DE-EE0006828

Nanoscale Interfacial Engineering for Stable Lithium Metal Anodes (Stanford University)

Yi Cui, Principle Investigator
Stanford University
Department of Materials Science and Engineering, Stanford University
Stanford, CA 94305
Phone: (650) 723-4613; Fax: (650) 736-1984
E-mail: yicui@stanford.edu

Tien Duong, DOE Program Manager
DOE EERE, Office of Vehicle Technology, Battery Materials Program (BMR)
E-mail: Tien.Duong@ee.doe.gov

Start Date: Oct. 1, 2014
End Date: June 30, 2018

Executive Summary

Li-ion battery has gain great success as the power source for portable electronics, electric vehicles and grid scale energy storage. However, its energy density has achieved a bottleneck which calls for the further innovation of battery technologies especially those beyond Li-ion. Li metal anode has long been regarded as the "holy grail" for Li battery research, which is not only due to its highest theoretical capacity of 3860 mAh/g and lowest electrochemical potential, but also its key role in Li-S and Li-air battery systems, both of which are the most prominent battery chemistries for the next-generation energy storage technology. However, many challenges have been encountered on its way to commercialization. Among all problems of Li metal, there are two root causes, namely high reactivity of Li and its infinite relative volume change during cycling. On one hand, the high reactivity of Li results in the excess side reactions once is exposed to liquid electrolyte, which further lead to complex interfacial chemistry, blocked ion transport and the consumption of materials. On the other hand, the infinite relative volume change makes the solid electrolyte interphase (SEI) prone to fracture, which not only creates hot spots for uneven Li-ion flux distribution and thus dendritic deposition, but also exposes fresh Li for further side reactions, leading to low Coulombic efficiency. Under the circumstance, it is necessary to develop surface protection techniques as well as to improve the electrode volume stability in order to solve all the above-mentioned problems. Correspondingly, we successfully developed a set of nano-synthesis techniques to realize the proposed concepts in this study.

The major achievements through this study include:

- The development of novel, three-dimensional Li composites to minimize the electrode-level volume change and excessive interfacial fluctuation during cycling.

- The development of various Li metal surface coating materials (inorganic materials, polymers, composites, etc.) and fundamentally studied the relationships between material properties and the electrochemical performance of Li metal anode
- The combination between three-dimensional Li and effective surface coating rendered significant improvement in Li metal cycling efficiency and safety

Results

1. Three-dimensional Li metal composites

Li metal is the ultimate anode for Li batteries, but dendritic deposition and the infinite relative dimension change during cycling severely impede its practical applications. To realize Li metal anodes, continuous effort has been made for decades to understand the mechanism of Li deposition and tackle dendrite formation, as well as unstable solid electrolyte interphase (SEI). The strategies employed previously can be broadly divided into three categories: (i) developing electrolyte additives for the stabilization of SEI; (ii) engineering high-modulus solid electrolytes to prevent dendrite penetration; and (iii) designing electrochemically and mechanically stable artificial interfaces for SEI stabilization and dendrite suppression. All of the above are efficacious to a certain extent for mitigating either or both dendritic Li growth and SEI collapse. Nevertheless, none of them is capable of addressing the infinite relative electrode dimension change caused by the ‘hostless’ Li plating/stripping. The stabilization of the electrode dimension is recognized to be equally important for practical applications of Li anodes. With infinite relative volume change, the resulting huge internal stress fluctuations and the floating interface can damage the cells, leading to potential safety hazards and causing tremendous engineering challenges for implementing the battery in a confined space. More importantly, SEI stability is also strongly correlated with dimension stability. The SEI may not be able to accommodate the drastic volume variation and would thus face the danger of collapse during continuous cycling. Such SEI collapse can in turn exacerbate the locally favorable Li dendrite growth and the continuous electrolyte decomposition. As a consequence, a new approach capable of solving these multifaceted problems would be indispensable.

The infinite dimension change of Li is originated from its ‘hostless’ nature. To address the problem, rational design of a ‘host’ for metallic Li is necessary. Carbon-based materials are the ideal hosts for Li due to the reason that they are among the lightest materials available for scaffold construction and can be engineered to have appealingly high surface area with excellent mechanical strength. Moreover, carbon materials are generally stable under the redox environment in Li batteries. Thus, we studied the relative affinity of Li for different carbon materials by contacting them with molten Li. It was found that different from other carbon materials, reduced graphene oxide (rGO) have a remarkably high 'lithiophilicity' thanks to the abundancy of polar surface functional groups (**Figure 1**). The intrinsic lithiophilicity of GO was utilized by directly contacting vacuum-filtrated GO film with molten Li and Li can be drawn rapidly into the matrix without any additional surface modification (**Figure 2**). The resulting electrode can be described as a layered structure with Li uniformly infused into the nanogaps between rGO layers. This layered Li-rGO composite electrode can not only realize highly reduced dimension change during electrochemical cycling, effective dendrite suppression due to increased surface area and lithiophilic surface, but also the rGO cap layer can serve as a scaffold for SEI stabilization, improving the cycling Coulombic efficiency.

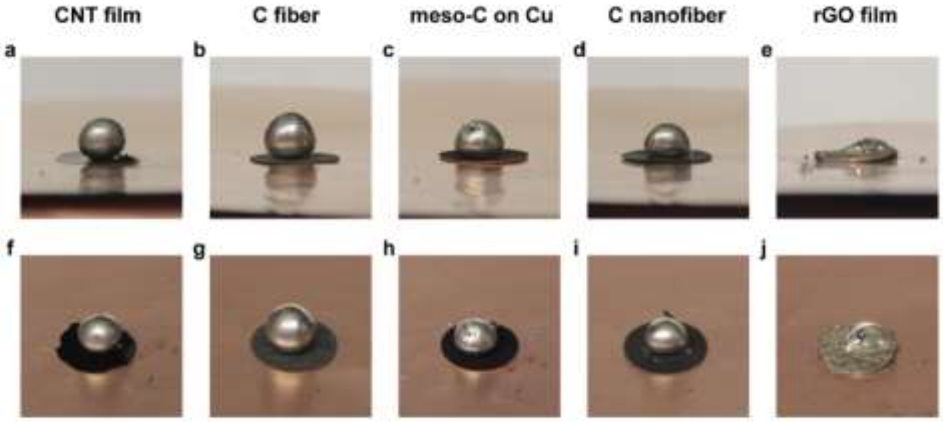

Figure 1: Surface wetting of molten Li on different carbon materials, including carbon nanotubes (CNT) film (a,f), carbon fiber paper (b,g), mesoporous carbon coated on Cu foil (c,h), electrospun carbon nanofiber (d,i) and GO film.
D. Lin, Y. Cui et al. Nature Nanotechnology, 2017

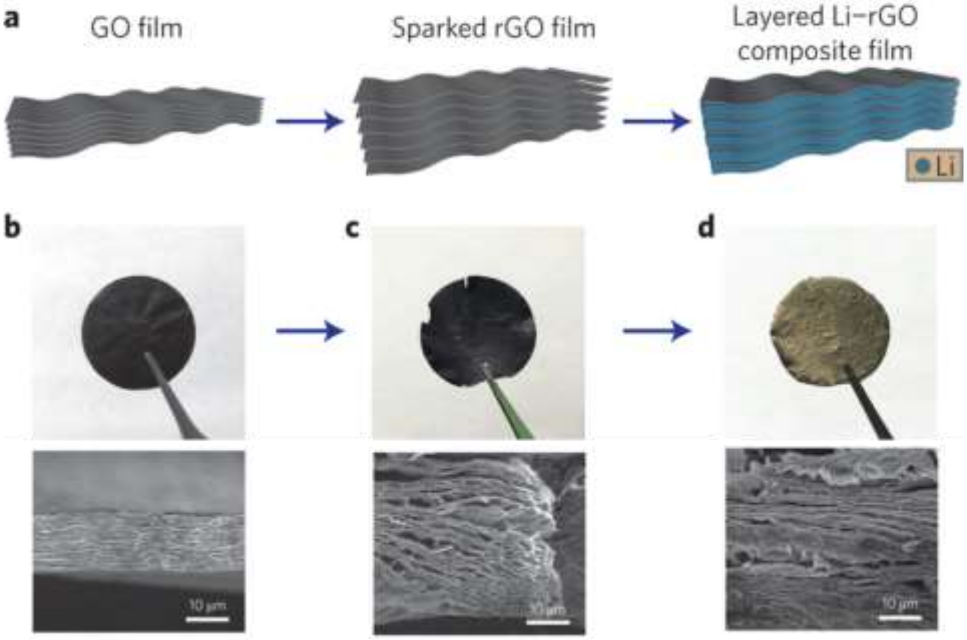

Figure 2: Schematic of the material design and the consequent synthetic procedures from a GO film (left) to a sparked rGO film (middle) to a layered Li–rGO composite film (right). b–d, Corresponding digital camera images and SEM images of the GO film (b), sparked rGO film (c) and layered Li–rGO composite film (d). The diameters of the films shown in b–d are ~ 47 mm.
D. Lin, Y. Cui et al. Nature Nanotechnology, 2017

To evaluate the cycling stability of the Li-rGO composite, symmetric cells were assembled and compared (**Figure 3**). It was found that the Li-rGO symmetric cells exhibits much more stable cycling for prolonged cycles, while the Li foil counterpart encountered soft short circuit within tens of cycles, which is a result of the dendrite propagation. In addition, consistently low overpotential with flat voltage plateaus was attained at various current density from 1-3 mA/cm^2, which can be attributed to the increased active surface area and the pre-engineered nucleation sites within the composite.

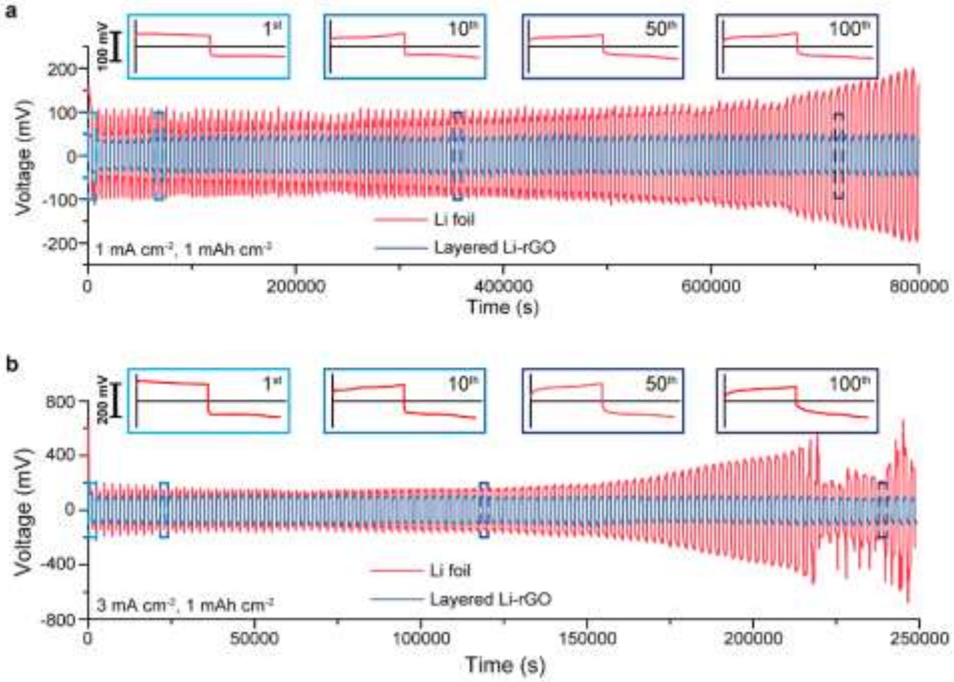

Figure 3: Comparison of the cycling stability of the layered Li-rGO and the bare Li electrode at a current density of (a) 1 mA/cm^2 and (b) 3 mA/cm^2 with a fixed capacity of 1mAh/cm^2.
D. Lin, Y. Cui et al. Nature Nanotechnology, 2017

When paired with LCO cathode, the layered Li–rGO anodes consistently exhibited a much better rate capability and lower hysteresis compare to Li foil (**Figure 4**). With Li–rGO anodes, a much higher LCO capacity can be retained especially at a high rate (∼110 mAh g^{-1} at 4 C and ∼70 mAh g^{-1} at 10 C).

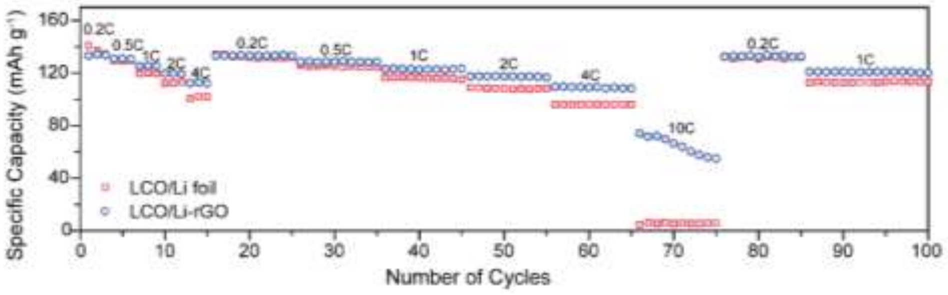

Figure 4: Rate capability of the LCO/Li–rGO and LCO/Li foil cells at various rates from 0.2 C to 10 C.
D. Lin, Y. Cui et al. Nature Nanotechnology, 2017

Excellent lithiophilicity of the host materials is required for molten Li infusion. However, unlike rGO, most available materials cannot be well-wetted by molten Li. In this circumstance, we further developed a universal surface functionalization method to afford lithiophilicity. Specifically, a conformal layer of ZnO can be coated on to the host material by atomic layer deposition (ALD) such that the rapid chemical reaction between ZnO and molten Li can draw extra Li into the host matrix. Highly heat-resistant polyimide (PI) nanofibers were used as an example to demonstrate the effectiveness of ZnO coating on creating 'lithiophilicity' (**Figure 5**). The properties of the resulting Li-PI composite electrode were evaluated. The inert PI fiber served as stable host matrix for Li metal, which achieved minimum volume change during electrochemical cycling and stable voltage profiles in symmetric cell configuration (**Figure 6**).

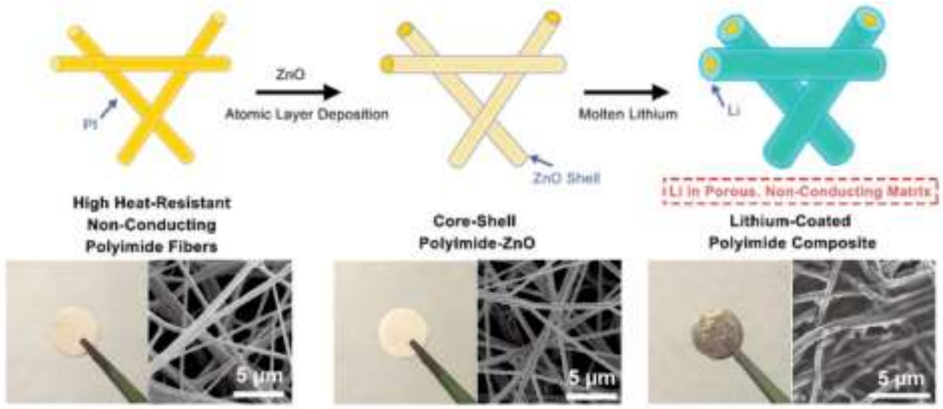

Figure 5: Schematic of the fabrication of the Li-PI composite electrode. Electrospun PI was coated with a layer of ZnO via ALD to form core-shell PI-ZnO. The existence of ZnO coating renders the matrix "lithiophilic" such that molten Li can steadily infuse into the matrix. The final structure of the electrode is Li coated onto a porous, non-conducting polymeric matrix.

Y. Liu, Y. Cui et al. Nature Communications, 2016

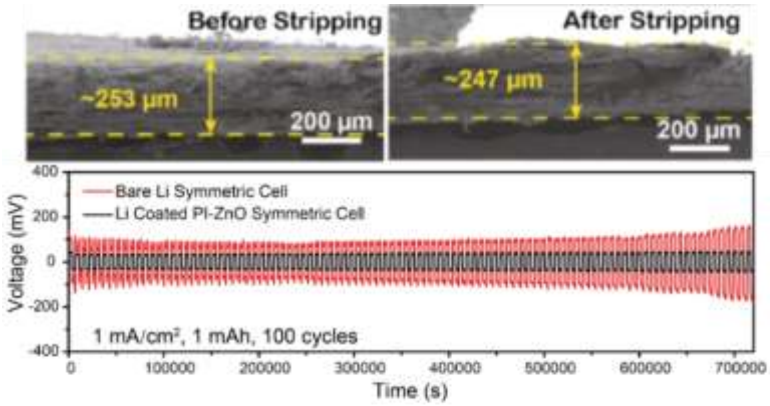

Figure 6: Electrochemical behaviors of the Li-PI electrodes in EC/DEC electrolyte. (top) Cross-sectional SEM images of nanoporous Li-PI anode before and after complete Li stripping. (bottom) Comparison of the cycling stability of the Li-PI and the bare Li electrode at a current density of 1 mA/cm^2 with fixed capacity of $1mAh/cm^2$.

Y. Liu, Y. Cui et al. Nature Communications, 2016

We studied the detailed plating/stripping behavior of the electrode and found that Li can be well-confined within the matrix during galvanostatic cycling (**Figure 7**). Top fibers were exposed after stripping away 5 mAh/cm^2 Li indicating the top Li layers were dissolved more favorably during stripping. Subsequently, when 3 mAh/cm^2 Li was plated, Li was deposited into the matrix and partially filled the space between the fibers. When all the stripped Li was plated back, the top surface of the matrix was covered again by Li with no discernable dendrites. The well-confined behavior can be rationalized by the electrically insulating polymeric surface such that the metallic Li confined within the matrix served as the only electron conductor for Li deposition. On the contrary, if electrons could be efficiently transported to the electrolyte-facing top surface, undesirable stripping/plating behavior may occur after recurrent cycles. Direct Li nucleation on the top surface might be easier due to the high availability of both electrons and Li ions, which provides favorable sites for dendrite growth while leaving the interior voids empty.

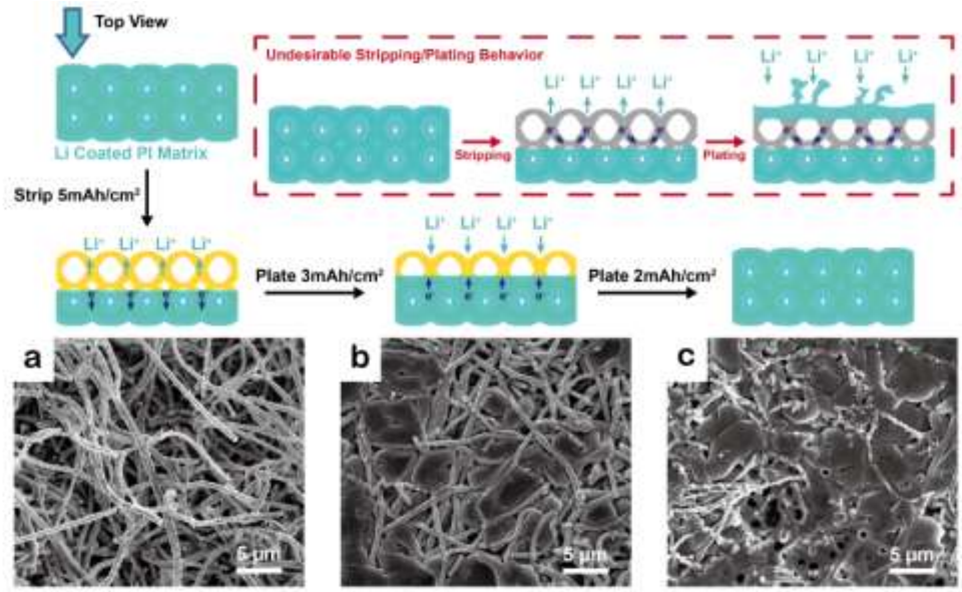

Figure 7. SEM images and schematics showing the well-confined stripping/plating behavior of the Li-PI electrode. (a) exposed top fibers after stripping away 5 mAh/cm^2 Li, (b) exposed top fibers partially filled with Li when plating 3 mAh/cm^2 Li back and (c) completely filled matrix after plating an additional 2 mAh/cm^2 Li back. The top-right schematic illustrates the alternative undesirable Li stripping/plating where after striping, Li nucleate on the top surface, leading to volume change and dendrites shooting out of the matrix.

Y. Liu, Y. Cui et al. Nature Communications, 2016

To test the Coulombic efficiency, hereby, the obtained nanoporous Li-PI (10 mAh/cm^2) electrode was paired with lithium titanate (LTO, 3 mAh/cm^2) cathode to study its performance in a full cell configuration (**Figure 8**). The slightly oversized nanoporous Li-LTO exhibited outstanding cycling stability of more than 100 cycles compare to bare Li foil (50 µm, ~10 mAh/cm^2) or electrodeposited Li, confirming the improved Coulombic efficiency of the Li-PI nanoporous electrode.

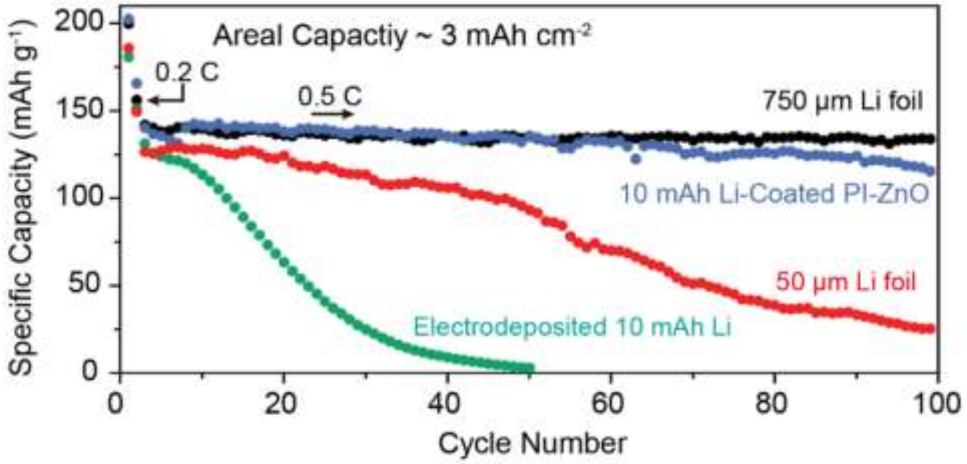

Figure 8: Discharge capacity of various Li metal anode- LTO cathode full cells for the first 100 galvanostatic cycles in EC/DEC with 1 vol % vinylene carbonate. Rate was set at 0.2 C for the first 2 cycles and 0.5 C for later cycles (1 C = 170 mA/g).
Y. Liu, Y. Cui et al. Nature Communications, 2016

2. Inorganic-organic composite interface

The introduction of stable hosts for metallic Li such as layered rGO and nanofibers with lithiophilic coatings has been proven a success in minimizing the volumetric change at the whole electrode level as well as reducing the effective current density and the degree of interface fluctuation during cycling, leading to more uniform Li deposition with greatly improved cycling stability. Engineering the SEI layer on 3D porous Li electrodes shall be the next step needed to further improve the cycling efficiency. Several requirements need to be satisfied for an ideal SEI layer: (1) High degrees of homogeneity (composition and morphology, etc.) to prevent only limited locations of Li metal nucleation and growth; (2) High elastic modulus and compact structure to mechanically suppress Li dendrite; (3) Sufficient flexibility to accommodate the ineligible interface fluctuation during cycling without repeated breakdown/repair; (4) And importantly, high ionic conductivity to facilitate the uniform transport of Li-ions throughout the whole electrode surface.

We proposed a composite artificial SEI layer design for the stabilization of Li metal anode, which shall be composed of a mechanically robust and Li-ion conducting inorganic phase connected by a flexible organic binder to maintain structural integrity during cycling. Cu_3N nanoparticles were chosen as the inorganic phase and a common binder material, styrene-butadiene rubber (SBR) as the polymeric phase (**Figure 9**). Sub 100-nm Cu_3N nanoparticles can be facilely obtained by a one-step solution reaction and afford a stable dispersion with SBR in solvents such as tetrahydrofuran. Notably, the Cu_3N nanoparticles will be passivated spontaneously when in contact with metallic Li to form Li_3N, which is among one of the fastest Li-ion conductors.

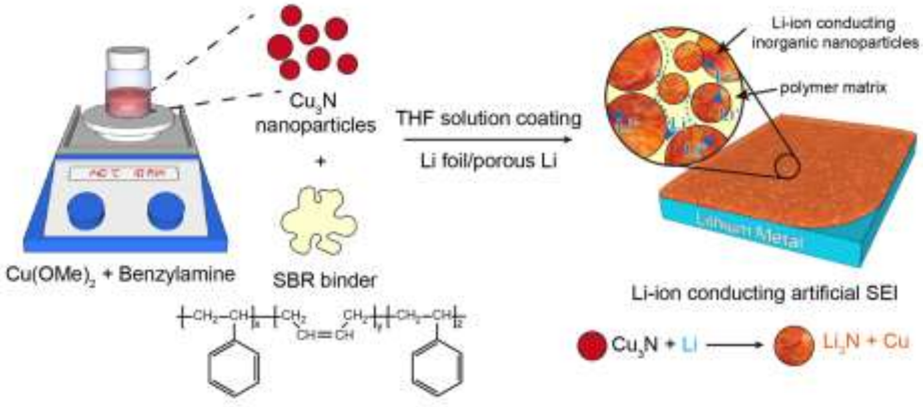

Figure 9: Schematic illustration of the fabrication of the highly Li-ion conducting composite artificial SEI.
Y. Liu, Y. Cui et al. Advanced Materials,2017

Though it remains a great challenge to determine the exact Coulombic efficiency of anodes with pre-stored Li, measuring the value on Cu3N+SBR protected Cu current collectors could serve as a direct evidence of the stabilizing effect our proposed artificial SEI layer when applied on Li metal surface. As can be seen from **Figure 10**a, at a current density of 1 mA/cm^2 in carbonate electrolyte (1 M lithium hexafluorophosphate in 1:1 ethylene carbonate/diethyl carbonate with 10 wt% fluoroethylene carbonate additive, EC/DEC), 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. The Cu_3N+SBR protected Cu demonstrated a much-improved Coulombic efficiency of ~97.4% averaged between the 20th to 70th cycle and such high efficiency performance was able to sustain for more than 100 cycles. In addition, the overpotential increase due to the existence of the artificial SEI was minimal, 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/cm2 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 10b). To further investigate the stabilizing effect of the artificial SEI layer, Cu_3N+SBR was doctor bladed on Li foil surface (Figure 10c), and electrochemical impedance spectroscopy (EIS) measurements in symmetric cell configuration were performed during continuous cycling in EC/DEC electrolyte (Figure 10d). Noticeably, a continuous increase in the R_{SEI} (impedance of the SEI layer) value was observed for bare Li foil, which indicates the repeating breakdown/repair of the native SEI during cycling. Nevertheless, Li protected by the artificial SEI layer showed nearly constant R_{SEI} throughout 200 cycles. Thus, it is evident that the Cu_3N+SBR coating is beneficial in forming a stable and less resistive SEI layer on Li metal surface during prolonged battery cycling.

Finally, when tested on 3D Li-PI metal anode pairing with LTO, 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) compared to ~ 70 cycles for the unprotected one. The indirect method demonstrates the effectiveness of the artificial SEI coating on further improving the performance of porous Li metal anode towards practical battery applications.

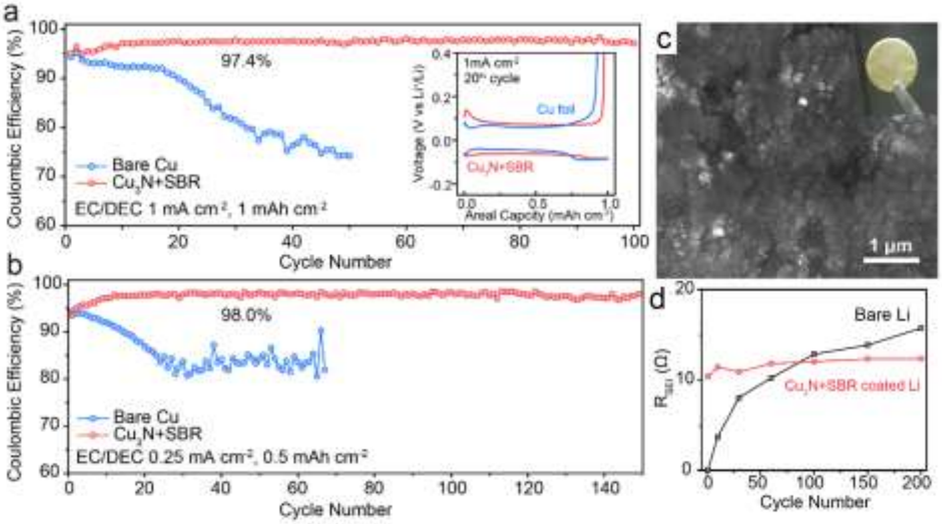

Figure 10: Coulombic efficiency of Cu3N+SBR artificial SEI protected Cu foil and bare Cu foil at a current density of (a) 1 mA/cm^2 (cycling capacity 1 mAh/cm^2; inset, the corresponding voltage profiles at the 20th cycle) and (b) 0.25 mA/cm^2 (cycling capacity 0.5 mAh/cm^2). (c) SEM image and digital photography of the Cu_3N+SBR protected Li metal foil. (d) Summary of the RSEI value as a function of cycle number using symmetric cell configuration.

Y. Liu, Y. Cui et al. Advanced Materials, 2017

3. Viscoelastic polymer interface

The chemical versatility of polymers makes them another class of materials promising for Li metal stabilization. In another study, we took the advantages of the "solid-liquid" hybrid behavior of Silly Putty (SP), a popular children's toy, as the interfacial layer for Li metal anodes. SP can reversibly switch between its "liquid" and "solid" properties in response to the rate of Li growth to provide uniform surface coverage and dendrite suppression, respectively, therefore enabling the stable operation of Li metal electrodes.

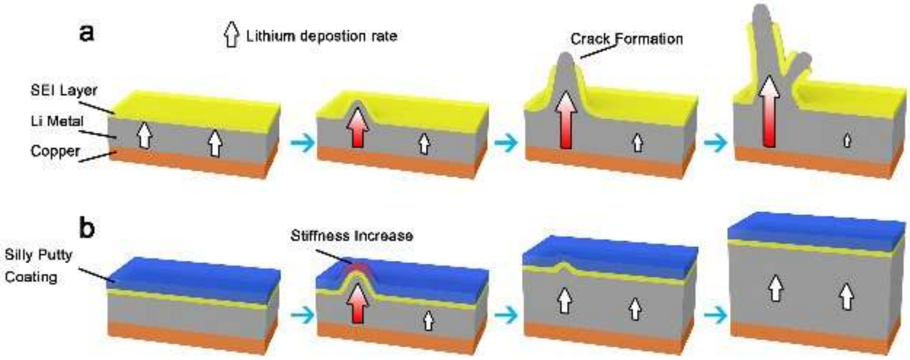

Figure 11: Schematic showing the design of silly putty (SP) modified Li anode. Top shows the conventional Li dendrite evolution process, while the bottom shows the Li deposition behavior on a SP modified surface.
k. Liu, Y. Cui et al. Journal of the American Chemical Society, 2017

The idea is illustrated schematically in **Figure 11**. SP, primarily comprised of polydimethylsiloxane (PDMS) crosslinked by transient boron-mediated bonds, is technically termed as a "shear thickening material". Namely, the rigidity of SP increases significantly as the deformation rate increases. It can even temporarily become an elastic solid if the deformation rate is too fast for the dynamic crosslinks to temporally break and reconnect. Therefore, when coated on the surface of Li metal, SP flows on the time scale of each charging and discharging circle and can uniformly covers the electrode surface to serve as a stable interface between the Li metal and the electrolyte. However, if occasionally there are some "hot-spots" where the deposition and expansion of Li is faster than at other places on the electrode, the stiffness of the local SP coating consequently increases. As such, SP acts as a clamping layer to help eliminate fast local overgrowth or expansion of Li metal and the SEI breakage, effectively suppressing Li dendrite growth.

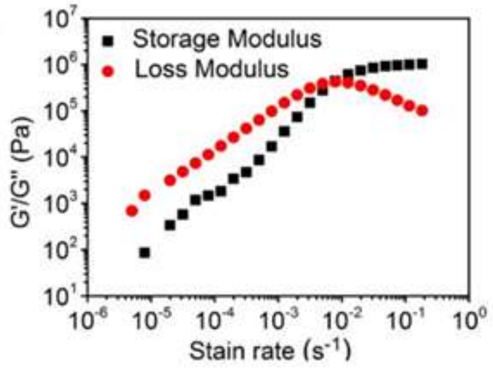

Figure 12: The rheological properties of SP.
k. Liu, Y. Cui et al. Journal of the American Chemical Society, 2017

The viscoelastic behavior of the SP was first studied by rheometer. As shown in **Figure 12**, when the stain rate is low ($<10^{-2}$ s^{-1}), the loss modulus (G'', which represents the viscous property), is significantly larger than the storage modulus (G', which represents the elastic property), indicating that the viscous property dominates the behavior and the SP behaves more like a flowable liquid. As the strain rate increases, G' increases significantly, indicating that the SP becomes stiffer. G' even exceeds G'' by almost an order of magnitude at high strain rates, at which SP exhibits more elastic solid-like behaviors. Therefore, similar to our expectation, SP indeed possess the interesting viscoelastic behavior, which makes it a favorable candidate as artificial SEI for Li metal anode.

The Li stripping/plating Coulombic efficiency of SP-coated Cu electrode was tested (**Figure 13**). The SP-coated electrode showed good cycling performance, maintaining an average efficiency of 97.6% for over 120 cycles at 0.5 mA cm^{-2}. In comparison, control electrodes without SP coatings exhibited poor performance, with Coulombic efficiency dropping below 90% after only 75 cycles. At a higher current density of 1 mA cm^{-2}, the SP-modified electrode achieved an average CE of 97.0% over 120 cycles, while the control electrode maintained efficiency of over 90% for only 65 cycles.

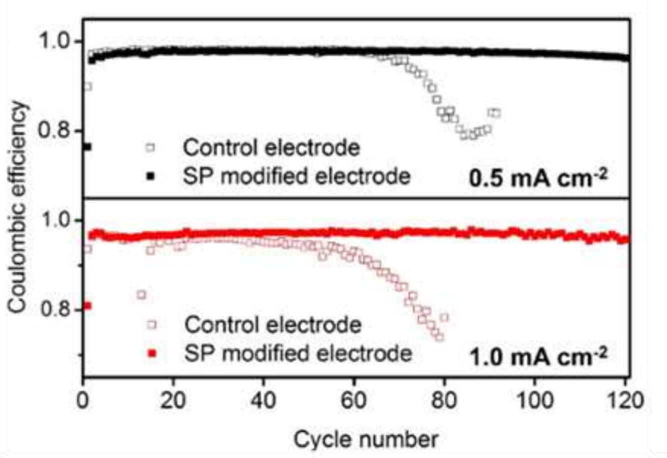

Figure 13: Coulombic efficiency of Li deposition/stripping (1 mAh cm^{-2}) on SP-modified electrodes and control Cu electrodes at different current densities.
k. Liu, Y. Cui et al. Journal of the American Chemical Society, 2017

4. LiF coating via gas-phase reaction

Among the inorganic surface protection materials, Li fluoride (LiF) has gained special attention due to its wide electrochemical stability window with negligible solubility in most of the electrolytes as well as its capability of regulating surface tension. In the early stage, it was found that the addition of HF or fluorinated compounds into electrolyte would help form LiF in SEI and enable more uniform Li deposition. However, these methods are unlikely to produce high-quality continuous and conformal LiF coating on Li metal. Instead, dispersive LiF domains would form with many weakly linked grain boundaries, which would easily fracture during Li metal plating and stripping. Moreover, HF and other fluorinated compounds are highly hazardous reagents, which might impose extra challenges in either industrial processing or battery packaging. Herein, we explored the possibility of gas phase reaction (using Freon R134a, 1,1,1,2-tetrafluoroethane, as the reagent) in attempt to produce high-quality LiF passivation layers conformally on 3D Li metal anode. The idea is illustrated schematically in **Figure 14**. By exposing Li metal to Freon R134a gas, assisted with controlled gas pressure, and reaction temperature, we were able to coat a dense and uniform LiF layer with tunable thickness directly onto metallic Li.

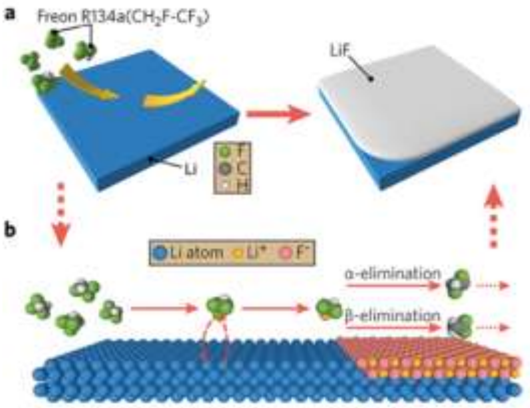

Figure 14: (a) Schematic showing the surface treatment of Li metal with Freon R134a.(b) Proposed major chemical reactions at the early stage of surface treatment.
D. Lin, Y. Cui et al. Nano Letters, 2017

It was found that at a fixed temperature, increasing gas pressure would accelerate the reaction and afford rougher surface; and when gas pressure was fixed, the reactivity increased with temperature. At temperature below 150 °C, the surface was smooth without visible domains, while once the temperature was increased to approaching the melting point of Li metal, the reaction occurred in a much more vigorous fashion and formed micron-sized and porous LiF domains. Thus, to obtain high-quality LiF coating and sufficient reaction rate, 150 °C and 0.5 atm is a good condition for conducting the surface coating. **Figure 15** shows the SEM images of a LiF-coated Li foil, where the top view shows smooth LiF surface, and the cross-section indicates a uniform thickness of ~40 nm.

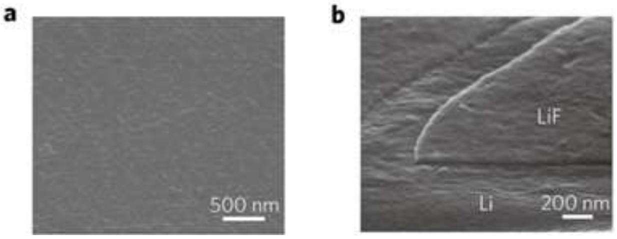

Figure 15: High-resolution SEM images showing the (a) surface morphology and (b) cross-section of a LiF-coated Li foil.
D. Lin, Y. Cui et al. Nano Letters, 2017

To study the efficacy of the LiF coating for improving electrochemical stability of 3D Li metal anode (Li metal infused into layered graphene oxide matrix, Li-rGO), time-dependent electrochemical impedance spectroscopy studies were carried out, as shown in **Figure 16**. LiF-coated Li-rGO do not show obvious increase in impedance within the tested period of time, indicating robust surface passivation that suppressed continuous side reactions and reduced the initial SEI formation. In addition, more stable symmetric cell cycling with suppressed increase in polarization was also observed.

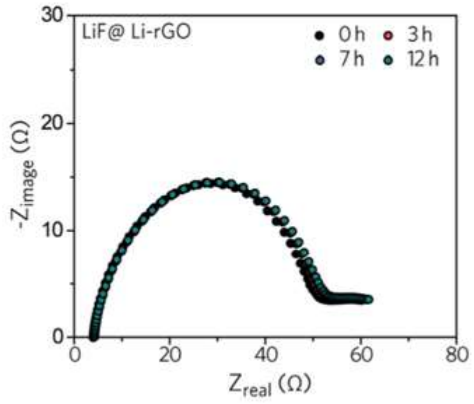

Figure 16: Time-dependent electrochemical impedance measurement on 3D Li metal symmetric cells with LiF coating.
D. Lin, Y. Cui et al. Nano Letters, 2017

5. Two-dimensional materials as nanoscale interface

h-BN, a two-dimensional (2D) atomic crystal with superior chemical inertness and mechanical strength has shown recent success as a stable coating to suppresses dendrite formation during electrochemical lithium metal plating. However, the h-BN grown by chemical vapor deposition (CVD) has numerous defects intrinsic to the synthesis and transfer processes, which may compromise the effectiveness of h-BN as a stable interfacial layer. To further improve the efficacy of the lithium metal protection layer, herein, we take the advantage of the dangling bonds at the defective sites to selectively stitch CVD grown h-BN domains by ALD. Selective ALD of LiF primarily on the line and point defects of h-BN was demonstrated in this study, and the protected lithium electrodes exhibited good cycling behavior with more than 300 cycles at relatively high coulombic efficiency (>95%) in an additive-free carbonate electrolyte.

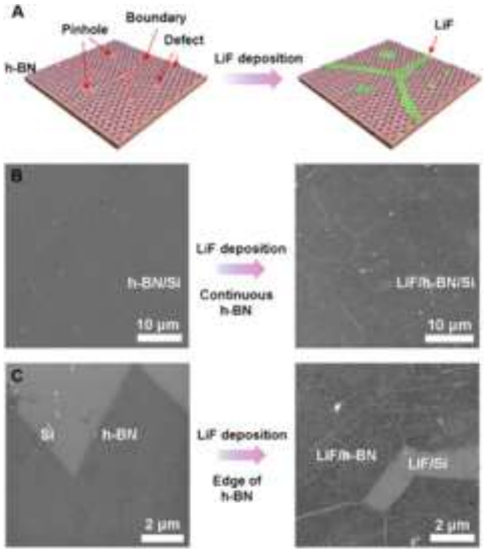

Figure 17: (A) Schematics of selective ALD LiF deposition on h-BN. (B) SEM characterization of 50 cycles of ALD LiF deposition on continuous h-BN. (C) SEM characterization of 50 cycles of ALD LiF deposition on the edge of h-BN.
J. Xie, Y. Cui et al. Science Advances, 2018

ALD of LiF in this study was carried out using lithium tert-butoxide and titanium fluoride as precursors at a growth temperature of 250°C. ALD is typically known for its ability to achieve a conformal coating. Conversely, the ALD LiF deposition on h-BN is selective and does not cover the entire substrate. For comparison, h-BN before and after ALD LiF deposition was characterized by SEM (**Figure 17**). Although pristine h-BN appears to form complete coverage on Si, point and line defects cannot be revealed by SEM due to the limitation of resolution. After LiF deposition, there were considerable numbers of nanowires and nanoparticles deposited on the continuous h-BN layer, indicating the nature of selective ALD LiF deposition on h-BN. The formation of nanowires and nanoparticles might relate to the preferred nucleation of LiF on the line and point defects of CVD h-BN.

Our previous results before this funding have also shown that h-BN can be lifted by the lithium plated underneath. However, in spite of a high theoretical in-plane Young's modulus, the grain boundaries are predicted to be the weak points of h-BN when tensile stress is applied. Although we started with a continuous CVD h-BN film, holes appeared after plating. Using the LiF/h-BN hybrid film as the interfacial layer combines the advantages of both components. First, the weak physical interaction between h-BN and Cu allows lithium to be plated in between h-BN and Cu. Second, with the addition of chemically stable LiF linkers, the overall mechanical strength of LiF/h-BN is improved. It also helps to seal any pinholes or cracks induced in the CVD synthesis and transfer. The superior chemical and mechanical stability of the LiF/h-BN combination effectively suppressed the dendrite formation. Long-term lithium plating/stripping experiments were also conducted in corrosive carbonate electrolyte without any additives. The Li plating/stripping on the LiF/h-BN/Cu substrate maintained a high average coulombic efficiency above 96% for over 300 cycles, which improved significantly compare to pristine h-BN without sealing the defects.

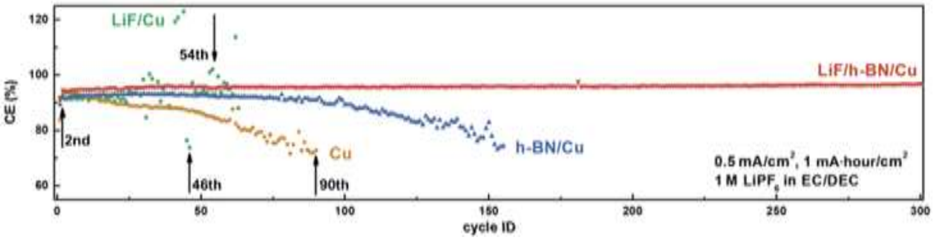

Figure 18: Coulombic efficiency during long-term cycling.
J. Xie, Y. Cui et al. Science Advances, 2018

6. Nanoscale interfacial engineering using ultra-strong bilayered nanodiamond

Interfacial engineering is among the essential means to answer the formidable challenges of Li metal anode caused by its unstable SEI. This approach relies on the introduction of an artificial scaffold on the current collector to reinforce the spontaneously formed SEI layer, and ideally the two can move together during battery cycling without fracturing and side reactions. To fulfill the goal, exacting requirements are imposed for the interfacial layer design: 1) It needs to be absolutely stable against Li, which precludes most of the polymeric and inorganic coatings explored so far as the ideal candidates. 2) A high elastic modulus and compact structure is especially desirable, for the mechanical strength of Li interface can play the key role in retarding dendrite propagation. 3) Certain degree of flexibility is required to accommodate the volume change of electrode during cycling. 4) It shall enable homogenous Li-ion flux without local hot spots. 5) The interfacial layer needs to be designed with low electrical conductivity and weak binding to the substrate such that Li deposition could solely take place underneath the film. Considering the requirements, diamond, a material well-known for its highest bulk modulus, chemical inertness, and electrically-insulating nature, is ideal for Li metal protection

Herein, we present an ultrastrong interface constructed with high-quality nanodiamonds for Li metal that is rationally designed to strictly satisfy all the above-mentioned requirements (**Figure 19**). The nanodiamond interface was synthesized by microwave-plasma chemical vapor deposition and detailed considerations are put into material fabrication to render diamond compatible as interfacial layer: by subtly choosing the correct substrate together with graphene oxide (GO) as a release layer, polycrystalline nanodiamond thin film with long-range homogeneity but only weak adhesion to the substrate can be obtained for Li deposition to occur underneath. Notably, an extremely high modulus of over 200 GPa was obtained via nanoindentation test on our nanodiamond interfacial layer, which is the highest value from real measurement reported so far among the artificial coatings for Li metal. Importantly, a unique double-layer film design was proposed for the first time to circumvent the adverse effect of local defects, which was often the failure mechanism of single-layer Li metal interfaces developed previously.

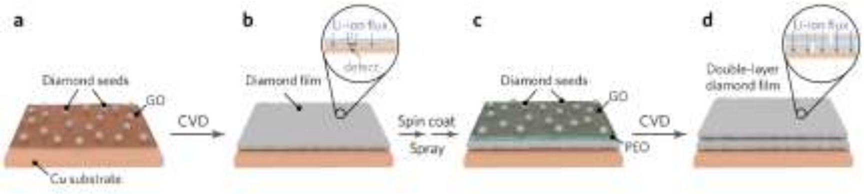

Figure 19: Fabrication process of nanodiamond interfacial layer for Li metal.
Y. Liu, Y. Cui et al. Joule, 2018

The multi-fold advantages of the double-layer nanodiamond interface, the average Li metal anode coulombic efficiency over 10 cycles can be as high as 99.4% at a current density of 1 mA cm^{-2} and an areal capacity of 2 mAh cm^{-2}, and the performance can be well-sustained during prolonged cycling. Prototypical Li-sulfur (S) cells were also constructed. With ~250% excess Li, more than 400 stable cycles can be obtained at a current density of 1.25 mA cm^{-2}, corresponding to an average Li anode coulombic efficiency of above 99% (**Figure 20**)

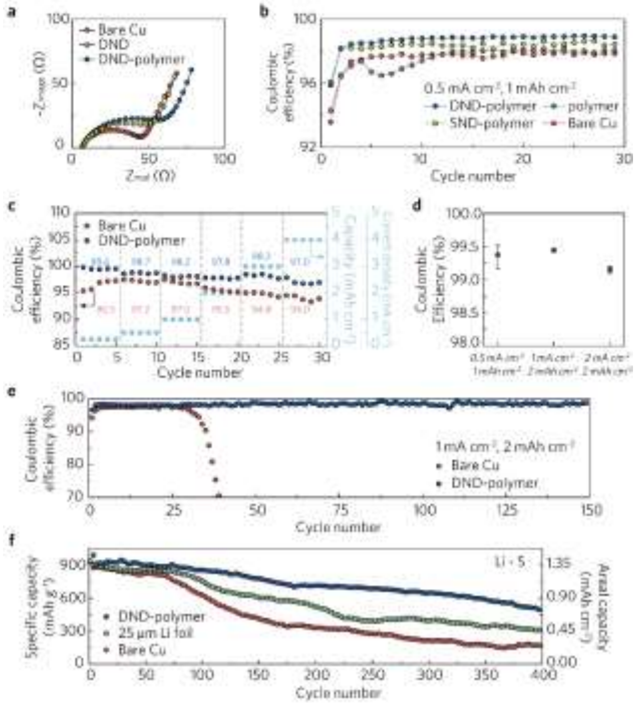

Figure 20: Electrochemical characterizations of the nanodiamond interface. (a) The electrochemical impedance spectra of bare Cu, DND and DND-polymer electrodes. (b) The CE of different anode architectures cycled at a current density of 0.5 mA cm^{-2} and a capacity of 1 mAh cm^{-2}. (c) The CE of bare Cu and DND-polymer electrode cycled at varying current densities and capacities. (d) Summary of the 10-cycle average CE of DND-polymer electrode measured according to the method developed by Aurbach and co-workers. (e) Long-term cycling CE of bare Cu and DND-polymer electrode at a current density of 1 mA cm^{-2} and a capacity of 2 mAh cm^{-2}. (f) Cycling performance of the prototypical Li-S cells at 0.5 C with 25 µm Li foil (~ 5 mAh cm^{-2}), bare Cu with 5 mAh cm^{-2} electrodeposited Li or DND-polymer with 5 mAh cm^{-2} electrodeposited Li as the anode. The areal mass loading of the S cathode is 1.5 mg cm^{-2}. The rate is calculated based on the theoretical capacity of S, where 0.5 C is equivalent to 1.25 mA cm^{-2}.

Y. Liu, Y. Cui et al. Joule, 2018

7. Interfacing three-dimensional Li with solid electrolytes

To address the challenges and make Li metal anode a viable technology, an attractive strategy is to replace the volatile liquid electrolytes with nonflammable solid counterparts that are electrochemically stable against Li and mechanically robust to suppress dendrite growth. Although a wide variety of solid electrolytes for Li batteries have been developed throughout the years, the same critical challenge, which is the interfacial detachment between solid electrolytes and electrodes, awaits to be solved for all the systems.

Unlike liquid electrolytes, solid electrolytes barely have any fluidity to form a continuous contact with active materials inside the electrodes. Therefore, the electrochemical process can be severely limited by the contact area, leading to great interfacial resistance and low utilization of electrode capacity. The issue is even more pronounced for the Li metal anode, whose interfacial fluctuation in practical applications can be as large as tens of micrometers, making it difficult to cycle the solid-state Li batteries at high capacity and current density. Here, we present a paradigm shift on the structural design of solid-state Li batteries: Unlike all the previous studies where solid-state cells were constructed using planar Li foil, we adopted 3D Li anode with high electroactive surface area for the first time, and the challenge of creating a conformal and continuous ionic contact between the 3D Li anode and the bulk solid electrolyte was successfully addressed via a flowable ion-conducting interphase (**Figure 21**). This structural design has several major advantages: first, the adoption of a 3D Li anode significantly increases the electrode-electrolyte contact area, dissipating the current density to facilitate charge transfer and offering the opportunities to high-power operation. Second, by dividing bulk Li into small domains, the interfacial fluctuation during cycling can be reduced to the sub-micrometer scale, enabling the cells to be cycled at a much higher capacity. More importantly, the incorporation of a flowable interfacial layer can accommodate the varying morphology at the 3D Li anode surface during cycling, which is desirable for maintaining a continuous electrode-electrolyte contact. Finally, the 3D Li anode design can be adopted as a general approach in solid-state Li batteries, which is compatible with both solid polymer and inorganic ceramic electrolytes.

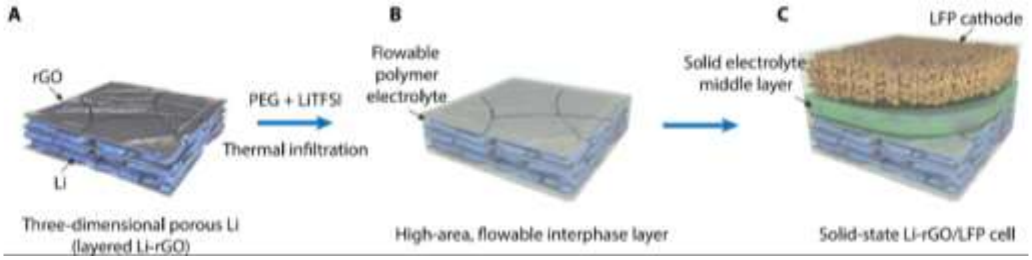

Figure 21: Schematics illustrating the fabrication process of the 3D Li anode with flowable interphase for solid-state Li battery. (A) 3D Li-rGO composite anode was first fabricated. (B) A flowable interphase for the 3D Li-rGO anode was created via thermal infiltration of liquid-like PEG-LiTFSI at a temperature of 150°C. (C) A CPE layer consisting of PEO, LiTFSI, and fumed silica or an LLZTO ceramic membrane was used as the middle layer, and high–mass loading LFP cathode with the CPE as the binder was overlaid to construct the solid-state Li-LFP full cell.

Y. Liu, Y. Cui et al. Science Advances, 2018

The electrochemical performance was tested pairing with $LiFePO_4$ (LFP) cathode. Notably, different from many previous studies on solid Li batteries where the cathode mass loading was kept low to minimize the interfacial delamination, a relatively high capacity cathode (~1 mAh cm^{-2}) was used here to highlight the effectiveness of our design strategy toward improving the interfacial contact. As can be seen from **Figure 22**, significantly improved rate performance and cycling stability can be achieved.

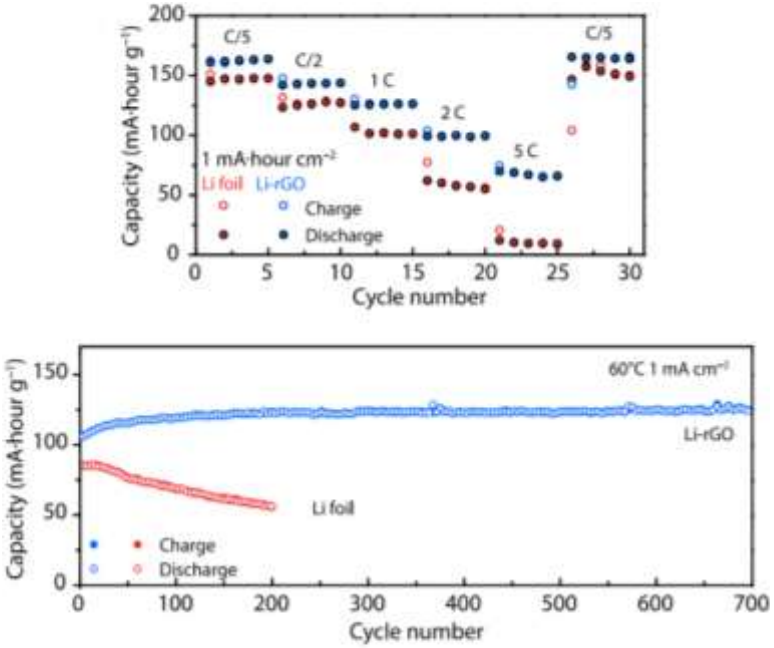

Figure 22: Electrochemical performance of solid-state Li-LFP batteries.
Y. Liu, Y. Cui et al. Science Advances, 2018

Conclusions

In all, during the duration of this project, we have made exciting progress in designing stable host for Li metal to afford minimal volume change. The new design principle, which emphasizes the importance of minimal volume change on interfacial stability, Li-ion flux homogeneity and dendrite suppression, is proposed and widely accepted. To fulfill the design, layered Li-rGO composite electrodes were developed. Due to the unique "lithiophilic" nature of rGO, Li can be easily infused into the nanoscale interlayer gaps of rGO to afford a composite. The composite electrodes exhibit highly reduced volume change from infinity to ~20%, offering more stable electrode dimension during cycling. With the rGO as the support, SEI can be stabilized and thus more uniform Li deposition with suppressed dendrite can be observed. Since Li-ion flux was homogenized with 3D form of Li, more stable cycling at high current density various from 1 to 3 mA/cm2 was achieved, outperforming the conventional Li foil counterpart. Moreover, full cells with LCO as the cathode were further proven, which exhibits highly improved rate capability especially at high rate of 4-10 C.

To fabricate the 3D form of composite with pre-stored Li in the matrix, it is important to afford "lithiophilic" property for the matrix, which is, however, not observed for most of the materials. As a consequence, it is of great promise to develop surface modification techniques to turn a 'lithiophobic' surface into 'lithiophilic'. In this consideration, we developed a universal surface coating technique to achieve the goal. It was found that these surface coatings can be applied universally to all kinds of materials to afford lithiophilic surface, which largely extend the material choices for constructing the stable host.

Once the stable dimension has been obtained, it is necessary to further protect the Li surface. Due to the 3D form of Li, the exposed surface area is highly increased. As a consequence, passivating the surface is meaningful to reduce the initial SEI formation reactions and build a more stable interface. A wide range of materials haven been rationally selected and their nanoscale architectures have been carefully designed to make them suitable for Li metal surface protection. The coating materials explored include, shear-hardening polymers, self-healing polymers, two-dimensional materials with sealed grain boundaries, highly stable inorganics via gas-phase coating reaction, ultrastrong nanodiamond thin films and inorganic-organic composites. Each coating has distinctive advantages for Li metal and the effects of which have been carefully studied.

Finally, the 3D form of Li and the resulting minimal volume change offers the opportunity to design all-solid-state batteries with much better interfacial contact. In this consideration, we combined a flowable interface with 3D Li-rGO composite anode to build all-solid-state batteries. By pairing with $LiFePO_4$ cathode, we demonstrated highly improved rate capability and cycling stability in the all-solid-state full batteries.

We have fulfilled the major milestones of the projects, including:

1) Fabrication of interconnected carbon hollow spheres with various sizes (03/31/2015)
2) Synthesize of layered hexagonal boron nitride and graphene with different thicknesses and defect levels (03/31/2015)
3) Demonstrate the guiding effect of polymer nanofibers for improved Li metal cycling performance (06/30/2015)
4) Achieve minimum relative volume change during electrochemical cycling via host-Li composite electrode design (12/31/2015)
5) Study the relative affinity of Li for different materials (03/31/2016)
6) Demonstrate facile, low-cost, scalable fabrication of porous host-Li composite electrodes. (06/30/2016)
7) Propose promising material design strategies for the surface protection of three-dimensional nanoporous Li metal anode (09/30/2016)
8) Rational design of composite artificial solid electrolyte interphase for the stabilization of three-dimensional nanoporous Li metal anode (12/30/2016)
9) Explore novel polymeric materials and their properties as artificial SEI layer on Li metal (03/31/2017)
10) Explore surface coating techniques for Li metal stabilization (06/30/2017)
11) Stabilizing three-dimensional Li metal anode with solid electrolytes (09/30/2017)
12) Further improve the efficacy of Li metal protection layers (12/31/2017)
13) Improve the Coulombic efficiency > 99.2% (03/31/2018)
14) Demonstrate > 800 cycles of Li metal anode with stable host and interphase (06/30/2018)

Presentations

1. (Invited talk) “Re-inventing Batteries: What’s Possible?” Condensed Matter Physics Seminar, Stanford University, Oct. 9, 2014.
2. (Invited talk) “Inventing Next Generation of Batteries: Materials Design and Advanced Characterization” CARA-BASF Battery Workshop, UC Berkeley, Nov. 7, 2014.
3. (Invited Closs Lectureship) “Nanomaterials Design for Energy and Environment”, Department of Chemistry, University of Chicago, Nov. 10, 2014.
4. (Invited talk) “Inorganic Nanostructure-Organic Hybrid Materials for Next Generation of Energy Storage”, Symposium P, Materials Research Society Fall Meeting, Boston, Nov. 30-Dec. 5, 2014.
5. (Plenary talk) “Nanomaterials Design for Energy and Environment”, The First International Conference on Nanoenergy and Nanosystems, Beijing, China, Dec. 8-10, 2014,
6. (Invited talk) “Nanomaterials Design for Energy Conversion and Storage”, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China, Dec. 10, 2014.
7. (Invited talk) “Nanomaterials Design for Energy Conversion and Storage”, Beijing University of Science and Technology, China, Dec. 11, 2014.
8. (Invited talk) “Nanomaterials Design for Energy and Environment”, Institute of Chemical Processing, Chinese Academy of Sciences, Beijing, China, Dec. 11, 2014.
9. (Plenary talk) “Nanomaterials Design for Energy and Environment” 2nd International Symposium on Bio, Organic & Nano Electronics (ISBONE-2014), Nanjing, China, Dec. 12-14, 2014.
10. (Invited talk) “Nanomaterials Design for Energy and Environment”, Guanxi University, Nanning, China, Dec. 19, 2014.
11. (Invited talk) “Nanomaterials Design for Energy Conversion and Storage”, Beijing University of Science and Technology, China, Dec. 11, 2014.
12. (Plenary talk**)** “Nanomaterials Design for Energy Conversion and Storage”, The 10th International Symposium for Chinese Inorganic Chemists (ISCIC-10), Xiamen, China, Dec. 19-22, 2014.
13. (Invited talk) “Rechargeable Batteries for Transportation and Grid: What’s Possible?” The AAAS Annual Meeting, Feb. 13-16, 2015, San Jose, CA.
14. (Invited talk) “Materials Selection And Design For Batteries With High Energy Density, Ultralong Cycle Life and Excellent Safety” The 32nd International Battery Seminar, Mar 9-12, 2015, Fort Lauderdale, Florida.
15. (Schlumberger Lectureship) two lectures: “Nanomaterials Design for Energy and Environment” and “Nanomaterials Design For Electrochemical Technologies: Batteries and Electrocatalysts”, Department of Chemistry, University of Cambridge, Mar 25-27, 2015.
16. (Invited talk) “High Capacity Anodes from Fundamental Research to Commercial Success" The 10th US-China Electrical Vehicle and Battery Workshop, Beijing, China, Mar 29-30, 2015.
17. (Invited talk) “Materials Design to Increase Energy and Improve Safety of Batteries" The Knowledge Foundation's Lithium Battery Safety meeting this, April 21-22, 2015, San Diego, California.
18. (Invited talk) “Materials Design for Battery Breakthroughs: from Fundamental Science to Commercialization” The 9th Annual CAFE Electric Aircraft Symposium, May 1-2, 2015, Sonoma County, California.
19. (Invited talk) “Batteries for the Future: What’s Possible?” SLAC Science Lecture, May 18, 2015.
20. (Keynote) “Lithium Sulfur Batteries: Fundamental Understanding and Materials Design” The 20th International Conference on Solid State Ionics, Jun 14-19, 2015, Keystone, Colorado.
21. (Keynote) “High Efficiency Air Filtration Technology with Nanotechnology” China-US Clean Air Conference, Jul 24-25, 2015, Beijing, China.
22. (Invited) two lectures “Materials Design for Energy” and “Materials Design for Environment” Shanghai Tech University, Jul 27-30, 2015.
23. (Keynote) “Nanotechnology for Energy, Air and Water”, China Nano, Sep. 3-5, 2015, Beijing, China.
24. (Plenary) “Nanomaterials Design for Energy Conversion and Storage” 1st International Symposium on Energy Chemistry and Materials”, October 29-31, 2015, Fudan University, Shanghai, China.

25. (Plenary) “Electrochemical Nanotechnology: Batteries and Electrocatalysts” International Conference on Innovative Electrochemical Energy Materials and Technologies (EEMT2015), Nanning, China, November 8-11, 2015.
26. (Invited session chair) Future Directions Workshop for Power and Energy, January 19-20th 2016 , California Institute of Technology.
27. (Invited Panelist) Vail Global Energy Forum, Jan 29-31, 2016.
28. (Invited) “Nanomaterials Design of Batteries Guided by *In-Operando* Characterization and Atomistic Simulation”, Gordon Research Conference on Batteries, Feb. 21-26, 2016, Ventura, California.
29. (Invited), “Crossing Nanoscience and Electrochemistry: Battery and Electrocatalysty” Department of Chemistry Seminar, Harvard University, March 7, 2016.
30. (Invited) “Batteries: Now and Future”, MIT Energy Seminar, Mar 8, 2016.
31. (Invited) “Batteries: Now and Future”, MRSEC Colloquium, Columbia University, Mar 15, 2016.
32. (Invited tutorial) “Materials Selection And Design For Batteries With High Energy Density, Ultralong Cycle Life and Excellent Safety” The 33rd International Battery Seminar, Mar 21-24, 2016, Fort Lauderdale, Florida.
33. (Invited) “Reviving Lithium Metal Anodes with New Materials Design Strategies” The 33rd International Battery Seminar, Mar 21-24, 2016, Fort Lauderdale, Florida.
34. (Invited) “Batteries: Now and Future” Materials Engineering Seminars, Mar 25, 2016, Arizona State University.
35. (Invited) “Reinventing Batteries” SLAC Public Lecture, Mar 29, 2016.
36. (Invited) “Batteries Today and Tomorrow” System X Seminar, Stanford University, Apr 21, 2016.
37. (Invited) “State of The Art Batteries”, Sustainable Aviation Symposium, May 6-7, 2016.
38. (Invited) “Multiple approaches to enable Li metal anode: from nanoscale to electrolyte design” Beyond Lithium Ion Conference, May 24-25, 2016, Pacific Northwest National Lab.
39. (Keynote) “Materials Design for Energy Storage” Nature Conference on Materials for Energy, Jun 11-14, 2016.
40. (Plenary) “Materials Design for Energy Storage”, The 2nd International Symposium on Energy Conversion and Storage, Xiamen University, Jun 15-16, 2016.
41. (Invited) “Materials Design for Battery Anodes: Silicon, Lithium Metal and Phosphorus” International Meeting for Lithium Ion Batteries, Jun 19-24, 2016.
42. (Invited) “Materials Design at Nanoscale for Energy and Environment”, UCSD Nanoengineering Seminar, Oct. 10, 2016.
43. (Plenary) Materials Design at Nanoscale for High Energy Batteries the 9th International Conference on Advanced Lithium Batteries for Automotive Applications (ABAA9), Huzhou, China, Oct 17-21, 2016.
44. (Invited) “Materials Design for Energy and Environment” KAIST Workshop on Energy, Environment and Water, Oct. 20-21, 2016.
45. (Invited) “Materials Design at Nanoscale for High Energy Batteries” China Energy Storage Conference, Shenzhen, China, Oct. 22-24, 2016.
46. (Plenary) “Energy Materials Design at Nanoscale” The 2nd International Symposium on Energy Chemistry and Materials, Hefei, China, Oct. 28-30, 2016.
47. (Invited) “Reviving Lithium Metal Anode Through Materials Design”, Samsung Forum, Nov. 1, 2016.
48. (Invited) “Energy Storage”, GCEP Symposium, Stanford, California, Nov. 2-3, 2016.
49. (Invited) “Nanomaterials Design for Energy and Environment”, Frontiers in Nanotechnology Seminar Series, Northwestern University, Nov 11, 2016.
50. (Invited) “Nanomaterials Design for Energy and Environment”, Argonne National Lab, Nov. 17, 2016.
51. (Plenary) “New Aspects for Electrical Batteries”, Pontifical Academy of Sciences, Vatican, Nov. 26-29, 2016.
52. (Invited) “Low-Cost Battery Chemistries for Grid Scale Energy Storage”, Materials Research Society Fall Meeting, Boston, Nov 27 to Dec 2, 2016.
53. (Invited) “Nanomaterials Design for Energy and Environment”, Rowland Institute Seminar, Harvard University, Dec. 1, 2016.

54. (Invited) “Nanomaterials Design for Energy and Environment”, Guilin Normal University, Dec. 30, 2016.
55. (Plenary) “Nanomaterials Design for Energy” International Conference on Materials for Energy Applications, City University of Hong Kong, Jan 3-6, 2017.
56. (Invited) “Reviving Lithium Metal Anode Through Materials Design”, HKUST-Argonne National Lab Workshop on Energy Storage Systems, Jan 4, 2017, Hongkong University of Science and Technology.
57. (Invited) “Nanomaterials Design for Energy and Environment” Institute of Textiles and Clothing seminar, Hongkong Polytech University, Jan 6, 2017.
58. (Keynote) “Reviving Lithium Metal Anode Through Materials Design”, The International Battery Association (IBA) 2017 Meeting, Nara, Japan, March 5-10, 2017.
59. (Invited) “Materials Selection and Design for Batteries with High Energy Density, Ultralong Cycle Life and Excellent Safety”, International Battery Seminar, Fort Lauderdale, March 22-23, 2017.
60. (Plenary) “Nanoscience for Energy Storage: Success and Future Opportunity” Basic Research Needs for Next Generation Electrical Energy Storage, Gaithersburg, Maryland, March 27-29, 2017.
61. (Invited) “Electrochemical and Chemical Storage of Electrons at Nanoscale for Sustainable Future”, American Chemical Society Spring meeting, San Francisco, Presidential Symposium on “Science for a Sustainable Energy Future”.
62. (Invited) “Tuning Electrocatalyst”, American Chemical Society Spring meeting, Symposium on Holy Grail in Chemistry Future, San Francisco, Apr 2-6, 2017.
63. (Invited) “Reviving Li Metal Anodes”, the 12th U.S.-China Electric Vehicle and Battery Technology Meeting, Zhuhai, China, April 16 to 18, 2017.
64. (Invited) “Lithium Sulfur Batteries: Fundamental Understanding and Materials Design”, Symposium ES13: Interfaces and Interphases in Electrochemical Energy Storage and Conversion, Materials Research Society Meeting, April 17- 21, 2017 Phoenix, Arizona.
65. (Invited) “Battery 500Wh/kg: Reviving Lithium Metal Anode Through Materials Design”, Symposium ES2: High Capacity Electrode Materials for Rechargeable Energy Storage, Materials Research Society Meeting, Phoenix, Arizona, April 17- 21, 2017.
66. (Invited) “Electrochemical Materials: Batteries and Electrocatalysts”, CARA anniversary symposium, University of California, Berkeley, California April 24-25, 2017.
67. (Keynote) “Energy and Environment Technology Innovation and Commercialization”, Silicon Valley Entrepreneurs Festival, Santa Clara Convention Center, May 2, 2017.
68. (Invited) “Nanomaterials Design for Energy Storage”, 4th Euro-Mediterranean Conference on Nano Materials and Renewable Energies (EMCMRE-4), Marrakech, Morocco, May 8-11, 2017
69. (Invited) “Electrochemical nanomaterial design for energy and water”, The 12th Sino-US Nano Forum, Beijing, China, May 26-28, 2017.
70. (Invited) “Electrochemical Materials: Energy Conversion, Storage and Beyond”, The 2nd ShanghaiTech Advance in Research (STAR) Symposium, Shanghai Tech University, Shanghai, China, Jun 22-23, 2017.
71. (Invited) “Nanoscience for Energy Storage: Success and Future Opportunity” 2017 China-America Frontiers of Engineering Symposium, organized by Chinese Academy of Engineering and US National Academy of Engineering , Shanghai, China, June 22-24, 2017.
72. (Plenary) “Electrochemical Materials: Energy Conversion, Storage and Beyond” Materials Design for Energy Storage”, The 3nd International Symposium on Energy Conversion and Storage, Nanjing University, Jun 24-25, 2017.
73. (Plenary) “Electrochemical Materials: Energy Conversion, Storage and Beyond” 4th China -United States Symposium on Energy, Shanghai, China, June 25~27，2017.
74. (Invited) “Reviving Lithium Metal Anode Through Materials, Interfacial and Solid Electrolyte Design”, The 10th Beyond Li-Ion Symposium (BLI-X). IBM Research-Almaden, June 27-29, 2017.
75. (Invited) “Batteries for Energy Storage”, International School for Materials for Energy and Sustainability, California Institute of Technology, July 16-22, 2017.
76. (Invited) “Electrochemical Materials: Energy Conversion, Storage and Beyond”, 2017 Blavatnik Science Symposium, New York City, Jul 17-18, 2017.

77. (Plenary) “Advanced materials for energy and environment” The 17th Congress, Asian Pacific Confederation of Chemical Engineering, Hong Kong Convention and Exhibition Center, 23-27 August 2017
78. (Keynote) “Electrochemical Nanotechnology: Energy and Environment” ChinaNano 2017, Beijing, Aug. 29-31, 2017.
79. (Invited) “Nanoscience for energy and environment” ChinaNano 2017, ACS Publications Forum, Beijing, Aug. 29-31, 2017.
80. (Invited) “Nanomaterials Design for Energy and Environment” ZJU-Stanford Symposium on Materials Science, Zhejiang University, Hangzhou, China, Oct. 10-13, 2017.
81. (Invited) “Nanomaterials Design for Energy and Environment” School of Materials Science, Zhejiang Institute of Technology, Hangzhou, Oct. 12, 2017.
82. (Invited) “Pathway to 500Wh/kg Batteries”, GCEP Research Symposium 2017, Stanford University, Oct. 17-18, 2017.
83. (Invited) “Nanoscience for Energy and Water”, Berkeley Nano Seminar, UC Berkeley, Oct 20, 2017.
84. (Invited) “Nanotechnology for Energy and Environment” Future Forum, Beijing, China, Oct. 28-29, 2017.
85. (Invited) “Nanomaterials Design for Energy Storage”, Stanford-Chalmers Workshop on Advancing Materials Innovatively, Charmers University of Technology, December 13-15, 2017.
86. (Invited) “Nanotechnology for Energy, Environment and Textile”, Hongkong Polytech University seminar, Dec. 29, 2017.
87. (Keynote) “Nanoscale Design And Cryogenic Electron Microscopy For Energy Storage” *Nature Conference* entitled ‘Materials Electrochemistry: Fundamentals and Applications’. Shenzhen, China, January 13-15, 2018.
88. (Invited) “Nanotechnology for Energy, Environment and Textile”, Seminar, Peking University School of Materials Science at Shenzhen, China, Jan 14, 2018.
89. (Invited) “Nanotechnology for Energy, Environment and Textile”, seminar, Dalian Institute of Chemical Physics, Dalian, China, Jan 16, 2018.
90. (Keynote) “Nanoscale Design And Cryogenic Electron Microscopy For Energy Storage”International Coalition for Energy Storage and Innovation (ICESI), which will beheld in Dalian, China, from Jan 16 to 19, 2018.
91. (Invited) “Nanotechnology for Energy, Environment and Textile”, seminar, Dalian Institute of Technology, Dalian, China, Jan 19, 2018.
92. (Invited) “Nanotechnology for Energy, Environment and Textile”, seminar, UC Irvine, Feb. 2, 2018.
93. (Invited) “Pathways of Batteries Towards Sustainable Electric Transportation and Stationary Storage”, Stanford Energy Seminar, Stanford University, Feb. 12, 2018.
94. (Invited) “Nanotechnology for Energy, Environment and Textile”, seminar, Tsinghua University, Beijing, China, Mar 5, 2018.

Publications

1. Yan, Kai, et al. "Ultrathin two-dimensional atomic crystals as stable interfacial layer for improvement of lithium metal anode." *Nano letters* 14.10 (2014): 6016-6022.
2. Liang, Zheng, et al. "Polymer nanofiber-guided uniform lithium deposition for battery electrodes." *Nano letters* 15.5 (2015): 2910-2916.
3. Li, Weiyang, et al. "The synergetic effect of lithium polysulfide and lithium nitrate to prevent lithium dendrite growth." *Nature communications* 6 (2015): 7436.
4. Liang, Zheng, et al. "Composite lithium metal anode by melt infusion of lithium into a 3D conducting scaffold with lithiophilic coating." *Proceedings of the National Academy of Sciences* 113.11 (2016): 2862-2867.
5. Liu, Yayuan, et al. "Lithium-coated polymeric matrix as a minimum volume-change and dendrite-free lithium metal anode." *Nature communications*7 (2016): 10992.
6. Lin, Dingchang, et al. "Layered reduced graphene oxide with nanoscale interlayer gaps as a stable host for lithium metal anodes." *Nature nanotechnology* 11.7 (2016): 626.

7. Yan, Kai, et al. "Selective deposition and stable encapsulation of lithium through heterogeneous seeded growth." *Nature Energy* 1.3 (2016): 16010.
8. Sun, Yongming, et al. "Graphite-encapsulated Li-metal hybrid anodes for high-capacity Li batteries." *Chem* 1.2 (2016): 287-297.
9. Liu, Wei, et al. "Stabilizing lithium metal anodes by uniform Li-ion flux distribution in nanochannel confinement." *Journal of the American Chemical Society* 138.47 (2016): 15443-15450.
10. Liu, Yayuan, et al. "An artificial solid electrolyte interphase with high Li-ion conductivity, mechanical strength, and flexibility for stable lithium metal anodes." *Advanced Materials* 29.10 (2017): 1605531.
11. Zheng, Guangyuan, et al. "High-performance lithium metal negative electrode with a soft and flowable polymer coating." *ACS Energy Letters* 1.6 (2016): 1247-1255.
12. Pei, Allen, et al. "Nanoscale nucleation and growth of electrodeposited lithium metal." *Nano letters*17.2 (2017): 1132-1139.
13. Liu, Wei, et al. "Core–shell nanoparticle coating as an interfacial layer for dendrite-free lithium metal anodes." *ACS central science* 3.2 (2017): 135-140.
14. Lin, Dingchang, Yayuan Liu, and Yi Cui. "Reviving the lithium metal anode for high-energy batteries." *Nature nanotechnology* 12.3 (2017): 194.
15. Lin, Dingchang, et al. "Three-dimensional stable lithium metal anode with nanoscale lithium islands embedded in ionically conductive solid matrix." *Proceedings of the National Academy of Sciences* (2017): 201619489.
16. Lin, Dingchang, et al. "Conformal lithium fluoride protection layer on three-dimensional lithium by nonhazardous gaseous reagent freon." *Nano letters* 17.6 (2017): 3731-3737.
17. Lin, Dingchang, et al. "Nanoscale perspective: Materials designs and understandings in lithium metal anodes." *Nano Research* 10.12 (2017): 4003-4026.
18. Zhao, Jie, et al. "Surface fluorination of reactive battery anode materials for enhanced stability." *Journal of the American Chemical Society* 139.33 (2017): 11550-11558.
19. Liu, Yayuan, et al. "Transforming from planar to three-dimensional lithium with flowable interphase for solid lithium metal batteries." *Science advances*3.10 (2017): eaao0713.
20. Xie, Jin, et al. "Stitching h-BN by atomic layer deposition of LiF as a stable interface for lithium metal anode." *Science advances* 3.11 (2017): eaao3170.
21. Li, Yanbin, et al. "Robust Pinhole-free Li3N Solid Electrolyte Grown from Molten Lithium." *ACS central science* 4.1 (2017): 97-104.
22. Liu, Yayuan, et al. "An Ultrastrong Double-Layer Nanodiamond Interface for Stable Lithium Metal Anodes." *Joule* (2018).
23. Liu, Yayuan, et al. "Solubility-mediated sustained release enabling nitrate additive in carbonate electrolytes for stable lithium metal anode." *Nature communications* 9.1 (2018): 3656.
24. Lopez, Jeffrey, et al. "Effects of Polymer Coatings on Electrodeposited Lithium Metal." *Journal of the American Chemical Society* 140.37 (2018): 11735-11744.

Patents

1) Paten disclosure (15-382) to Stanford, “Composite Lithium metal anodes for Lithium batteries with minimal volumetric fluctuation during cycling and dendrite suppression functions”, Inventors: Yi Cui, Zheng Liang, Dingchang Lin, Yayuan Liu.

2) Paten disclosure (15-171) to Stanford, “A structure that encapsulates lithium metal for high energy density battery anode” Inventors: Yi Cui, Kai Yan, Steven Chu.