Efficient and stable operation of a lithium (Li) metal anode has become the enabling factor for next-generation high capacity energy storage systems. Due to its highest theoretical specific energy (3860 mAh g⁻¹), low density (0.534 g cm⁻³), and the lowest electrochemical potential (−3.040 V vs standard hydrogen electrode), a Li metal anode has long been considered the “Holy Grail” of battery chemistry. Nevertheless, fundamental challenges remain for a Li metal anode despite almost five decades of research, which prevents it from practical applications in rechargeable batteries.

A natural solid electrolyte interphase (SEI) is known to form on Li metal surfaces when in contact with organic electrolytes and functions as a passivation layer. However, as a “hostless” electrode, the virtually infinite volumetric change during Li stripping/plating induces significant mechanical instability in the relatively fragile SEI layer, leading to the formation of cracks. The cracks locally enhance the Li-ion flux, which result in nonuniform Li deposition with dendritic morphology that can trigger an internal short circuit and compromise the safety of battery operation. Moreover, the high-surface-area ramiﬁed Li and the recurring breakdown/repair of SEI bring about continuous side reactions, severely reducing the cycle life.

In recognition of the problems associated with the “hostless” nature of Li metal, stable hosts such as layered reduced graphene oxide and nanofibers with “lithiophilic” coatings have been successfully introduced for metallic Li. For the first time, the approach minimized the volumetric change at the whole electrode level during Li plating/stripping. Moreover, porous Li with highly increased surface area can be obtained, which reduces the effective current density and the degree of interface fluctuation during cycling, leading to more uniform Li deposition with greatly improved cycling stability. Other approaches exploring 3D conductive current collectors demonstrated similar effects in confining Li dendrites and improving cycling efficiency. Thus, further engineering of the SEI layer on porous Li nanocomposite electrodes shall be the next leap needed to push the cycling efficiency closer to real battery operation requirements.

It is apparent from the above discussion that the quality of the SEI layer is critical for the efficient and stable operation of Li metal anodes and several requirements need to be satisfied for an ideal SEI layer. First, it has to be homogeneous in all aspects (composition, morphology, etc.) to prevent only limited locations of Li metal nucleation and growth. Second, it shall possess high elastic modulus and compact structure, for theoretical predictions have shown that a solid film with modulus on the order of 1 GPa should be sufficient in suppressing dendrite. Third, the SEI layer has to be ﬂexible enough to accommodate the ineligible interface ﬂuctuation during battery cycling without repeated breakdown/repair. And more importantly, high ionic conductivity of the SEI layer is essential to facilitate the easy and uniform transport of Li-ions throughout the whole electrode surface. However, native SEI can hardly meet all the requirements, which necessitates the rational design of artificial SEI.

The concept of artificial SEI has been actively explored in previous studies, and various artificial coatings have been applied on Li foil surfaces, such as polyacetylene, tetraethoxysilane, lithium phosphorus oxynitride, Al₂O₃ particles, and ultrathin Al₂O₃ film via atomic layer deposition. Admittedly, these coatings are effective to some extent in suppressing side reactions and Li dendrite formation, especially under static conditions or at the initial stage of cycling. Nevertheless, the protective effects often wear off after prolonged battery operations. This can be attributed to the fact that most of these studies focused only on a single aspect of the SEI requirement, such as providing strong physical barriers or certain Li-ion conductivity, while failed to take the whole picture into consideration. Inadequate thickness or compositional control of the coatings may lead to compromised SEI homogeneity and more importantly, given the limited Li-ion conductivity or poor ﬂexibility of the coating materials, the cracking of the artificial SEI layers during cycling will induce even greater inhomogeneity on Li metal surface, exacerbating dendrite growth and side reactions.

Herein, we propose the rational design of an artificial SEI layer, composed of Cu₃N nanoparticles joined together by styrene butadiene rubber (Cu₃N + SBR), which can simultaneously possess high mechanical strength, good flexibility, and high Li-ion conductivity being all indispensable for...
an ideal SEI. Notably, the Cu₃N nanoparticles will be passivated spontaneously when in contact with metallic Li to form Li₃N, which is among one of the fastest Li-ion conductors with ionic conductivity on the order of \( \approx 10^{-3} - 10^{-4} \, \text{S cm}^{-1} \) at room temperature [27–29]. This can effectively facilitate the transport of Li-ions across the electrode surface, resulting in more uniform Li-ion flux. Moreover, compared to pure inorganic phase coatings, composite artificial SEI with both inorganic nanoparticles and a polymeric binder can better maintain structural integrity during Li plating/stripping thanks to the good flexibility of the SBR, which is also desirable for SEI homogeneity. Furthermore, the proposed artificial SEI can be applied via a facile solution coating process with good thickness and compositional control and also applicable to porous Li electrodes. The introduction of such an artificial SEI layer with superior Li-ion conductivity, mechanical strength, and flexibility significantly enhanced the stability of the Li metal anode both under static condition and during prolonged cycling. The Coulombic efficiency can be improved to above 97.4% with a current density up to 1 mA cm⁻² in corrosive carbonate electrolyte on copper (Cu) current collector and if applied on porous Li-coated polyimide–zinc oxide electrode (Li-coated PI–ZnO), the coating rendered a 40% increase in cycle life when paired with Li titanate (LTO).

Figure 1a schematically illustrates the fabrication process of the Cu₃N + SBR artificial SEI layer and its microstructure. Cu₃N nanoparticles with a size of sub-100 nm were synthesized via a facile one-step reaction between Cu(II) methoxide (Cu(OMe)₂) and benzylamine (Figure S1, Supporting Information) [30]. The resulting nanoparticles can be readily dispersed in tetrahydrofuran (THF) with SBR to form a stable colloidal solution, which can then be applied on the Li surface via doctor blade casting or drop casting to afford a conformal protection layer. When in contact with Li, Cu₃N nanoparticles can be converted to Li₃N, rendering a protective Li metal surface coating with a mechanically strong Li-ion conducting inorganic phase connected tightly within a flexible polymeric matrix. Compare to unprotected Li, the highly Li-ion conducting artificial SEI not only mechanically suppresses Li dendrite but also contributes to the even distribution of Li-ion flux across the electrode surface, resulting in more uniform Li plating/stripping behavior (Figure 1b).

Figure 2a shows the scanning electron microscopy (SEM) image of the as-synthesized Cu₃N nanoparticles, which clearly reveals nonagglomerated nanoparticles with size below 100 nm. A powder X-ray diffraction (XRD) pattern confirms the crystallinity of the nanoparticles, which matches well with the Cu₃N standard (JCPDS No. 55-0308, Joint Committee on Powder Diffraction Standards, Figure 2b). Noticeably, the Cu₃N nanoparticles can afford a stable dispersion in THF for days without precipitation nor chemical degradation, as little changes in the XRD pattern can be detected for samples dispersed overnight in THF (Figure 2b). Such small particle size, good dispersity and chemical stability make the Cu₃N nanoparticles desirable to yield a uniform and conformal coating on the Li metal surface.
In order to evaluate the electrochemical properties of the Cu$_3$N+SBR artificial SEI layer, it was first applied on a Cu foil current collector via doctor blading. Figure 2c shows the top-view SEM image of the artificial SEI layer, where a dense and uniform composite coating can clearly be observed. The thickness (400 nm and above) of the coating layer can be changed easily by adjusting the gap size of the blade, demonstrating the facileness and great tunability of our proposed method for Li metal surface stabilization (Figure S2, Supporting Information). Cyclic voltammetry (CV) were carried out to confirm the conversion of Cu$_3$N to Li$_3$N in the presence of metallic Li (Figure 2d). During the first CV cycle, a main cathodic peak at $\approx$0.48 V (vs Li$^+/\text{Li}$) can be observed, confirming the lithiation of Cu$_3$N to Li$_3$N and Cu. It shall be noted that the conversion reaction of Cu$_3$N is only partially reversible. During the first delithiation, the anodic peak centered at $\approx$1.3 V corresponds well with the oxidation of Cu$_0$ to Cu$^+$ in Cu$_3$N, while the anodic peak at $\approx$2.1 V shall be associated with the oxidation of Cu$^+$ to Cu$^{2+}$ in Cu$_2$O. And redox peaks belonging to both nitride and oxide can be seen in subsequent CV cycles.$^{[30,31]}$ Fortunately, the electrochemical potential of the Li metal anode will usually not exceed the decomposition voltage ($\approx$0.5 V theoretically) of Li$_3$N under normal operation conditions.$^{[32]}$ which guarantees the validity of our proposed coating as a Li-ion conducting artificial SEI on Li metal electrode. Raman spectra of the Cu$_3$N+SBR artificial SEI after lithiation exhibited distinctive peaks in accordance with those of standard Li$_3$N powder, corroborating the CV measurements (Figure S3, Supporting Information).$^{[33]}$

The morphology of Li deposition on a Cu$_3$N+SBR protected Cu current collector was then studied to evaluate the dendrite suppression capability of the artificial SEI. Specially fabricated crimped separators with a Li-ion conducting area of 0.5 cm$^{-2}$ were used for all the electrochemical measurements, which can provide a more accurately defined effective area, and thus current density, compare to normal separators (Figure S4, Supporting Information). The protected Cu current collectors were subjected to ten activation cycles between 0 and 0.4 V at a low current density of 0.01 mA cm$^{-2}$ to ensure the complete conversion of Cu$_3$N before being cycled galvanostatically at different current densities, and an upper cut-off voltage of 0.4 V was set for the cycling to prevent the decomposition of Li$_3$N. After five galvanostatic plating/stripping cycles at a current density of 0.5 mA cm$^{-2}$ and a capacity of 0.5 mAh cm$^{-2}$, there were no observable dendrites on Cu foil protected by the mechanically robust and highly Li-ion conducting Cu$_3$N+SBR artificial SEI (Figure 3a), while excessive wire-shaped Li with diameter around 1–2 µm has already formed on the bare Cu counterpart (Figure 3b). The color of the Li deposit on the protected Cu foil remained silver and shiny, similar to that of pristine Li metal (Figure 3c). In contrast, dark gray Li was observed for deposition directly on bare Cu, stemming from a less compact Li deposition morphology (Figure 3d).$^{[34]}$ The effective dendrite
suppression can be attributed to the Li-ion conducting artificial SEI that fostered a uniform Li-ion flux to prevent local “hot spots” as well as the high elastic modulus of the inorganic nanoparticles that mechanically impeded the dendrite formation.

The mechanical properties of the artificial SEI were evaluated using nanoindentation. The elastic modulus versus depth curves are shown in Figure S5 (Supporting Information), in which the modulus of the artificial SEI increased from 0.71 to 0.81 GPa. The slight increase in modulus was due to densification of the artificial SEI resulting from the Cu3N nanoparticle packing under compression.15,36 The low modulus from depth 0 to ≈1.5 µm was likely due to a combination of imperfect alignment between the flat punch indenter and the artificial SEI surface, and the effect of surface roughness. A simple analysis was performed to verify the effect of misalignment as shown in Figure S6: the indenter was found to be at θ = 2.3° relative to the artificial SEI surface and began contact starting from one side of the circular punch as indicated by r. Since r = h/θ, the contact area was a function of the indentation depth and a corrected modulus was calculated. A representative elastic modulus versus depth curve was corrected based on this analysis and is shown by the red curve in Figure 3f. The “dip” in modulus at h < 0.7 µm was related to the surface roughness of the artificial SEI (arithmetic mean roughness, Ra = 0.44 µm, and root mean squared roughness, Rq = 0.58 µm) as shown in Figure S6 (Supporting Information). An elastic modulus on the order of 1 GPa is known to help suppress Li dendrites.

Coulombic efficiency, which is defined as the ratio between the extractable and the deposited capacity, is another crucial parameter to examine for a practical Li metal anode. Although it remains a great challenge to determine the exact Coulombic efficiency of anodes with prestored Li,11,12 measuring the value on Cu3N + SBR protected Cu current collectors could serve as direct evidence of the stabilizing effect our proposed artificial SEI layer when applied on Li metal surface. As can be seen from Figure 4a, at a current density of 1 mA cm−2 in carbonate electrolyte (1 M lithium hexafluorophosphate in 1:1 ethylene carbonate/diethyl carbonate (EC/DEC) with 10 wt% fluoroethylene carbonate additive), the Coulombic efficiency of bare Cu started at around 95% and quickly decayed to merely 70% within 50 stripping/plating cycles due to the growth of Li dendrites and the continuous breakdown/repair of SEI that consumed both Li and the electrolyte. Surprisingly, the Cu3N + SBR protected Cu demonstrated a much improved Coulombic efficiency of ≈97.4% averaged between the 20th and 70th cycles and such high efficiency performance was able to be sustain for more than 100 cycles. In addition, the overpotential increase due to the existence of the artificial SEI was minimal (Figure 4a inset), thanks to its relatively high ionic conductivity. Since the effective current density can be significantly reduced on porous Li metal anodes, Coulombic efficiency at a lower current density of 0.25 mA cm−2 was also studied to better resemble the real working condition of the artificial SEI protected porous Li. With reduced current density, the Coulombic efficiency increased to as high as ≈98%, which was stable for at least 150 cycles (Figure 4b). It is known that higher cycling efficiency can be expected in ether electrolyte due to the formation of a relatively flexible oligomer SEI that could better withstand the volumetric change during battery cycling.37 Accordingly, with
the protection of the Cu₃N + SBR artificial SEI, the Coulombic efficiency at 0.25 mA cm⁻² was on average 98.5% for more than 300 cycles in ether electrolyte (Figure S7, Supporting Information, 1 M lithium bis(trifluoromethanesulfonyl)imide in 1:1 w/w 1,3-dioxolane/1,2-dimethoxyethane with 1 wt% lithium nitrate additive). Such significant improvement in cycling efficiency, especially in the corrosive carbonate electrolyte, strongly indicates that the Cu₃N + SBR artificial SEI layer can indeed suppress Li dendrite propagation and retard the continuous breakdown/repair of the SEI on a Li metal surface. Moreover, the drastic morphological differences in the SEI layer after prolonged battery cycling strongly support the Coulombic efficiency measurements (Figures S8 and S9, Supporting Information). SEI as thick as tens of micrometers was accumulated on the bare Cu electrode while the SEI layer on the protected electrode was thin and uniform. Finally, it shall be noted that the composite coating outperformed coatings with Cu₃N nanoparticles or SBR alone (Figure S10, Supporting Information). The Coulombic efficiency of the pure inorganic coating started high with a much faster decay for it is more prone to cracking without

Figure 4. Coulombic efficiency of Cu₃N + SBR artificial SEI protected Cu foil and bare Cu foil at a current density of a) 1 mA cm⁻² (cycling capacity 1 mAh cm⁻²; inset, the corresponding voltage profiles at the 20th cycle) and b) 0.25 mA cm⁻² (cycling capacity 0.5 mAh cm⁻²). c) SEM image and digital photography of the Cu₃N + SBR (1 mil) protected Li metal foil. d) The equivalent circuit for the interpretation of the impedance spectra. e) Summary of the $R_{SEI}$ value as a function of cycle number.
the flexible polymeric binder, demonstrating the synergistic effect between the inorganic and the polymeric phase. And there existed an optimal coating thickness (=1 μm, 1 mil doctor blade) for the artificial SEI layer; coatings that are too thin do not provide sufficient mechanical property to suppress Li dendrite propagation while coatings that are too thick compromise the impedance of the cell (Figure S11, Supporting Information).

To further investigate the stabilizing effect of the artificial SEI layer, Cu3N + SBR was doctor bladed onto a Li foil surface (Figure 4c), and electrochemical impedance spectroscopy measurements in a symmetric cell configuration were performed under both static and continuous cycling conditions in a EC/DEC electrolyte. The equivalent circuit for the interpretation of the impedance spectra is shown schematically in Figure 4d. The Ohmic part of the cell (RΩ) reflects a combined resistance of the electrolyte, separator, and electrodes. RSEI and CPE1 are the resistance and capacitance of the SEI layer on the surface of two electrodes, which corresponds to the semicircle at high frequencies. Rct and Cdl are the charge transfer resistance and its relative double-layer capacitance, which appear as a semicircle at medium frequencies. Zw represents the Warburg impedance related to a combined effect of Li-ions diffusing across the electrode–electrolyte interfaces, corresponding to the sloped line at low frequency end. Under an open circuit potential condition (Figure S12, Supporting Information), the impedance of bare Li foil increased with increasing storage time, indicating that the native SEI on Li metal cannot fully passivate the surface. On the contrary, only a small increase in impedance was observed for the protected Li foil thanks to the compact Cu3N + SBR layer that hindered the reaction between the Li metal and the electrolyte. When the symmetric cells were cycled galvanostatically at a current density of 0.5 mA cm−2 and a capacity of 1 mAh cm−2 (Figure S13, Supporting Information), the size of the semicircle at medium frequency decreased significantly with the cycle number for a bare Li foil due to the increase in Li surface area (dendrite formation) while the variation in Rct was much smaller for the protected Li foil. This further confirmed the dendrite suppression capability of the artificial SEI. More importantly, a continuous increase in the RSEI value was observed for the bare Li foil, which indicates the repeated breakdown/repair of the native SEI during cycling (Figure 4e). Nevertheless, Li protected by the artificial SEI layer showed nearly constant Rs at throughout 200 cycles. Thus, it is evident that the Cu3N + SBR coating is beneficial in forming a stable and less resistive SEI layer on Li metal surface during prolonged battery cycling.

Finally the protective effects of the Cu3N + SBR artificial SEI was tested on a novel 3D porous Li metal anode, which was fabricated via thermal infusion of molten Li into zinc oxide coated polyimide nanofibers (Li-coated PI–ZnO, Figure S15, Supporting Information). Thanks to the high porosity and rapid liquid intake of the Li-coated PI–ZnO, the coating solution can be drop casted and evenly spread across the electrode to afford conformal coating. Due to the reason that it remains challenging to determine the exact Coulombic efficiency value of electrodes with prestored Li,[11,12] a semiquantitative method was adopted instead. Namely, the high areal capacity LTO electrode (=3 mAh cm−2) was paired with an oversized Li metal anode (=10 mAh cm−2). Figure 5a) such that the cycle life of the cells can reflect the Coulombic efficiency of the anode well. If the Li metal electrode has a Coulombic efficiency of ≈90%, 0.3 mAh cm−2 of Li will be lost at each cycle and the cell will start to decay at ≈23 cycles (0.3 mA cm−2 × 23 = oversize 7 mAh cm−2 of Li). If the efficiency is lower, the cycle life will be even shorter (80%: 12 cycles; 70%: 8 cycles). Notably, LTO is a good choice as the counter electrode for it has no prestored Li and the cycling efficiency can be nearly 100% despite the initial cycle (=90%, Figure 5b black line shows the stable cycling of LTO with highly oversized Li, 750 μm) so that Li lost can be mainly attributed to the anode side. As can be seen in Figure 5b, at a cycling current density of ≈1.5 mAh cm−2, a Li foil with 50 μm in thickness (theoretical capacity 10 mAh cm−2, orange line) started to decay at 20 cycles, indicating that the Coulombic efficiency is ≈88.3%. The performance was even worse for an electrodeposited Li (green line), which started to decay only at eight cycles (Coulombic efficiency ≈70%). However, with the introduction of a stable host for Li, no obvious decay can be observed for a Li-coated PI–ZnO electrode for the first 65 cycles, corresponding to a Coulombic efficiency of ≈96.4% (blue line).

Figure 5. a) Stripping capacity of Li-coated PI–ZnO anode after the application of the Cu3N + SBR artificial SEI with an areal capacity of 10 mAh cm−2. b) Discharge capacity of various Li metal anode-LTO cathode cells for the first 100 galvanostatic cycles in EC/DEC with 1 vol% vinylene carbonate. Rate was set at 0.2 C for the first two cycles and 0.5 C for later cycles (1 C = 170 mA g−1). The areal capacity of the cathodes was ≈3 mAh cm−2.
Further improvement in cycle life can be clearly observed after the artificial SEI protection (red line), where stable cycling was sustained for at least 90 cycles (Coulombic efficiency ≈97.4%), the actual value shall be even higher considering the low first cycle Coulombic efficiency of LTO). The indirect method demonstrates the effectiveness of the artificial SEI coating on further improving the performance of porous Li metal anode toward practical battery applications.\[39\]

In conclusion, the quality of the SEI layer is a critical determinant for the efficient and stable operation of Li metal anodes, which needs to be mechanically strong yet flexible enough to accommodate volume change during cycling and be extremely homogeneous in all aspects including not only composition, morphology but also ionic conductivity. To realize such a goal, we proposed the rational design of a composite artificial SEI layer, consisted of sub-100 nm Cu$_3$N nanoparticles connected tightly within a polymeric binder matrix, which can be converted into a highly Li-ion conducting Li$_3$N phase on a Li metal surface. Compared with single-component artificial SEI layers, pronounced synergistic effects can be observed between the inorganic nanoparticles and the polymeric binders; namely, the closely packed inorganic phase provided mechanical stiffness to suppress Li dendrite propagation while the polymeric phase maintained the integrity of the film without cracking in the presence of the significant interface fluctuation during battery cycling. More importantly, the high Li-ion conductivity of the artificial SEI guaranteed uniform Li-ion flux across the whole electrode surface and prevented the formation of local “hot spots.” And the facile solution processing of the artificial SEI not only offered great tunability of the film but also made it applicable to porous Li anodes with stable host. Thanks to its outstanding Li-ion conductivity, mechanical properties, and chemical stability, the artificial SEI layer can effectively suppress Li dendrite formation and protect the Li metal surface from repeated SEI breakdown/repair under both static and long-term cycling conditions. Moreover, the cycling efficiency of the protected porous Li metal anode can be clearly improved when paired with LTO, demonstrating our proposed approach as a promising way to tackle the problem of Li metal, and push porous Li one step closer toward practical applications for next-generation rechargeable batteries.

Experimental Section
The experimental methods can be found in the Supporting Information.

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

Acknowledgements
The work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the US Department of Energy under the Battery Materials Research (BMR) program and the Battery 500 Consortium program.

Received: October 13, 2016
Revised: November 7, 2016
Published online:

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