Constructing a Phosphating–Nitriding Interface for Practically Used Lithium Metal Anode

Siyuan Li,^{†,||} Qilei Liu,^{‡,||} Xinyang Wang,[†] Qian Wu,[†] Lei Fan,[†] Weidong Zhang,[†] Zeyu Shen,[†] Linyan Wang,[§] Min Ling,^{*,†,||} and Yingying Lu^{*,†,||}

[†]State Key Laboratory of Chemical Engineering, Institute of Pharmaceutical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

[‡]Institute of Chemical Process Systems Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

[§]Department of Ophthalmology, The Second Affiliated Hospital, Zhejiang University School of Medicine, Hangzhou, Zhejiang 310009, China

S Supporting Information

ABSTRACT: Low cycling reversibility and safety concerns are hindering the practical application of high-energy lithium metal batteries. Rational design of an artificial electrode/electrolyte interface is regarded as an effective way to circumvent the above problems. Herein, a phosphating–nitriding method is developed through the reaction between lithium metal and a $\text{PCl}_5\text{--LiNO}_3$ complex. An as-formed hybrid interface, consisting of Li_3N , Li_3PO_4 , and nanocrystalline LiCl , offers high ionic conductivity and strong mechanical stability for uniform lithium electrodeposition. The dendrite-free behavior is further investigated through ex situ and in situ techniques. Accordingly, the modified 50 μm Li anode exhibits a high-current-density durability of 10 mA cm^{-2} and a long-term cycling performance of greater than 300 h at a high Li-metal utilization of 30.6% under a conventional EC/DEC electrolyte. A full cell paired with a high-voltage cathode $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) displays a 4-fold improvement in cell lifetime under a low negative to positive electrode capacity ratio (N/P ratio) of 3.92. This work paves a new way to construct an advanced artificial interface for next-generation high-capacity/high-voltage Li-metal-based batteries.

The current lithium ion battery (LIB) consisting of a graphite anode (372 mAh g^{-1}) and a transition metal oxide cathode has reached its theoretical energy density ($\leq 250 \text{ Wh kg}^{-1}$) and cannot meet the needs of large electric equipment.^{1–3} To promote the energy density of batteries, lithium metal with high theoretical specific capacity and the lowest electrochemical potential (3860 mAh g^{-1} , -3.04 V vs standard hydrogen electrode) and cathodes with aggressive chemistries, such as Li-S and Li-O_2 , are explored.^{4,5} Such configuration, offering an energy density exceeding 500 Wh kg^{-1} , is considered to be an attractive power system for future electric vehicles and unmanned aircraft.^{6,7}

To realize the commercialization of lithium metal batteries (LMBs), basic research issues and industrial amplification need to be carefully considered. Due to the high reactivity, lithium metal can react with an electrolyte to form an intrinsic unstable solid electrolyte interface (SEI) on its surface.⁸ The

heterogeneous mosaic-like SEI cannot endure the large electrode expansion, and fresh Li will be consumed, resulting in a low Coulombic efficiency (CE) and harmful dendrite growth. Such irreversibility impedes further industrialization, because the anode capacity utilized in a practical cell is limited (negative to positive electrode capacity ratio, N/P ratio < 1.5).^{9,10} The exhaustion of the lithium source becomes the main reason for battery failure, rather than dendrite growth or an internal short circuit.¹¹

Various strategies have been proposed to protect the Li-metal anode and improve its reversibility in a liquid-state cell. Accommodating Li in a 3D host framework effectively alleviates the large volume expansion during cycling and

Received: September 30, 2019

Accepted: November 18, 2019

Published: November 18, 2019

Figure 1. Preparation and characterizations of the PN interface on a Li anode. (a) Schematic illustration of formation of PN interface on Li metal. (b) Top-view SEM image and (c) cross-sectional SEM image of PN–Li anode. (d) High-resolution TEM image of PN interface. (e) XPS spectra of N 1s, P 2p, and Cl 2p for PN interface. (f) EDS elemental mapping images of Cl, N, and P for PN–Li anode.

meanwhile lowers the local current density.^{12–16} Artificial SEIs with high Li ionic conductivity can mechanically suppress the dendrite growth.^{17–21} Tailoring electrolyte components such as Li salts, additives, and solvents can in situ form a chemically stable SEI layer to enhance plating efficiency.^{22–30} In general, the key towards a dendrite-free anode is to construct a protective layer that is ionically conductive, electronic insulating, mechanically robust, and electrochemically stable to regulate the deposition behavior of lithium metal.^{31,32} Moreover, although these efforts have been proven to be effective to some extent, the lifespan test under practical conditions (for example, using 50 μm Li foils) is still a huge challenge for the Li-metal anode. Combining ultrathin Li-metal foils with a high areal capacity cathode (>2.5 mAh cm⁻²) would be indispensable to examine the expected effect in a real soft-package cell.³³

Herein, a phosphating–nitriding interface (denoted as a PN interface) strategy is proposed via a reaction between an ultrathin lithium anode and a PCl₅–LiNO₃ complex to smooth the lithium deposition on interface. The complex gradually decomposes on the lithium surface to form a dense and stable interface consisting of inorganic Li₃PO₄, Li₃N, and nanocrystalline LiCl. Owing to the fast Li-ion conductor and strong

mechanical stability of the polycrystalline inorganic interface, the homogeneous lithium electrodeposition behavior of the PN–Li anode can be observed through ex situ focused ion beam scanning electron microscopy (FIB-SEM) and in situ optical microscope. Meanwhile, the modified 50 μm Li anode exhibits a high-current-density durability of 10 mA cm⁻² and a long-term cycling performance of greater than 300 h under a high areal capacity loading of 3 mA h cm⁻². Full cells paired with a high-voltage cathode LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (NCM523) or LiFePO₄ display an obvious improvement in cell lifetime under a low N/P ratio of 3.92.

The procedures for preparing an PN interface are detailed in the [experimental section](#) and schematically illustrated in [Figure 1a](#). Firstly, PCl₅ and LiNO₃ are dissolved in dimethyl ether (DME) solvent to obtain a transparent solution, after which two solutions are mixed together to form a yellow solution ([Figure S1](#)). Raman spectra show the almost same pattern before and after mixing, indicating the chemical reaction between PCl₅ and LiNO₃ does not change the solvent structure ([Figure S2](#)). Then, lithium metal is immersed into a single or mixed solution for 24 h, separately. As can be seen, the lithium foils in pure DME and LiNO₃-containing solution show the shiny surface after soaking, revealing that LiNO₃ salt

Figure 2. Cycling performance of symmetrical cells using PN-Li electrode. (a) Voltage profiles of bare, LiNO_3 , PCl_5 , and PN treated Li anode at 2 mA cm^{-2} and 1 mA h cm^{-2} . Voltage profiles of PN-Li anode at (b) 10 mA cm^{-2} and 1 mA h cm^{-2} and (c) 1 mA cm^{-2} and 3 mA h cm^{-2} . (d) Enlargement of green bar in (b). (e) Nyquist plot of the impedance spectra of the Li anode treated by different materials.

and solvent almost remain stable against lithium metal and it is hard for them to form an effective protective layer under normal condition. As a comparison, the surfaces of lithium foils in PCl_5 - and PN-containing solution turns to yellow and gray, indicating that adding PCl_5 into LiNO_3 -DME solution absolutely changes the reaction behavior as compared with each single one (Figure S3). Scanning electronic microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and X-ray photoelectron spectroscopy (XPS) were conducted to investigate the detailed compositions of the PN interface. Before immersion, the pristine Li shows a relatively smooth surface with some slip lines (Figure S4a). The Li anode possesses an ultrathin thickness of $50 \text{ }\mu\text{m}$, corresponding to a specific capacity of 9.8 mA h cm^{-2} (Figure S4b,c). For a Li anode exposed to mixed PN solution, an as-formed interface is composed of a nanoflake-like structure from top-view, which is different from the dense structure formed in PCl_5 solution (Figures 1b and S5). This protective layer with a thickness of $2 \text{ }\mu\text{m}$ tightly adheres to the Li surface, which is beneficial to maintain the integrity of interface/electrode during cycling (Figure 1c). HRTEM is utilized to further identify the composition of the PN coating. Compared with a routine SEI layer formed in EC/DEC electrolyte, the polycrystalline nature of inorganic nanoparticles in the PN

layer is demonstrated by selected area electron diffraction (Figure S6). A high-resolution TEM image (Figure 1d) demonstrates the existence of noncrystal phases and ultrafine nanocrystals with sizes ranging from 2 to 5 nm in PN interface. The lattices spacing of 0.387, 0.401, and 0.256 nm can be attributed to the typical lattice planes of Li_3N (001), Li_3PO_4 (120), and LiCl (200). This result is also validated by XPS measurement (Figure 1e). From N 1s spectra, the peaks located at 407.3, 402.4, and 399.6 eV can be ascribed to NO_3^- , N_xO_y^- and N_3^- , respectively. The P 2p and Cl 2p spectra indicate that the PCl_5 decomposes into phosphate and lithium chloride, which is consistent with the observation results in HRTEM. The energy dispersive spectroscopy (EDS) elemental mapping shows a uniform element distribution of Cl, N, and P, reflecting that the nanocrystals are well-distributed in the whole interface. Owing to the fast Li-ion conducting property of Li_3N and LiN_xO_y and the strong mechanical stability of inorganic nanoparticles, it is reasonable that the PN layer can reinforce the interface stability and homogenize the Li-ion flux at the electrode/electrolyte interface. The detailed formation process of the PN interface is also detected by density functional theory (DFT) calculation and nuclear magnetic resonance (NMR) spectra. From Table S1, the energy change by the complexation between each PCl_5 -

Figure 3. Morphology of cycled Li and the deposition behavior analysis. In situ optical microscopy observations of the electrode/electrolyte interface during electrodeposition on (a) PN-Li and (b) bare Li under a current density of 3 mA cm^{-2} . (c) Cross-sectional FIB images of (c) PN-Li and (d) bare Li after 20 cycles at 1 mA cm^{-2} and 3 mA h cm^{-2} . (e,h) Schematic diagrams of remaining active Li on bare Li and PN-Li after long cycling. (f,i) Top-view and (g,j) cross-sectional SEM images of bare Li and PN-Li anodes after 30 cycles at 1 mA cm^{-2} and 3 mA h cm^{-2} .

LiNO_3 pair is determined to be -0.297 eV , which can be translated to $-28.64 \text{ kJ mol}^{-1}$. It suggests that the complexation between PCl_5 and LiNO_3 is favorable, as the energy of the $\text{PCl}_5\text{--LiNO}_3$ binary system is lower after complexation. The ^{31}P NMR spectra of the PN solution also show an obvious PCl_5 peak at -84 ppm at the beginning (Figure S7), indicating the existence of $\text{PCl}_5\text{--LiNO}_3$ complex. After Li foil immersion, the ^{31}P peaks at -3.5 , -3.8 and -4.6 ppm can be observed,

which are attributed to the decomposition intermediate due to the P-Cl cleavage. After immersion for 24 h, the complex is fully transformed to phosphate ($\sim 0 \text{ ppm}$), which is in accordance with the XPS results. The supposed reaction mechanism is evaluated through DFT calculations thermodynamically (Figure S8). In the pure LiNO_3/DME electrolyte, lithium nitrate can spontaneously react with metallic lithium to form Li_3N . However, its reaction thermodynamic tendency is

small ($\Delta G = -29.485$ eV). When the $\text{PCl}_5\text{-LiNO}_3$ complex was applied, the reaction Gibbs free energy changes ΔG equal to -177.135 eV (decomposition products: Li_3N) and -51.799 eV (decomposition products: LiNO_2), indicating that the reaction is more favorable for the $\text{PCl}_5\text{-LiNO}_3$ complex and Li than for pure LiNO_3 and Li.

Galvanostatic charge/discharge measurements were performed under a carbonate-based electrolyte without additives to evaluate the cell lifetime of the modified $50\text{ }\mu\text{m}$ Li anode. The solvent type and material ratio are studied to determine the optimal conditions for interface formation. In Figure S9, the cell prepared using the $\text{PCl}_5\text{-LiNO}_3$ complex with a mass ratio of 5:1 dissolved in DME shows the longest lifespan of more than 180 h compared with that using mass ratios of 5:2 or 7.5:1. Then, ester-based electrolyte was used to evaluate the effects of solvent types on the interface formed (Figure S10). Compared with the high reactivity of EC to form the heterogeneous mosaic-like SEI, the SEI formed in DME solution becomes more homogenous, thus rendering an even Li^+ flux on PN interface. As a comparison, the single LiNO_3 and PCl_5/DME treated cells were also investigated to study their interfacial stability (Figure 2a, top). The interface obtained in 5% LiNO_3/DME solution is easy to be washed away and shows limited protection on deposited Li (lifetime 95 h). For the interface obtained in PCl_5/DME solution, due to the lack of lithium nitride that rapidly conducts lithium ions, the cell also exhibits a middle lifespan of 120 h under a current density of 2 mA cm^{-2} with a fixed capacity of 1 mA h cm^{-2} . Inheriting the advantages of nitride and phosphide, the PN/Li anode shows a stable voltage profile with a small hysteresis of about 50 mV for more than 320 h, while the bare Li anode quickly fails after just 170 h of cycling under the current density of 1 mA cm^{-2} (Figure S11a). When the current density increases to 5 mA cm^{-2} , dead lithium rapidly grows during each plating and stripping process in the bare Li-metal cell, resulting in a depletion of the lithium source over 40 cycles. In contrast, the PN-Li anode offers a fast ion transport pathway and enough mechanical strength for uniform Li deposition, leading to an excellent lithium retention for more than 100 cycles (Figure S11b). Even in an extreme condition of 10 mA cm^{-2} , the fast ion migration in the PN interface can also guarantee the smooth operation of symmetrical cells for more than 60 cycles, while a bare Li cell represents random voltage curves with sluggish ion transport kinetics (Figure 2b). The detailed voltage profiles are represented in Figure 2d; the curve of bare Li anode shows lots of burrs, reflecting severe side reactions or an internal short circuit under such a high current density. However, the PN-Li anode exhibits nearly constant voltage hysteresis (~ 250 mV), implying the outstanding stability and compatibility of PN at the anode interface. In addition, a high areal capacity of 3 mA h cm^{-2} for commercial use was tested to verify the stability of PN interface against large volume change (Figures 2c and S11c). The routine SEI on a bare Li anode is brittle and easily damaged by a sharp Li dendrite and surface fluctuation, which leads to a short lifetime of 110 h under the current density of 1 mA cm^{-2} . In contrast, the PN-Li cell can cycle more than 300 h without failure. The fast ionic pathway of the PN layer is also proven by electrochemical impedance spectra measurement in that PN interface possesses the lowest interfacial resistance ($\sim 10\text{ }\Omega$ in the first cycle, Figure 2e). The long lifespan of modified Li can be ascribed to the high cyclic Coulombic efficiency upon the PN interface (Figure S12). The PN-Li delivers 7.99 mA h of

active Li (CE: 96.12%) after 51 cycles in the EC/DEC electrolyte under the conditions of 1 mA cm^{-2} and 0.5 mA h cm^{-2} , which is much higher than bare Li (6.80 mA h , CE = 91.45%). When adding 30 wt % fluorinated carbonate into DEC, the CE of PN-modified Li can reach 98.04%. The high reversible capability of the PN interface is indispensably important to reduce the irreversible consumption of active Li materials.

The morphology of Li electrodeposits on the PN interface and bare Li can be probed directly using optical visualization studies. All cells were operated under a fixed current density of 3 mA cm^{-2} for 30 min to obtain the optical images. For the bare Li symmetrical cell, mossy Li electrodepositions are apparent as early as 8 min after the beginning of deposition. The uneven loose Li deposits are ramified growth on the surface of the Li anode, triggering the irreversible Li consumption and a severe safety hazard. The PN-Li anode shows a smooth Li deposition behavior without obvious Li protrusion (Figure 3a,b). Figure S13 provides more detailed information about Li deposition at 0.8 mA h . Sliced focused ion beam (FIB) images reveal the morphology evolution beneath the SEI (Figure 3c,d). After cross-sectioning by a Ga^+ ion beam, PN-Li exhibits a dense and compact Li deposition (black region) under the PN layer (white layer). The PN layer is tightly adhered to the Li surface without any interspace, indicating a good conformal ability of the PN layer. For the cycled bare Li, FIB images offer the textural information that Li deposition is porous, which means that a large volume expansion as well as accumulated SEI formation occurs after cycling (Figure S14). With the continuous plating and stripping process, the fragile SEI cannot endure such a large volume change, and fresh Li is exposed to the electrolyte to generate more SEI, which conversely aggravates the active Li consumption and dead Li formation (Figure 3e). SEM images confirm this behavior that the Li source is completely exhausted. The surface of the bare Li anode is full of disordered Li dendrites, and the electrode thickness dramatically increases to $150\text{ }\mu\text{m}$, 3-fold thicker than pristine Li (Figure 3f,g). In contrast, the PN interface can effectively insulate electrolyte intrusion, and fresh Li can finely protect beneath the SEI interface (Figure 3h). As a result, the cycled Li exhibits a flatter surface morphology and small volume exchange of $66\text{ }\mu\text{m}$ due to the smooth deposition kinetics (Figure 3i,j). Ex situ XPS shows that the nitrate fully changes to Li_3N , and the peaks of Cl 2p and P 2p can still be detected, indicating the PN interface finely coats the Li surface after 30 cycles (Figure S15).

The commercial process of the lithium metal anode encounters many difficulties. The most significant indicator for practical application of lithium metal batteries is the N/P ratio. However, many measurements are carried out under a Li unlimited condition with a small cathode loading ($500\text{ }\mu\text{m}$ thick Li and N/P ratio > 50). In this kind of configuration, cells always fail due to an internal short circuit or accumulated resistance rather than Li source depletion, which cannot reflect a practical cycling condition of real utilization. Therefore, it is urgent to design a full cell test with a low N/P ratio and high cathode loading for industrialization. In this work, we utilized the limited Li anode to pair with LiFePO_4 (LFP) and $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) to validate the cycling ability under an anode controlling condition. The characterizations of the LFP and NCM cathodes are exhibited in Figure S16. The LFP and NCM electrodes offer an areal capacity of 1.5 and 2.5

Figure 4. Electrochemical performance of Li/LFP and Li/NCM523 full cells. Long-term cycling performance of (a) Li/LFP and (b) Li/NCM523 full cells with mass loadings of 9.9 and 15.206 mg cm⁻². (c) Voltage profiles of bare Li/LFP and PN-Li/LFP cells at different cycles. (d) Voltage profiles of bare Li/NCM and PN-Li/NCM cells at different cycles.

mA h cm⁻², respectively. Figure 4a shows the long cycling stability of PN-Li/LFP and bare Li/LFP at a 0.5 C rate (1 C = 170 mA g⁻¹), from which a modified LFP cell possesses a higher and more stable cycling performance. Specifically, the initial specific capacity of 155 mA h g⁻¹ is obtained by a modified LFP cell and maintains 86.4% capacity retention after 180 cycles. Meanwhile, the bare Li/LFP cell can only effectively work for around 90 cycles and drops fast to 0 mA h g⁻¹ at the 130th cycle due to the depletion of the Li source in cells. The Coulombic efficiency confirms the lithium exhaustion in cells that the bare Li cell shows a declined CE after 90 cycles, while the PN-Li cell provides a high average CE of 99.8% during the whole cycling. The lithium exhaustion becomes more worse when the N/P ratio arrives at 3.92 by using an NCM cathode (Figure 4b). The bare Li/NCM cell has a 80% capacity retention of 25 cycles and quickly fails after 60 cycles at such a high N/P ratio. The cycled bare Li cell is disassembled, and remaining Li is measured to be 0.158 mA h cm⁻², which is difficult for normal operation (Figure S17). As a comparison, the PN-Li/NCM cell successfully works for more than 100 cycles with a high CE of 99.8%, which displays a 4-fold improvement in cell lifetime. The superior cycling performance is also supported by the galvanostatic voltage profiles in Figure 4c,d in that reduced voltage hysteresis can be found in modified LFP and NCM cells after the 90th and 20th cycles, suggesting that faster charge-transfer behavior at the PN/electrolyte interface effectively improves the cycling performance.

In conclusion, a functional phosphating–nitriding interface has been developed to improve cycling reversibility as well as suppress dendrite growth in high-energy-density cells. The

stable and high-ionic-conductivity interface consisting of inorganic Li₃PO₄, Li₃N, and nanocrystalline LiCl offers a high ionic pathway for fast Li⁺ transfer. As a result, symmetrical Li/Li cells utilizing 50 μm Li foils can operate steadily under an ultrahigh current density of 10 mA cm⁻² using a conventional EC/DEC electrolyte. Owing to the homogeneous lithium electrodeposition behavior of the PN-Li anode, the superior electrochemical cycling performance is achieved in high-capacity/high-voltage NCM/Li full cells for 100 cycles with a low N/P ratio of 3.92. This work provides a promising route to synthesize a stable liquid–solid interface with optimized components to solve the uneven deposition with Li metal and sheds a new light on further research on an advanced artificial SEI layer for high-energy lithium-based batteries.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.9b00416>.

Experimental section; supporting tables and figures (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: yingyinglu@zju.edu.cn. (Y.L.)

*E-mail: minling@zju.edu.cn. (M.L.)

ORCID

Min Ling: 0000-0001-6727-9585

Yingying Lu: 0000-0001-9713-8441

Author Contributions

[†]S.-Y.L. and Q.-L.L. contribute equally to this work.

Author Contributions

All authors have given approval to the final version of the manuscript.

Funding

This work was supported by the National Key R&D Program of China (2018YFA0209600, 2016YFA0202900) and the Natural Science Foundation of China (NSFC, grant number 21878268, 21676242).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Mrs. Na Zheng at the State Key Laboratory of Chemical Engineering in Zhejiang University for performing SEM and Raman. The authors also thank the support of the National Key R&D Program of China (2018YFA0209600, 2016YFA0202900) and the Natural Science Foundation of China (NSFC, grant number 21878268, 21676242).

ABBREVIATIONS

LIB, lithium ion battery; LMBs, lithium metal batteries; SEI, solid electrolyte interface; CE, Coulombic efficiency; FIB-SEM, focused ion beam scanning electron microscopy; DME, dimethyl ether; HRTEM, high-resolution transmission electron microscopy; XPS, X-ray photoelectron spectroscopy; EDS, energy dispersive spectroscopy; DFT, density functional theory; NMR, nuclear magnetic resonance

REFERENCES

- (1) Armand, M.; Tarascon, J. M. Building better batteries. *Nature* **2008**, *451*, 652–657.
- (2) Li, S.; Jiang, M.; Xie, Y.; Xu, H.; Jia, J.; Li, J. Developing High-Performance Lithium Metal Anode in Liquid Electrolytes: Challenges and Progress. *Adv. Mater.* **2018**, *30*, 1706375.
- (3) Li, L.; Li, S.; Lu, Y. Suppression of dendritic lithium growth in lithium metal-based batteries. *Chem. Commun.* **2018**, *54*, 6648–6661.
- (4) Zeng, X.; Li, M.; Abd El-Hady, D.; Alshitari, W.; Al-Bogami, A. S.; Lu, J.; Amine, K. Commercialization of Lithium Battery Technologies for Electric Vehicles. *Adv. Energy Mater.* **2019**, *9*, 1900161.
- (5) Fan, L.; Wei, S.; Li, S.; Li, Q.; Lu, Y. Recent Progress of the Solid-State Electrolytes for High-Energy Metal-Based Batteries. *Adv. Energy Mater.* **2018**, *8*, 1702657.
- (6) Liu, J.; Bao, Z.; Cui, Y.; Dufek, E. J.; Goodenough, J. B.; Khalifah, P.; Li, Q.; Liaw, B. Y.; Liu, P.; Manthiram, A.; Meng, Y. S.; Subramanian, V. R.; Toney, M. F.; Viswanathan, V. V.; Whittingham, M. S.; Xiao, J.; Xu, W.; Yang, J.; Yang, X.-Q.; Zhang, J.-G. Pathways for practical high-energy long-cycling lithium metal batteries. *Nat. Energy* **2019**, *4*, 180–186.
- (7) Lu, Y.; Rong, X.; Hu, Y.-S.; Li, H.; Chen, L. Research and development of advanced battery materials in China. *Energy Storage Mater.* **2019**, *23*, 144.
- (8) Tikekar, M. D.; Choudhury, S.; Tu, Z.; Archer, L. A. Design principles for electrolytes and interfaces for stable lithium-metal batteries. *Nat. Energy* **2016**, *1*, 16114.
- (9) Niu, C.; Pan, H.; Xu, W.; Xiao, J.; Zhang, J. G.; Luo, L.; Wang, C.; Mei, D.; Meng, J.; Wang, X.; Liu, Z.; Mai, L.; Liu, J. Self-smoothing anode for achieving high-energy lithium metal batteries under realistic conditions. *Nat. Nanotechnol.* **2019**, *14*, 594–601.
- (10) Niu, C.; Lee, H.; Chen, S.; Li, Q.; Du, J.; Xu, W.; Zhang, J.-G.; Whittingham, M. S.; Xiao, J.; Liu, J. High-energy lithium metal pouch cells with limited anode swelling and long stable cycles. *Nat. Energy* **2019**, *4*, 551–559.

- (11) Ren, X.; Zou, L.; Cao, X.; Engelhard, M. H.; Liu, W.; Burton, S. D.; Lee, H.; Niu, C.; Matthews, B. E.; Zhu, Z.; Wang, C.; Arey, B. W.; Xiao, J.; Liu, J.; Zhang, J.-G.; Xu, W. Enabling High-Voltage Lithium-Metal Batteries under Practical Conditions. *Joule* **2019**, *3*, 1662–1676.

- (12) Li, S.; Liu, Q.; Zhou, J.; Pan, T.; Gao, L.; Zhang, W.; Fan, L.; Lu, Y. Hierarchical Co₃O₄ Nanofiber–Carbon Sheet Skeleton with Superior Na/Li-Philic Property Enabling Highly Stable Alkali Metal Batteries. *Adv. Funct. Mater.* **2019**, *29*, 1808847.

- (13) Li, Q.; Zhu, S.; Lu, Y. 3D Porous Cu Current Collector/Li-Metal Composite Anode for Stable Lithium-Metal Batteries. *Adv. Funct. Mater.* **2017**, *27*, 1606422.

- (14) Yun, Q.; He, Y. B.; Lv, W.; Zhao, Y.; Li, B.; Kang, F.; Yang, Q. H. Chemical Dealloying Derived 3D Porous Current Collector for Li Metal Anodes. *Adv. Mater.* **2016**, *28*, 6932–6939.

- (15) Zheng, X.; Li, P.; Cao, Z.; Luo, W.; Sun, F.; Wang, Z.; Ding, B.; Wang, G.; Huang, Y. Boosting the Reversibility of Sodium Metal Anode via Heteroatom-Doped Hollow Carbon Fibers. *Small* **2019**, *15*, 1902688.

- (16) Fan, L.; Li, S.; Liu, L.; Zhang, W.; Gao, L.; Fu, Y.; Chen, F.; Li, J.; Zhuang, H. L.; Lu, Y. Enabling stable lithium metal anode via 3D inorganic skeleton with superlithiophilic interphase. *Adv. Energy Mater.* **2018**, *8*, 1802350.

- (17) Liu, S.; Xia, X.; Deng, S.; Xie, D.; Yao, Z.; Zhang, L.; Zhang, S.; Wang, X.; Tu, J. In Situ Solid Electrolyte Interphase from Spray Quenching on Molten Li: A New Way to Construct High-Performance Lithium-Metal Anodes. *Adv. Mater.* **2019**, *31*, 1806470.

- (18) Li, S.; Fan, L.; Lu, Y. Rational design of robust-flexible protective layer for safe lithium metal battery. *Energy Storage Mater.* **2019**, *18*, 205–212.

- (19) Xu, R.; Zhang, X.-Q.; Cheng, X.-B.; Peng, H.-J.; Zhao, C.-Z.; Yan, C.; Huang, J.-Q. Artificial Soft-Rigid Protective Layer for Dendrite-Free Lithium Metal Anode. *Adv. Funct. Mater.* **2018**, *28*, 1705838.

- (20) Jiang, Z.; Jin, L.; Han, Z.; Hu, W.; Zeng, Z.; Sun, Y.; Xie, J. Facile Generation of Polymer-Alloy Hybrid Layers for Dendrite-Free Lithium-Metal Anodes with Improved Moisture Stability. *Angew. Chem., Int. Ed.* **2019**, *58*, 11374–11378.

- (21) Xu, R.; Cheng, X.-B.; Yan, C.; Zhang, X.-Q.; Xiao, Y.; Zhao, C.-Z.; Huang, J.-Q.; Zhang, Q. Artificial Interphases for Highly Stable Lithium Metal Anode. *Matter* **2019**, *1*, 317–344.

- (22) Ren, X.; Chen, S.; Lee, H.; Mei, D.; Engelhard, M. H.; Burton, S. D.; Zhao, W.; Zheng, J.; Li, Q.; Ding, M. S.; Schroeder, M.; Alvarado, J.; Xu, K.; Meng, Y. S.; Liu, J.; Zhang, J.-G.; Xu, W. Localized High-Concentration Sulfone Electrolytes for High-Efficiency Lithium-Metal Batteries. *Chem.* **2018**, *4*, 1877–1892.

- (23) Chen, S.; Zheng, J.; Mei, D.; Han, K. S.; Engelhard, M. H.; Zhao, W.; Xu, W.; Liu, J.; Zhang, J. G. High-Voltage Lithium-Metal Batteries Enabled by Localized High-Concentration Electrolytes. *Adv. Mater.* **2018**, *30*, No. 1706102.

- (24) Yan, C.; Yao, Y. X.; Chen, X.; Cheng, X. B.; Zhang, X. Q.; Huang, J. Q.; Zhang, Q. Lithium Nitrate Solvation Chemistry in Carbonate Electrolyte Sustains High-Voltage Lithium Metal Batteries. *Angew. Chem., Int. Ed.* **2018**, *57*, 14055–14059.

- (25) Yang, Y.; Davies, D. M.; Yin, Y.; Borodin, O.; Lee, J. Z.; Fang, C.; Olguin, M.; Zhang, Y.; Sablina, E. S.; Wang, X.; Rustomji, C. S.; Meng, Y. S. High-Efficiency Lithium-Metal Anode Enabled by Liquefied Gas Electrolytes. *Joule* **2019**, *3*, 1986–2000.

- (26) Fan, X.; Chen, L.; Borodin, O.; Ji, X.; Chen, J.; Hou, S.; Deng, T.; Zheng, J.; Yang, C.; Liou, S. C.; Amine, K.; Xu, K.; Wang, C. Non-flammable electrolyte enables Li-metal batteries with aggressive cathode chemistries. *Nat. Nanotechnol.* **2018**, *13*, 715–722.

- (27) Weber, R.; Genovese, M.; Louli, A. J.; Hames, S.; Martin, C.; Hill, I. G.; Dahn, J. R. Long cycle life and dendrite-free lithium morphology in anode-free lithium pouch cells enabled by a dual-salt liquid electrolyte. *Nat. Energy* **2019**, *4*, 683–689.

- (28) Zeng, Z.; Murugesan, V.; Han, K. S.; Jiang, X.; Cao, Y.; Xiao, L.; Ai, X.; Yang, H.; Zhang, J.-G.; Sushko, M. L.; Liu, J. Non-flammable

electrolytes with high salt-to-solvent ratios for Li-ion and Li-metal batteries. *Nat. Energy* **2018**, 3, 674–681.

(29) Zhang, Y.; Zhong, Y.; Shi, Q.; Liang, S.; Wang, H. Cycling and Failing of Lithium Metal Anodes in Carbonate Electrolyte. *J. Phys. Chem. C* **2018**, 122, 21462–21467.

(30) Zhang, Y.; Zhong, Y.; Liang, S.; Wang, B.; Chen, X.; Wang, H. Formation and Evolution of Lithium Metal Anode–Carbonate Electrolyte Interphases. *ACS Materials Lett.* **2019**, 1, 254–259.

(31) Kim, M. S.; Ryu, J.-H.; Deepika; Lim, Y. R.; Nah, I. W.; Lee, K.-R.; Archer, L. A.; Il Cho, W. Langmuir–Blodgett artificial solid-electrolyte interphases for practical lithium metal batteries. *Nat. Energy* **2018**, 3, 889–898.

(32) Wang, J.; Huang, W.; Pei, A.; Li, Y.; Shi, F.; Yu, X.; Cui, Y. Improving cyclability of Li metal batteries at elevated temperatures and its origin revealed by cryo-electron microscopy. *Nat. Energy* **2019**, 4, 664–670.

(33) Hwang, J.-Y.; Park, S.-J.; Yoon, C. S.; Sun, Y.-K. Customizing a Li–metal battery that survives practical operating conditions for electric vehicle applications. *Energy Environ. Sci.* **2019**, 12, 2174–2184.