AFM image j) of PPA-Li anode and k) corresponding Young’s modulus mapping.](image)
promotes the corrosion phenomenon, as reported by Aurbach’s group.\textsuperscript{13b} Because of the complicated reaction between the electrolyte and Li metal,\textsuperscript{3, 13a,c} all of the elements, including carbon, oxygen, and fluorine, are aggregated at the edge of these porous structures, as evident in Figure 2a–d. Minimal carbon is observed in the porous structure because Li$_2$O and LiOH can react with the electrolyte, whereas Li$_2$CO$_3$ is more stable during SEI formation.\textsuperscript{13b,c} The current density is locally enhanced at the porous structure,\textsuperscript{6a, 13b} thereby the Li dendrite formation and growth during cycling (Figure S5, Supporting Information, and Figure 2i,j). In comparison with Li metal, all of the elements, including carbon, oxygen, and fluorine, are uniformly distributed on the smooth surface of the PPA-Li (Figure 2e–h) after storage for 12 h at open-circuit potential. Thus, the PPA-Li anode has a stable and uniform interface. Furthermore, because of the high Li-ion conductivity of the thin Li$_3$PO$_4$ SEI layer, no obvious Li deposition product or Li dissolution structure forms on the surface of the PPA-Li sample (Figure S6a–d, Supporting Information) during the first charge/discharge process. Thus, the PPA-Li anode exhibits a uniform and smooth structure (Figure 2k,l) after cycling. In comparison with the PPA-Li anode, the PPA-LiT anode exhibits a porous structure (Figure S3c,d, Supporting Information) to some extent after cycling because of the low Young’s modulus (<6 Pa) in local region of the PPA-LiT anode. Various current densities have been used to evaluate the artificial Li$_3$PO$_4$ SEI layer (Figure S7, Supporting Information). It is found that the PPA-Li anode exhibits a smooth interface, even in the current density of 0.5 mA cm$^{-2}$. Although the artificial Li$_3$PO$_4$ SEI layer is partial destroyed at high rate, the dendrite structure on the surface of PPA-Li anode is effectively reduced.

XPS was used to analyze the element content and valence on the surface of these Li anodes. The surface of the Li metal contains primarily Li, C, and O, whereas the surface of the PPA-Li anode contains mainly Li, C, P, and O (Figure S8, Supporting Information). In the C 1s spectra (Figure 3a) of Li metal, the peaks at ≈286.5, 288.5, 289.7, and 290.1 eV are assigned to C-C-O (reduction product of DEC), C-O-CO$_2$Li (reduction product of ethylene carbonate or dimethyl carbonate), Li$_2$CO$_3$, and ROCO$_2$Li, respectively.\textsuperscript{13a, 16} Li$_2$O disappears during formation of the SEI, whereas O-C-O increases during SEI formation and during cycling (Figure S9a, Supporting Information). Thus, the native film of Li metal is partially dissolved in the electrolyte, and the reduction products of the electrolyte emerge during the SEI formation process. The concentrations of these reduction products increase after cycling. Combined with the previous morphology research on Li metal, these results indicate that the unstable SEI underwent repeated breakage and repair during cycling, leading to massive losses of both Li metal and electrolyte.

In the P 2p spectra of the PPA-Li anode (Figure 3b), because of spin–orbit coupling, the peaks at 133.5 and 134.3 eV are attributed to two split components 2p$_{3/2}$ and 2p$_{1/2}$, respectively, which correspond to the phosphate group (PO$_4^{3-}$).\textsuperscript{17} On the basis of the XPS results, the surface composition of the PPA-Li
anode is Li$_3$PO$_4$ with a small amount of adsorbed organic carbon and little residual DMSO (Figure S10, Supporting Information). In comparison with the Li metal, the native film of Li metal has been replaced by Li$_3$PO$_4$. Furthermore, except for a small amount of LiPF$_6$ and LiF, no obvious change in the surface composition of PPA-Li is evident after storage at open-circuit potential and even after cycling. Combined with the morphology of PPA-Li during cycling, the artificial Li$_3$PO$_4$ layer is stable in the Li metal battery system. In comparison with the Li metal anode, few electrolyte reduction products are present on the surface of the PPA-Li anode after storage at open-circuit potential and even after cycling. Thus, the artificial Li$_3$PO$_4$ layer effectively reduced the side reaction between Li metal and the electrolyte.

To further elucidate the interfacial stability of the PPA-Li anode, electrochemical impedance spectroscopy (EIS) measurements were performed on the symmetric cell. In the Nyquist plots (Figure S11, Supporting Information), the semicircle at high frequency is associated with the resistance through the SEI layer ($R_{SEI}$). In the cell assembled with the symmetric Li electrode, the initial $R_{SEI}$ is less than that of the cell assembled with the PPA-Li electrode. However, the $R_{SEI}$ value continuously increases with time, which is attributed to the gradual growth of a resistive surface layer due to the reaction between the Li metal and the organic electrolyte. Only a small increase is observed in the $R_{SEI}$ value of the PPA-Li electrode, indicating that the stable Li$_3$PO$_4$ layer effectively restrains the reaction between the Li metal and the electrolyte. Furthermore, the Nyquist plots of the Cu foil|Li half-cell and the LiFePO$_4$|Li full cell (Figures S12 and S13, Supporting Information) indicate that the artificial Li$_3$PO$_4$ SEI layer can enhance the Li-ion transport on the Li metal interface during cycling.

The performance of the Li|LiFePO$_4$ battery systems constructed using Li anodes is shown in Figure 4 and Figure S14 (Supporting Information). The capacity increase is attributed to the activation process of the LiFePO$_4$ materials.[19] (Figure 4a). After activation process, the polarization between the charge and discharge plateaus for the PPA-Li cell is lower than that for the Li metal cell (Figure 4b), which indicates that the kinetics of the full cell are significantly improved by the artificial Li$_3$PO$_4$ SEI layer.[20] The better cycling stability of the full cell using the PPA-Li anode is attributed to its stable interface in the Li|LiFePO$_4$ battery system. To assess the morphologies of Li anodes after long-term cycling in the Li metal batteries, we disassembled the Li|LiFePO$_4$ battery systems after 200 cycles. The Li metal exhibits a loose and porous structure with a thickness of ≈200 µm (Figure 4c,d). A large amount of bulk Li was consumed during the long-term cycling because of the repeated breakage/repair of the SEI layer.[22,4a] The PPA-Li anode still exhibits a smooth and compact interface without obvious dendrite structure after 200 cycles (Figure 4e,f). As no perfect artificial SEI layer is present, there are some inevitable cracks on the PPA-Li anode. However, the corrosion of bulk Li is obviously reduced after long cycling (Figure 4e). Thus, the smooth and compact interface on the PPA-Li anode can restrain the developing of the cracks, and can prevent further corrosion of Li metal. Furthermore, the PPA-Li anode also can be used in the Li-S battery (Figure S15, Supporting Information).

A symmetric Li|Li cell with a hollow spacer as the separator was used to further investigate the stability of the PPA-Li anode (Figure S16, Supporting Information). The Li|Li symmetric cell exhibits a large and irreversible voltage drop at 55 h (Figure S17, Supporting Information), which is attributed to cell failure by dendrite-induced short circuit.[10b,21] By contrast, the PPA-Li|LiFePO$_4$ symmetric cell is cycled for over 600 h without short circuiting (Figure S17, Supporting Information), indicating that the Li dendrite growth has been significantly restrained. This result further demonstrates the exceptional cycling stability of the PPA-Li anode.

Our results demonstrate an innovative strategy to restrain Li dendrite growth and reduce the side reaction between the electrolyte and the Li metal by inducing the formation of an artificial Li$_3$PO$_4$ SEI layer on the surface of the Li metal. The innovative design of the artificial SEI layer has four outstanding characteristics: (1) replacing the Li native film with a uniform Li$_3$PO$_4$ SEI layer via an in situ reaction, (2) excellent chemical stability in a highly reducing environment, (3) high Young’s modulus, and (4) high Li-ion conductivity. The native film of Li metal is not stable in the electrolyte.[13,4c] In our rational design, PPA can react with Li metal and its native film, including Li$_2$CO$_3$, Li$_2$O, and LiOH, and can form a uniform Li$_3$PO$_4$ film. Thus, the native film of Li metal can be removed and a uniform Li$_3$PO$_4$...
SEI layer can be obtained simultaneously. The uniform and smooth interface is not sufficient to restrain the formation of Li dendrites. As indicated by Aurbach et al., Li is thermodynamically unstable in organic solvents.\(^{13b,c}\) Thus, the chemical stability of the interface film is important for the Li metal anode. The partial dissolution of the native film and the formation of the SEI layer lead to a porous structure of the Li surface, thereby promoting Li dendrite growth during the Li deposition/dissolution process (Scheme 1). The repeated breakage and repair of the SEI layer consumes both Li metal and electrolyte, leading to the drying up of the electrolyte and to serious corrosion of the bulk Li metal.\(^{22}\) In our rational design, the uniform Li\(_3\)PO\(_4\) interface layer is chemically stable in the organic electrolyte, even during the Li deposition/dissolution process, thereby reducing the side reaction between Li metal and electrolyte.

Thus, the artificial Li\(_3\)PO\(_4\) SEI layer can restrain the breakage/repair of the SEI layer during the Li deposition/dissolution process. In addition, the high Young’s modulus is necessary to the artificial SEI layers. The artificial SEI layers with high Young's modulus around 10–11 GPa can effectively restrain the lithium dendrite growth. Furthermore, high ionic conductivity is necessary for the artificial SEI layer. In the absence of high ionic conductivity, the interface film would be rapidly destroyed during the Li deposition/dissolution process.\(^{22}\) Li\(_3\)PO\(_4\), especially the Li\(_3\)PO\(_4\) thin film, possesses good Li-ion conductivity.\(^{22}\) The PPA-Li anode with artificial Li\(_3\)PO\(_4\) SEI layer can enhance the Li-ion transportation on the Li metal interface during cycling. With these characteristics, the artificial Li\(_3\)PO\(_4\) SEI layer can effectively restrain Li dendrite growth and reduce the corrosion of bulk Li during long-term cycling in a Li|LiFePO\(_4\) battery.

Figure 4. a) Cycling performance of the Li|LiFePO\(_4\) battery system using Li metal and PPA-Li anodes. b) The typical charge/discharge profiles after activation at a current rate of 0.5 C. The inset of (b) shows enlarged profiles. c) Side-view SEM image and d) top-view SEM image of the Li metal anode after 200 cycles. e) Side-view SEM image and f) top-view SEM image of the PPA-Li anode after 200 cycles.
system. Consequently, the artificial Li$_3$PO$_4$ SEI layer approach is a promising strategy to address the Li metal anode problems in Li metal batteries. Numerous possible approaches could be used to improve the artificial SEI layer, including doping and optimization of the reactant.

In conclusion, we demonstrated that an artificial Li$_3$PO$_4$ SEI layer with high Young’s modulus can restrain Li dendrite growth and reduce the side reaction between Li metal and the organic electrolyte. In the ingenious design, the native film of Li metal was replaced by the stable and uniform Li$_3$PO$_4$ SEI layer via an in situ treatment process. The Li$_3$PO$_4$ SEI layer exhibits high chemical stability during the Li deposition/dissolution process without a breakage and repair mechanism. Thus, the uniform Li$_3$PO$_4$ SEI layer effectively restrains Li dendrite growth and reduces the corrosion of bulk Li after 200 cycles in a Li/LiFePO$_4$ battery. The artificial SEI strategy we described is a promising route to tackle the intrinsic problems of Li metal anodes and other metal-based anodes. Totally solving the problems of metallic Li anode will require strategies from a range of techniques including artificial SEI layers, functional electrolytes, current collectors, and separators, and their success will promote the development of next-generation rechargeable Li metal batteries.

Supporting Information

Supporting Information is available online from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51225204, 21127901, and 1103244), the National Basic Research Program of China (Grant Nos. 2013AA050903 and 2012CB932900), and the “Strategic Priority Research Program” of the Chinese Academy of Sciences (Grant No. XDA09010000).

Received: September 14, 2015 Revised: November 17, 2015 Published online: December 23, 2015


