

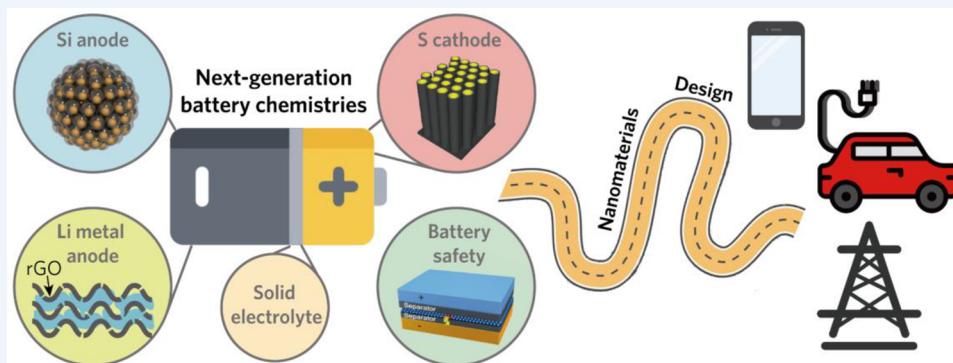
Design of Complex Nanomaterials for Energy Storage: Past Success and Future Opportunity

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CONSPECTUS: The development of next-generation lithium-based rechargeable batteries with high energy density, low cost, and improved safety is a great challenge with profound technological significance for portable electronics, electric vehicles, and grid-scale energy storage. Specifically, advanced lithium battery chemistries call for a paradigm shift to electrodes with high Li to host ratio based on a conversion or alloying mechanism, where the increased capacity is often accompanied by drastic volumetric changes, significant bond breaking, limited electronic/ionic conductivity, and unstable electrode/electrolyte interphase.

Fortunately, the rapid progress of nanotechnology over the past decade has been offering battery researchers effective means to tackle some of the most pressing issues for next-generation battery chemistries. The major applications of nanotechnology in batteries can be summarized as follows: First, by reduction of the dimensions of the electrode materials, the cracking threshold of the material upon lithiation can be overcome, at the same time facilitating electron/ion transport within the electrode. Second, nanotechnology also provides powerful methods to generate various surface-coating and functionalization layers on electrode materials, protecting them from side reactions in the battery environment. Finally, nanotechnology gives people the flexibility to engineer each and every single component within a battery (separator, current collector, etc.), bringing novel functions to batteries that are unachievable by conventional methods.

Thus, this Account aims to highlight the crucial role of nanotechnology in advanced battery systems. Because of the limited space, we will mainly assess representative examples of rational nanomaterials design with complexity for silicon and lithium metal anodes, which have shown great promise in constraining their large volume changes and the repeated solid–electrolyte interphase formation during cycling. Noticeably, the roadmap delineating the gradual improvement of silicon anodes with a span of 11 generations of materials designs developed in our group is discussed in order to reflect how nanotechnology could guide battery research step by step toward practical applications. Subsequently, we summarize efforts to construct nanostructured composite sulfur cathodes with improved electronic conductivity and effective soluble species encapsulation for maximizing the utilization of active material, cycle life, and system efficiency. We emphasize carbon-based materials and, importantly, materials with polar surfaces for sulfur entrapment. We then briefly discuss nanomaterials strategies to improve the ionic conductivity of solid polymer electrolytes by means of incorporating high-surface-area and, importantly, high-aspect-ratio secondary-phase fillers for continuous, low-tortuosity ionic transport pathways. Finally, critical innovations that have been brought to the area of grid-scale energy storage and battery safety by nanotechnology are also succinctly reviewed.

1. INTRODUCTION

The past 25 years have witnessed the rapid development of rechargeable lithium-ion batteries (LIBs) and their commercial success for portable electronics. Today, LIBs are playing an ever

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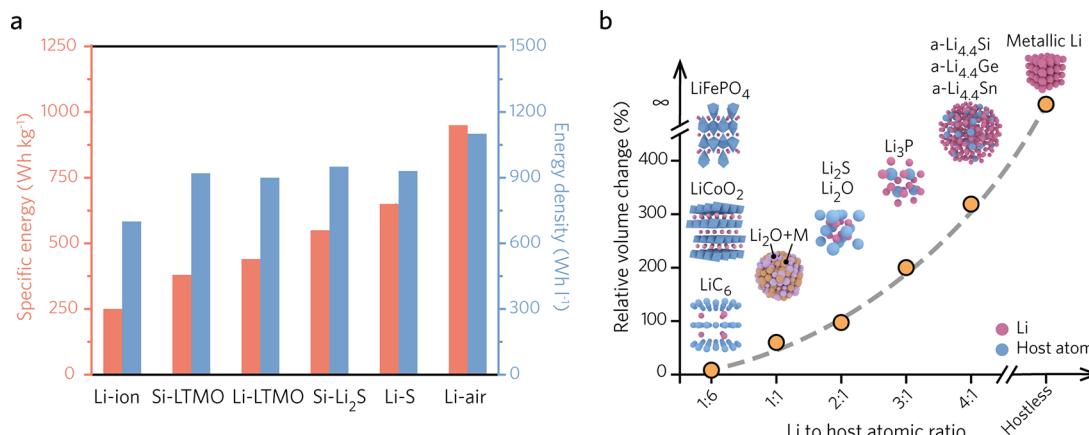


Figure 1. (a) Practical specific energies and energy densities of state-of-art LIBs (Li-ion), and advanced battery chemistries including Si–LTMO, Li metal–LTMO, Si–Li₂S, Li metal–S, and Li–air. Casings, separators, and electrolytes are all considered, and Li metal cells are calculated on the basis of 100% excess Li. (b) Increased specific capacity is accompanied by significantly increased volume change, bringing challenges to the practical applications of advanced electrode materials.

more important role in the sustainable energy landscape as the enabling technology for electric vehicles and grid-scale storage. The state-of-the-art LIBs are composed of graphite anodes and Li transition-metal oxide (LTMO)/phosphate cathodes that reversibly intercalate Li ions with minimal structural change thanks to the low atomic ratio of Li ions to host atoms. Nevertheless, the chemical bonding of the host structure limits the capacity of intercalation electrodes, and conventional battery chemistry is approaching its theoretical limits with narrow room to satisfy our unprecedented demand. Thus, battery chemistries beyond Li ion need to be developed.¹

Next-generation batteries call for a paradigm shift to electrodes with high Li to host ratios based on a conversion or alloying mechanism (Figure 1a). Replacing graphite with silicon or Li metal alone can nearly double the specific energy, while the adoption of sulfur and air cathodes would offer practical specific energies beyond 500 W h kg⁻¹ with further improved volumetric energy density. However, the increased capacity is often accompanied by drastic volumetric changes, significant bond breaking, and unstable electrode–electrolyte interphase, undermining the electrochemical performance. Figure 1b plots the relative volume expansion versus the Li to host atomic ratio. Existing electrode materials have less than 10% volume change with a small Li to host ratio (1:6). However, new chemistries such as Si can have 300% volume expansion with a large Li to host ratio (~4:1).

Over the past decade, nanotechnology has been offering unparalleled solutions to battery research.² With various complex nanostructural designs, researchers have come closer to tackling the problems of next-generation battery chemistries. Thus, it is a good time to review the progress made to date and look ahead to what is possible in the near future. This Account aims to summarize the crucial role of nanotechnology in advanced battery systems, highlighting representative examples of Si and Li metal anodes, S cathodes, and composite solid electrolytes. We then discuss nanomaterials for grid-scale storage and battery safety, albeit briefly because of limited space.

2. NANOMATERIALS FOR ANODES

2.1. Si Anode

Si is among the most prominent anode materials for next-generation batteries because of its high theoretical capacity (4200 mA h g⁻¹ based on the mass of Si), which is over 10 times that of graphite

(372 mA h g⁻¹). The high capacity, originating from its alloying mechanism, where each Si can host up to 4.4 Li ions, also brings poor cyclability due to the significant volume expansion (>300%) upon lithiation. The stress induced by the volume change cracks and even pulverizes the electrode, leading to loss of electrical contact and rapid capacity fading. Moreover, the continuous expansion/contraction during cycling can disrupt the solid–electrolyte interphase (SEI), resulting in low Coulombic efficiency (CE) due to repeated SEI formation.³ The Si anode is an exemplary case to illustrate the power of nanotechnology in addressing material challenges facing battery research. In our group alone, there have been 11 generations of nanostructural designs toward improving Si for practical applications (Figure 2).

The pulverization issue was first mitigated by reducing the size of the Si to the nanoscale. It was reported that with sizes less than 300 nm, known as the critical fracture size, Si will expand and contract without pulverization.⁴ For example, the first-generation Si anode reported by our group at the end of 2007 utilized Si nanowires grown directly on the current collector by a vapor–liquid–solid method,⁵ and a pronounced improvement in electrochemical performance was observed compared with thick films and large particles. Inspired by this, we subsequently explored Si crystalline–amorphous core–shell nanowires (Gen 2)⁶ and hollow nanospheres (Gen 3).⁷ In Gen 2, because of the difference in lithiation potentials, only the amorphous shell was selectively cycled, while the crystalline core was preserved as a mechanical support and electron transport pathway.

Although the above nanostructures demonstrated high resistance to pulverization, the SEI remained unstable because of their outward expansion when lithiated. To stabilize the interface, various approaches were explored, including double-walled Si–SiO_x nanotubes (Gen 4)⁸ and Si nanoparticle–carbon yolk–shell structures (Gen 5).⁹ With the existence of an internal void space and a strong mechanical clamping outer layer (SiO_x or carbon), Si could expand inward without breaking the SEI on the outer surface, allowing hundreds or even thousands of stable cycles to be achieved with CEs of up to ~99.9%.

Developing advanced binders for Si is also crucial. Conventional poly(vinylidene fluoride) binder attaches to Si only via weak van der Waals forces and fails to hold the particles together in the presence of large volume expansion.¹⁰ In 2013, a three-dimensional (3D) conducting hydrogel formed by *in situ* polymerization (Gen 6) and a self-healing polymer (Gen 7) were

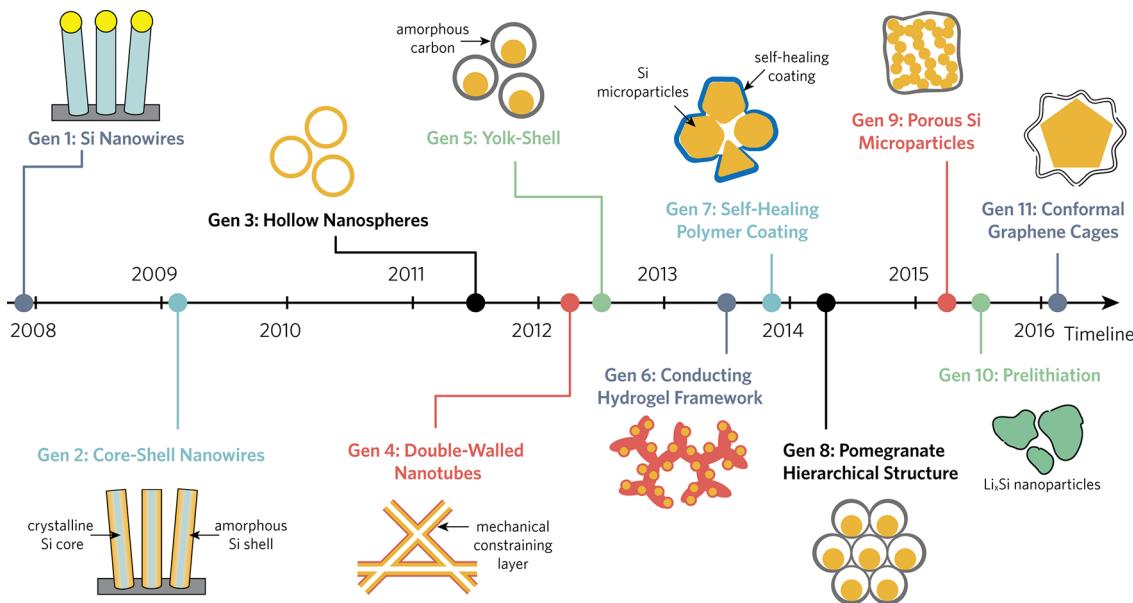


Figure 2. Roadmap of nanostructural designs for Si anodes.

proposed by Stanford groups as novel binders.^{11,12} Noticeably, the self-healing chemistry proved to be effective even on micron-sized Si, extending the cycle life over 10 times.

To realize viable Si anodes, two more issues have to be considered: (1) side reactions during the initial cycles need to be minimized, and (2) the areal and volumetric capacities must be increased to meet the industrial standards. The main obstacle facing nanosized Si is the high surface area, which exacerbates side reactions. Moreover, the tap density of nano-Si is relatively low, bringing about low volumetric capacity. To address these shortcomings, a pomegranate-inspired hierarchical Si structure (Gen 8) and nonfilling carbon-coated porous Si microparticles (Gen 9) were developed.^{13,14} Specifically, an ensemble of Si nanoparticles was encapsulated by a thicker, electrolyte-proof carbon layer to afford micron-sized secondary particles. This hierarchical arrangement lowered the electrode–electrolyte contact area, resulting in high CE, superior cyclability, and high volumetric capacity. Meanwhile, anode prelithiation reagents (Gen 10) were developed to compensate for the first-cycle capacity loss due to SEI formation. For example, we demonstrated the synthesis of Li_xSi–Li₂O core–shell nanoparticles by thermal alloying.¹⁵ The Li₂O shell imparted solvent and dry-air stability to the reactive Li_xSi core, realizing a high extraction capacity (1400 mA h g⁻¹).

Our latest design (Gen 11) extended the concept of nanomaterials encapsulation to Si microparticles, which are more viable toward industrial applications from an economic standpoint.¹⁶ Si microparticles were conformally encapsulated by multilayered graphene cages with pre-engineered empty space. Despite the fracture of Si during cycling, the mechanically strong and conductive graphene cage could confine the Si pieces while maintaining the essential electrical contact and stabilizing the SEI. Finally, the nanoscale design principles developed for Si over the years can be transferred to other battery materials that undergo large volume changes, such as Sn and Ge anodes and transition metal oxides.¹⁷

2.2. Li Metal Anode

Li metal is the ultimate anode of choice because of its highest theoretical capacity (3860 mA h g⁻¹, stemming from its “hostless”

nature) and lowest electrochemical potential (−3.04 V vs the standard hydrogen electrode).¹⁸ Despite five decades of research, there remained no workable solution to the challenges of the Li metal anode, the major two of which are its high reactivity and infinite relative volume change during cycling. The significant interfacial fluctuation cracks the fragile SEI layer, locally enhancing the Li-ion flux to promote dendritic Li deposition, which could trigger internal short circuit and compromise battery safety. Moreover, the high-surface-area dendrites and the recurring SEI breakdown/repair bring about continuous side reactions, severely shortening the cycle life. Recently, the development of nanotechnology has brought a renaissance in Li metal research, the progress of which has been well-summarized in several reviews.^{19–21} Therefore, we will mainly highlight representative nanotechnology-based solutions toward Li stabilization developed in our group.

Electrolyte additives are a long-lasting theme in Li metal research, and renewed interest has surfaced recently using additives such as fluorinated compounds and metal ions.^{22,23} We discovered the synergistic effect of Li polysulfide (LPS) and LiNO₃ in suppressing dendrites (Figure 3a).²⁴ With conventional LiNO₃ additive alone in ether electrolyte, as observed from the scanning electron microscopy (SEM) image, dendritic deposition still occurred (Figure 3b). However, the further presence of Li₂S₈ transformed the Li deposit into a pancake-shaped morphology (Figure 3c), which was attributed to the competing reactions between the two additives toward Li that formed a more stable SEI. Such a synergistic effect enabled high-CE cycling even at high current densities (>99% for over 300 cycles at 2 mA cm⁻²).

In 2014, we proposed the concept of nanoscale interfacial engineering, wherein mechanically and electrochemically stable interfaces can be fabricated on current collectors. During deposition, Li ions pass through the interface and deposit underneath, such that dendrites can be mechanically suppressed. Moreover, the SEI forms on top of the interface, and the two can move together during cycling without fracturing (Figure 3d). The first example was constructed with interconnected hollow carbon spheres (Figure 3e), which were elevated after Li plating (Figure 3f) due to their weak binding with the substrate, resulting

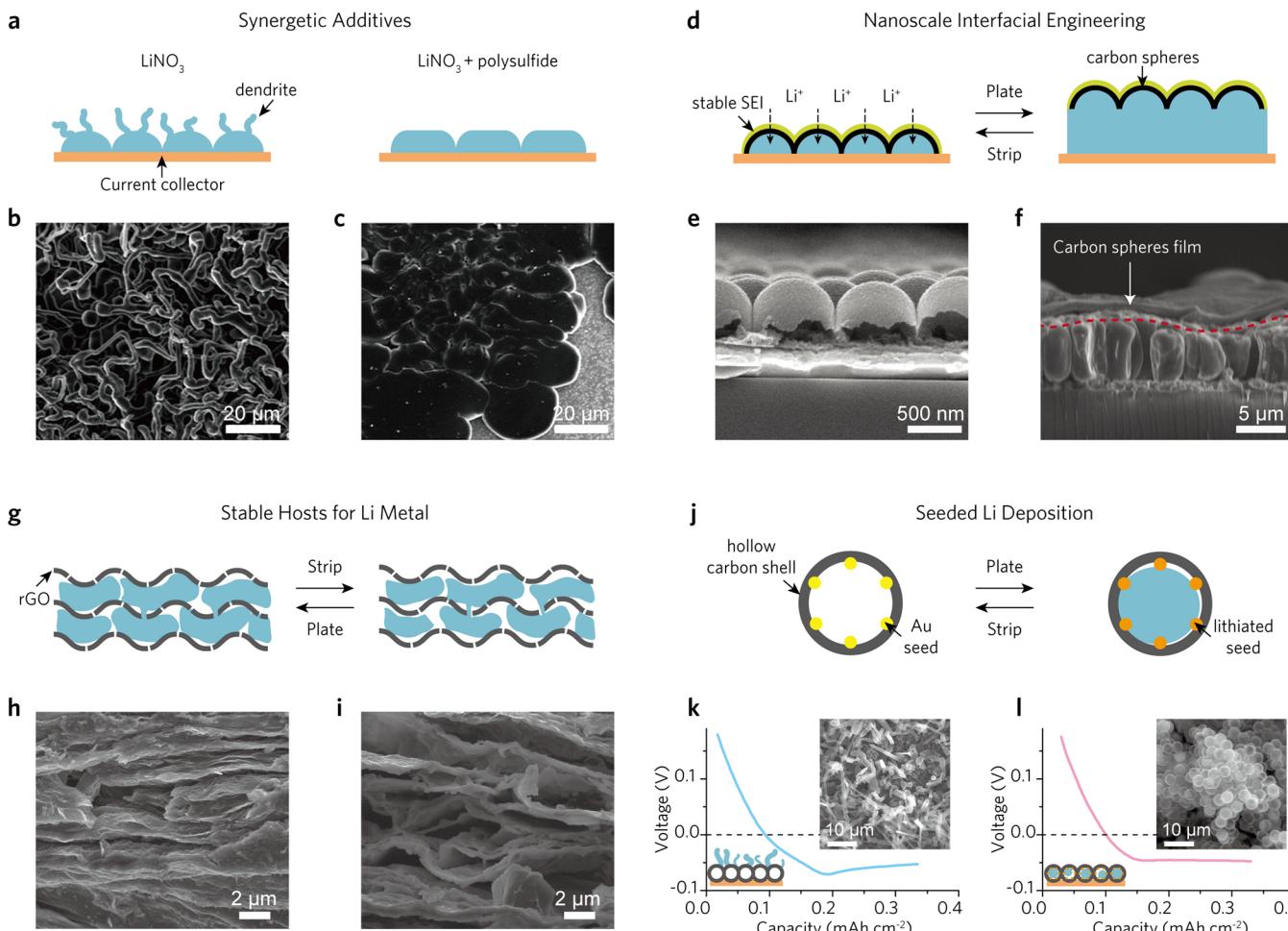


Figure 3. (a) Schematic of Li deposit morphologies with LiNO_3 alone and with both Li_2S_8 and LiNO_3 as synergistic additives and (b, c) the corresponding SEM images. Adapted with permission from ref 24. Copyright 2015 Nature Publishing Group. (d) Principles of nanoscale interfacial engineering, where Li deposits under the interface while this layer moves during cycling to stabilize the SEI. The first example was on (e) interconnected hollow carbon spheres, which (f) allowed the deposition of columnar Li. Adapted with permission from ref 25. Copyright 2014 Nature Publishing Group. (g) Schematic showing the effect of stable hosts in maintaining constant electrode volume and (h, i) the corresponding SEM images of the Li-rGO composite (h) in the pristine state and (i) after complete Li stripping. Adapted with permission from ref 29. Copyright 2016 Nature Publishing Group. (j) Schematic of spatially controlled Li deposition into Au-seeded carbon capsules and (k, l) deposition voltage profiles on carbon capsules (k) without and (l) with Au. The insets are SEM images after deposition. Adapted with permission from ref 39. Copyright 2016 Nature Publishing Group.

in columnar deposition and enhanced cyclability.²⁵ Nanostructuring of interfaces directly on current collectors unleashed the constraints of fabricating artificial SEIs on highly reactive Li metal, leading to various novel designs based on two-dimensional (2D) materials,²⁶ inorganic nanoparticles,²⁷ and polymers.²⁸

Though the above-mentioned approaches successfully hindered dendrite growth and improved CE, they were unable to tackle the critical problem of infinite volume change. This issue has long been overlooked until recently, when stable hosts were introduced to afford porous Li metal composites. In one example, a layered reduced graphene oxide (rGO) film was found to possess good wettability by Li (“lithiophilicity”), such that molten Li can rapidly infuse into the host upon contact.²⁹ The property was attributed to the strong interaction between molten Li and the oxygen-containing functional groups of rGO as well as the nanocapillary forces within the rGO gaps. The presence of the rGO skeleton successfully reduced the relative volume change to below 20% upon complete Li stripping (Figure 3g–i). Moreover, such composites demonstrated high electroactive surface area, dissipating the current density for reduced overpotential and more uniform Li deposition.

Lithiophilicity is a prerequisite for molten Li infusion, yet few materials possess this property. To expand the material choices for hosting Li, we also developed a general surface modification method that involves a thin and conformal lithophilic coating of ZnO or Si.^{30,31} The method enabled a series of studies on Li composites and the integration of Li metal with solid electrolytes.^{32,33} Overstoichiometric reaction between Li and hosts was also investigated as an alternative to obtain composite Li anodes.^{34,35}

Similar to Si, nanostructuring of Li increases the surface area, which may result in more side reactions during initial cycles. Solution-based coating of an artificial SEI is one option to passivate the Li surface.³⁶ Importantly, gas-phase reactions that can conformally coat 3D surfaces would be ideal. Recently reports have described the effective passivation of Li using atomic layer deposition³⁷ and gaseous reagents such as Freon.³⁸ Ultimately, combining nanostructured Li with a proper solid electrolyte may be the way toward a stable interphase.

Finally, basic questions about Li deposition await to be elucidated, as there is no conclusive understanding of the different morphologies formed under different conditions. The studies

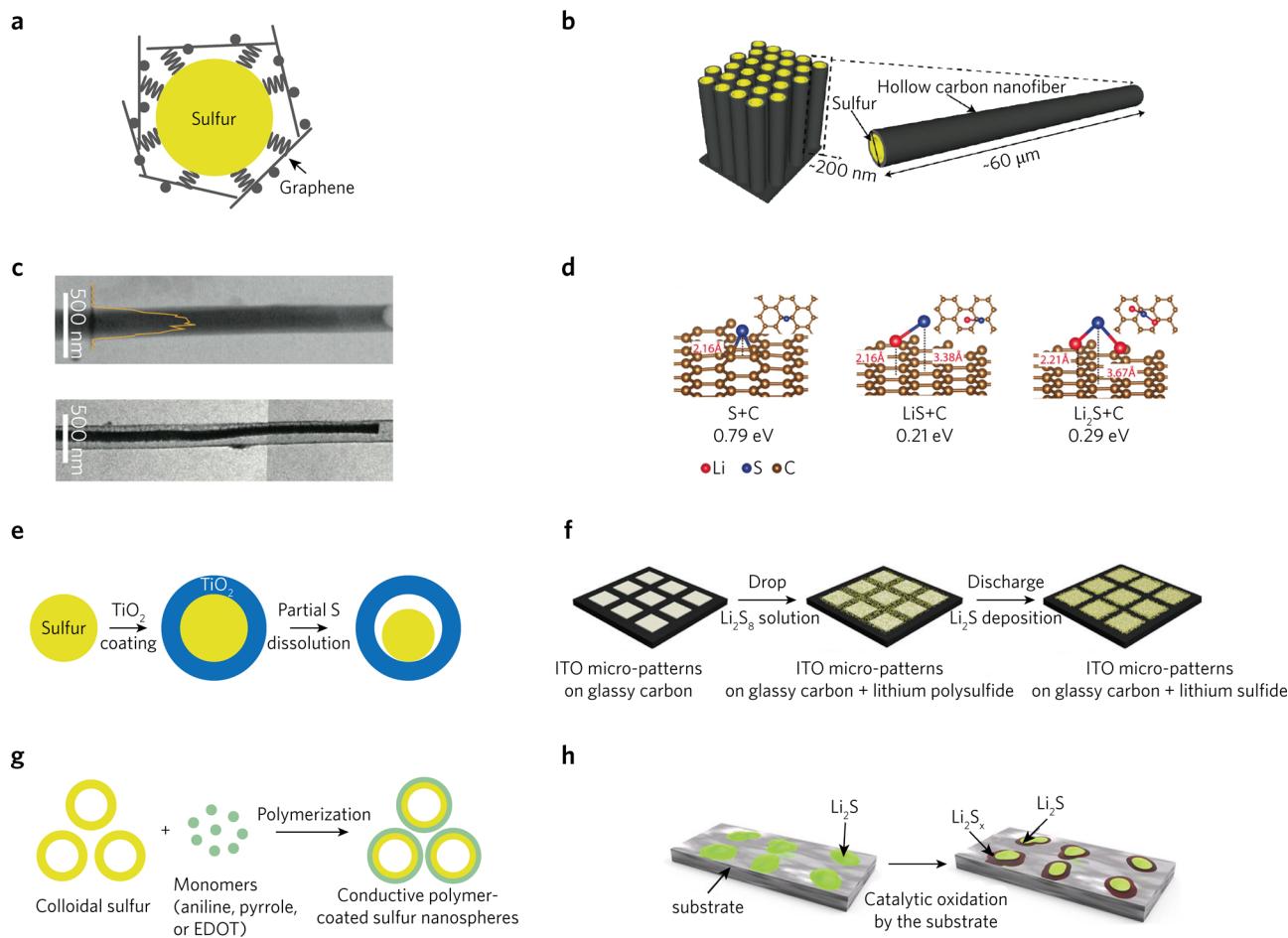


Figure 4. (a) Schematic of a graphene-wrapped sulfur composite. Adapted from ref 46. Copyright 2011 American Chemical Society. (b) Schematic of hollow carbon nanofibers for effective LPSs trapping. Adapted from ref 52. Copyright 2011 American Chemical Society. (c) TEM images of hollow-carbon-nanofiber-encapsulated sulfur (top) before and (bottom) after discharge and (d) results of first-principles calculations revealing the weak interaction between carbon and sulfur species. Adapted from ref 53. Copyright 2013 American Chemical Society. (e) Schematic of the synthesis of sulfur–TiO₂ yolk–shell structure. Adapted with permission from ref 56. Copyright 2013 Nature Publishing Group. (f) Schematic showing spatially preferred LPS deposition on the polar ITO surface. Adapted with permission from ref 58. Copyright 2014 Nature Publishing Group. (g) Schematic of the fabrication of conductive-polymer-coated hollow sulfur nanospheres. Adapted from ref 60. Copyright 2013 American Chemical Society. (h) Metal sulfides catalyze the oxidation of Li₂S to sulfur. Adapted with permission from ref 63. Copyright 2017 National Academy of Sciences.

are made complicated by the high reactivity of Li and the instant formation of a heterogeneous SEI during deposition. Therefore, future efforts to address these fundamental questions are needed. When exploring Li deposition on various metal substrates, we found that substrates with definite Li solubility (e.g., Au) exhibited low nucleation barriers, whereas substrates with no Li solubility (e.g., Cu) had appreciable nucleation barriers.³⁹ Taking advantage of this, we designed Au-seeded hollow carbon capsules that enabled spatially controlled Li deposition only inside the capsules without dendrite formation, while the SEI was stabilized by the carbon shell (Figure 3j–l). High CEs (>98%) can be obtained for over 300 cycles even in corrosive carbonate-based electrolytes.

3. NANOMATERIALS FOR CATHODES

Sulfur stands out as a promising cathode candidate because of its overwhelming advantage in specific energy (2600 W h kg^{-1}) and capacity (1675 mA h g^{-1}), which is 5-fold higher than that of state-of-the-art cathodes.¹ It is also abundant and environmentally friendly. However, enormous challenges remain for Li–S chemistry, including (i) the insulating nature of sulfur species, which leads to poor material utilization; (ii) dissolution of LPSs

into the electrolyte, which causes material loss and low CE due to the shuttling effect; and (iii) the 80% volume expansion during lithiation, which induces structural damage in electrode materials.⁴⁰ To address these issues, tremendous efforts have been made to design nanostructured composite cathodes.

Carbon materials are the most common hosts for confining sulfur because of their high electrical conductivity and large pore volume.⁴¹ The Nazar group pioneered this area by developing a highly ordered mesoporous carbon–sulfur cathode via melt diffusion.⁴² Our group also reported a full-cell design with a Li₂S–mesoporous carbon composite cathode and Si nanowire anode, which exhibited a high specific energy of 630 W h kg^{-1} based on the mass of Li₂S.⁴³ The groups of Gao⁴⁴ and Guo⁴⁵ both reported the encapsulation of metastable small sulfur molecules in carbon micropores, which effectively suppressed LPS dissolution.

Besides porous carbon, 2D-nanostructured graphene, with its large surface area and rich surface chemistry, also shows great promise. The Dai group utilized carbon-black-decorated graphene to wrap poly-(ethylene glycol)-coated sulfur particles (Figure 4a), which demonstrated 80% capacity retention over 100 cycles.⁴⁶ Other representative graphene–sulfur configurations include a

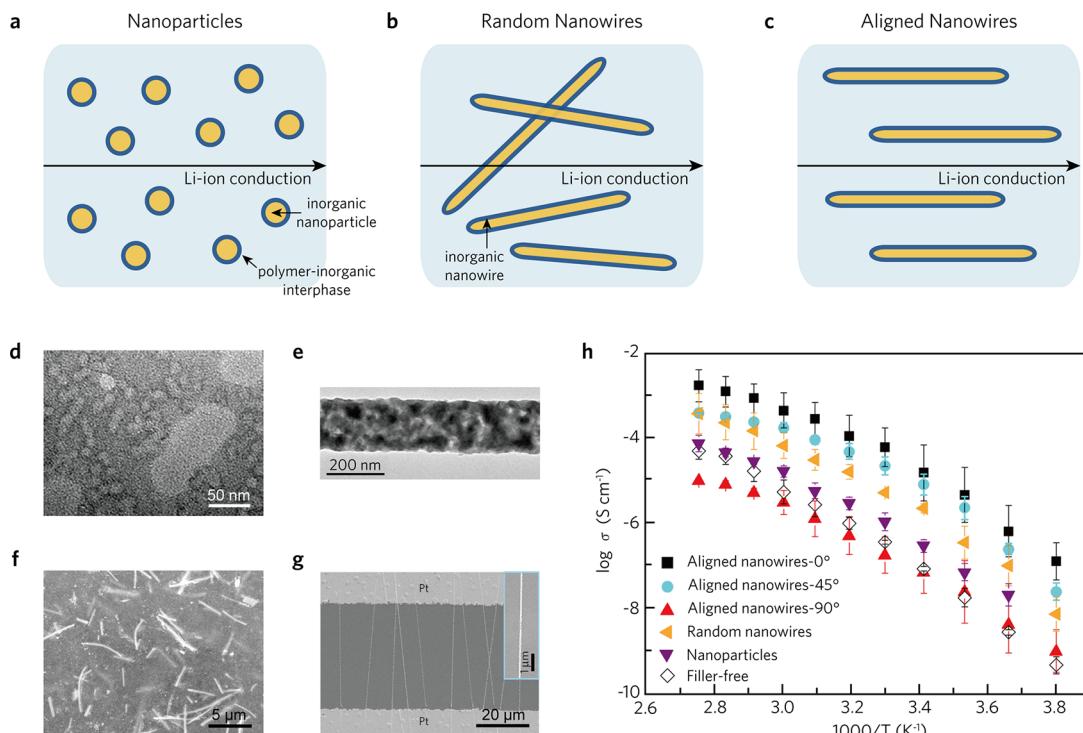


Figure 5. Li-ion conduction pathways in CPEs with (a) nanoparticles, (b) random nanowires, and (c) aligned nanowires as fillers. High-aspect-ratio nanowires supply a more continuous conduction pathway, and aligned nanowires further decrease the conduction tortuosity. (d) TEM image of the in situ 12 nm silica CPE. Adapted from ref 66. Copyright 2015 American Chemical Society. (e) TEM image of an LLTO nanowire. Adapted from ref 67. Copyright 2015 American Chemical Society. (f, g) SEM images of polyacrylonitrile CPEs with (f) random (adapted from ref 67; copyright 2015 American Chemical Society) and (g) aligned LLTO nanowires. (h) Arrhenius plots of CPEs with nanowires at various orientations, random nanowires, and filler-free electrolyte. Adapted with permission from ref 68. Copyright 2017 Nature Publishing Group.

sandwich-type structure,⁴⁷ a gradient structure,⁴⁸ unstacked graphene double layers,⁴⁹ etc.

One-dimensional carbon nanostructures have also been widely studied. Sulfur-coated carbon nanotube (CNT) coaxial structures⁵⁰ and vertically aligned CNT–sulfur composites have been studied to improve the electrochemical performance.⁵¹ However, sulfur residues outside of CNTs were hard to prevent, leading to sulfur dissolution during cycling. Correspondingly, a more effective encapsulation method was proposed, involving the synthesis of hollow carbon nanofibers with an anodic aluminum oxide (AAO) template (Figure 4b), such that sulfur infusion could be confined solely inside the nanofibers.⁵²

Although a substantial body of literature has reported good battery performance with sulfur–carbon composites, our group recognized early the relatively weak interactions between non-polar carbon and polar LPS species. The weak physical binding leads to significant detachment of active materials, as confirmed by ex situ transmission electron microscopy (TEM) and first-principles calculations (Figure 4c,d).⁵³ Thus, polar hosts are preferred for stronger sulfur anchoring. Metal oxides such as Al_2O_3 and SiO_2 ,^{54,55} with high surface area and abundant polar groups, have been extensively explored as LPS absorbents. We proposed a sulfur– TiO_2 yolk–shell nanoarchitecture to accommodate sulfur volume expansion and LPS dissolution inside the internal void space (Figure 4e), which realized an initial specific capacity of 1030 mA h g^{-1} with 67% retention after 1000 cycles.⁵⁶ However, as a semiconductor, TiO_2 has low electrical conductivity, so the coating thickness needs to be controlled elaborately. This issue can be resolved by reducing TiO_2 to a more conductive TiO_{2-x} phase.⁵⁷ Moreover, with patterned tin-doped indium oxide (ITO) on a glassy carbon electrode,

we provided clear visual evidence of the preferred LPS deposition on polar ITO surfaces (Figure 4f).⁵⁸

Another strategy to alleviate the shuttling effect and improve the electrical conductivity of sulfur is to adopt conductive polymers (e.g., polyaniline,⁵⁹ polypyrrole,⁶⁰ poly-(3,4-(ethylene-dioxy)-thiophene) (PEDOT),⁶¹ etc.) as coatings/binders. After systematic investigations on polymer-coated hollow sulfur nanospheres (Figure 4g), PEDOT was found to afford the best electrochemical performance because of its strongest sulfur binding from theoretical simulations.⁶⁰

Though strong research evidence has indicated the importance of a conductive matrix for electron transfer in sulfur electrodes, abundant insulating or semiconducting materials discussed above also improved the electrochemical performance. For a clearer mechanistic understanding, we examined various non-conductive metal oxides. Adsorption experiments and theoretical calculations revealed that LPSs are captured by these oxides via monolayer chemisorption and that better surface diffusion leads to higher Li_2S deposition efficiency.⁶² However, if the deposited Li_2S cannot be effectively activated, especially at high mass loading, rapid capacity decay can be expected. We then discovered a novel catalytic effect of metal sulfides toward Li_2S oxidation during charging, which is crucial for good cyclic stability (Figure 4h).⁶³ These understandings can guide the design of sulfur electrodes to achieve high capacity and long cycle life in Li–S batteries.

4. NANOMATERIALS FOR COMPOSITE SOLID ELECTROLYTES

Research on solid electrolytes has continued to grow recently because of the prospects in improving battery safety and energy

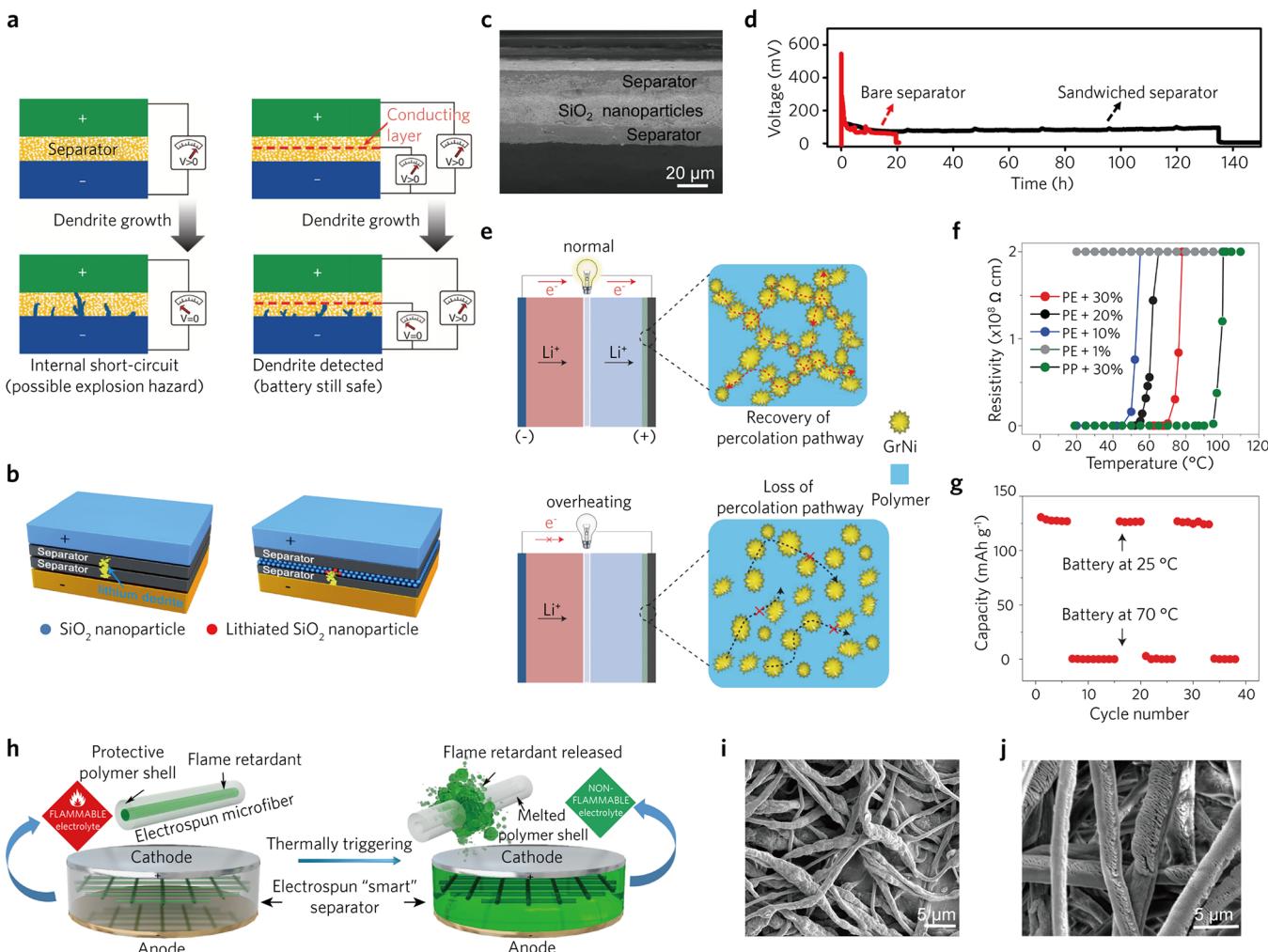


Figure 6. (a) Schematic of bifunctional separators for early dendrite detection. Adapted with permission from ref 71. Copyright 2014 Nature Publishing Group. (b) Schematic and (c) SEM image of a silica-nanoparticle-sandwiched trilayer separator. (d) Voltage vs time profile of Li/Li symmetric cells with conventional and trilayer separators. Adapted with permission from ref 72. Copyright 2017 Wiley. (e) Schematic illustrating the working principle of the TRPS current collector. (f) Resistivities of different TRPS films as functions of temperature and (g) demonstration of safe LiCoO₂ battery cycling between 25 °C and shutdown. Adapted with permission from ref 73. Copyright 2016 Nature Publishing Group. (h) Schematic and (i, j) SEM images of the electrospun separator with thermal-triggered fire-retardant properties. In (j) the microfiber was sputtered to reveal the core–shell structure. Adapted with permission from ref 75. Copyright 2017 AAAS.

density. Solid electrolytes are especially appealing when combined with Li metal anodes to potentially alleviate side reactions and mechanically suppress dendrites.⁶⁴ Solid electrolytes can be classified into two main categories: inorganic electrolytes (ceramics and glasses) and solid polymer electrolytes (SPEs). Compared with brittle inorganics, we believe that the flexible, low-cost SPEs hold great promise for large-scale applications. Nevertheless, since first being proposed in 1973, SPEs remain limited in ionic conductivity, necessitating solid-state cells to be operated at elevated temperatures.

It is recognized that the ionic conductivity of SPEs is largely contributed by the amorphous regions. Therefore, conventional wisdom to boost ionic conductivity would dictate incorporating secondary-phase fillers to afford composite polymer electrolytes (CPEs).⁶⁵ The fillers locally frustrate polymer crystallization, and the Lewis acid–base interactions between the filler surface and electrolyte anions promote salt dissociation. Our effort to improve CPEs via nanoengineering relies on maximizing the polymer–filler contact area and interconnection by reducing the filler size (Figure 5a)⁶⁶ and, notably, introducing high-aspect-ratio

nanowires as continuous, low-tortuosity ionic transport pathways (Figure 5b,c).^{67,68} Different from blending preformed particles with polymers, we introduced an *in situ* hydrolysis approach to synthesize monodispersed silica nanospheres down to 12 nm directly in a poly-(ethylene oxide) electrolyte (Figure 5d), which enabled much higher polymer–filler interfacial area for enhanced ionic conductivity.⁶⁶ However, with nanoparticle fillers, Li ions need to cross multiple particle–particle junctions for conduction. Therefore, shifting from zero-dimensional to one-dimensional fillers, such as Li_{3x}La_{2/3-x}TiO₃ (LLTO) nanowires further improved the performance by extending the fast transport pathways to much longer distances (Figure 5e,f).^{67,69} Finally, we demonstrated well-aligned LLTO nanowires along the normal direction of electrodes (Figure 5g), resulting in a 1 order of magnitude enhancement in ionic conductivity over the random counterpart due to fast ion conduction on nanowire surfaces across the electrodes without crossing junctions (Figure 5h).⁶⁸

With examples given, taking advantage of both highly conductive inorganic fillers and soft polymer electrolytes may be an

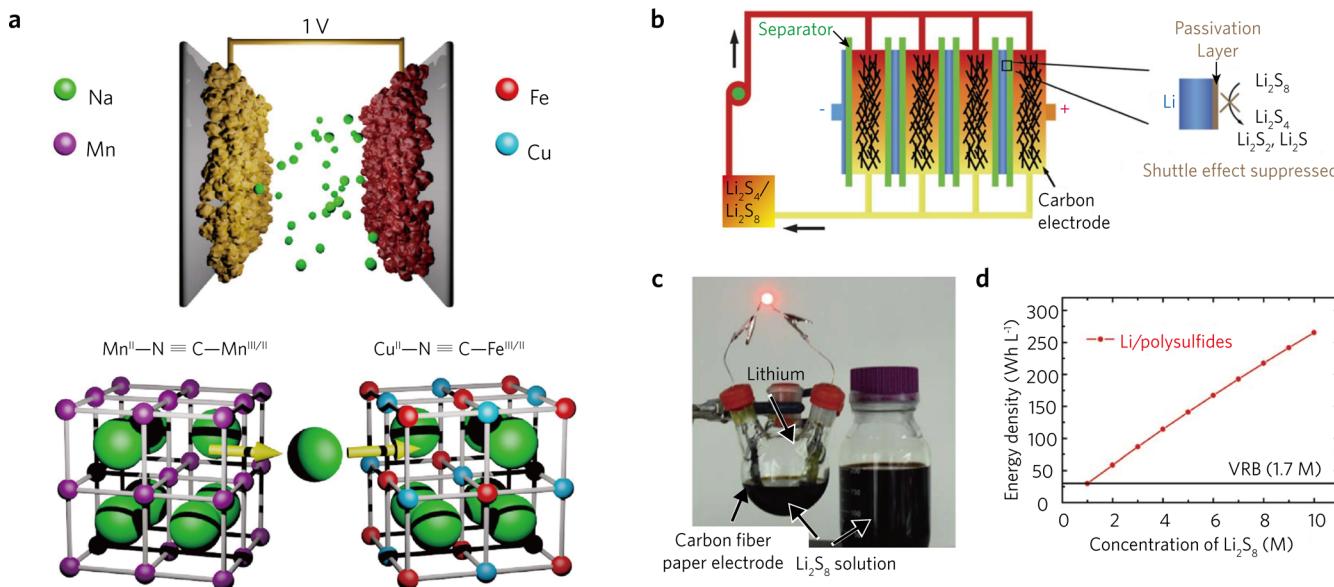


Figure 7. (a) Schematic of the Prussian Blue aqueous battery based on Na^+ insertion. Adapted with permission from ref 76. Copyright 2014 Nature Publishing Group. (b) Schematic of a membrane-free Li/PS semiliquid battery, (c) its experimental demonstration, and (d) the calculated volumetric energy density vs catholyte concentration with the value for a vanadium flow battery (30 Wh L^{-1}) as a reference. Adapted with permission from ref 77. Copyright 2013 Royal Society of Chemistry.

ultimate solution for solid electrolytes. Nevertheless, the exact nature of the filler–polymer interface is not fully answered, so fundamental studies remain necessary. Efforts are also needed to address the poor electrode–electrolyte contact, which is critical for realizing solid-state Li metal batteries.

5. NANOMATERIALS FOR BATTERY SAFETY

With increases in energy density, guaranteeing battery safety becomes critical.⁷⁰ There have been burgeoning research activities to build safer batteries. For example, our group designed a smart separator that monitors battery health *in situ*.⁷¹ This was achieved by a polymer–metal–polymer configuration that imparts an additional voltage-sensing function to the separator (Figure 6a). When a dendrite grows and reaches the metallayer, a sudden voltage drop between the anode and the metal layer can be sensed immediately, realizing early failure detection. Besides detection, a trilayer structure with silica nanoparticles sandwiched between two commercial polyethylene separators was also developed to consume Li dendrites by chemical reaction when they penetrate into the separator (Figure 6b,c). This achieved an ~5-fold battery life extension (Figure 6d).⁷²

The temperature increases abruptly when an internal short-circuit occurs, which will eventually lead to thermal runaway if not controlled in a timely manner. Thus, a fast and reversible thermoresponsive polymer switching (TRPS) mechanism was incorporated into the current collector (Figure 6e).⁷³ The TRPS film consisted of spiky graphene-coated nickel (GrNi) particles as conductive fillers inside a polyethylene matrix with a large thermal expansion coefficient. The TRPS film showed high electrical conductivity at room temperature, but when it was heated above the switching temperature (tunable from ~50 to 100 °C), the conductivity decreased within 1 s by 7–8 orders of magnitude as a result of the expansion of the matrix, which separated the conductive GrNi (Figure 6f). The insulating film above the critical temperature can quickly shut down the battery, and the process is highly reversible even after multiple overheating events (Figure 6g).

The safety issues of LIBs originate from the intrinsic flammability of liquid electrolytes, yet the direct addition of fire retardants into electrolytes generally deteriorates the electrochemical performance.⁷⁴ Therefore, we proposed a novel separator encapsulating fire retardants inside electrospun polymer microfibers (Figure 6h–j).⁷⁵ The protective polymer shell prevents direct exposure of the fire retardants to the electrolyte but can quickly melt during thermal runaway, releasing the fire retardants to suppress combustion.

Battery safety is a complex and systematic problem. More efforts should be devoted to understanding the origin of thermal runaway with the aid of advanced characterization techniques. Also, more reliable battery components should be developed, and nanomaterials can contribute to this greatly.

6. NANOMATERIALS FOR GRID-SCALE STORAGE

The urgent requirements to integrate renewable energy sources into the grid demands the development of high-energy-density stationary storage systems. Existing technologies including sodium–sulfur batteries, vanadium redox-flow batteries, lead-acid batteries, and liquid metal batteries have been implemented with success for grid-scale storage to regulate peak load. However, their high cost, high working temperatures, and/or low energy densities impede their widespread applications.

Recently, a new family of materials based on Prussian Blue analogues have been explored for grid-scale applications. The general chemical formula of this family is $A_x\text{PR-(CN)}_6\cdot n\text{H}_2\text{O}$, where A is an alkali cation, P is a transition-metal cation, and R-(CN)₆ is a hexacyanometallate anion. Both P and R-(CN)₆ sites can be electrochemically active with potentials controlled by composition. The wide channels between A sites enable rapid insertion and removal of cations in aqueous solutions with little lattice strain, resulting in extremely stable electrodes. Moreover, bulk quantities of the materials can be produced by room-temperature chemical synthesis from earth-abundant precursors, which is attractive for large-scale applications. By combination of a manganese hexacyanomanganate anode with a copper

hexacyanoferrate cathode, a safe, fast, inexpensive aqueous battery was demonstrated with no measurable capacity loss after 1000 deep-discharge cycles (Figure 7a).⁷⁶

Although Prussian Blue analogues exhibit ultralong cycle life and low cost, their specific energy remains low ($\sim 30 \text{ W h kg}^{-1}$). Thus, we proposed a room-temperature Li/polysulfide (Li/PS) semiliquid battery, which realized high energy density while maintaining the merits of flow batteries.⁷⁷ In this system, Li_2S_8 in ether solvent and passivated metallic Li were used as the catholyte and the anode, respectively (Figure 7b,c). Notably, the cell functioned without an expensive ion-selective membrane because of the addition of LiNO_3 , which formed a uniform SEI on the Li surface to prevent parasitic reactions. Furthermore, adverse effects on cycling due to the formation and volume change of Li_2S_2 and Li_2S could be avoided, as the catholyte was not discharged to these insoluble states. By calculation, with 5 M catholyte, the energy density of the semiliquid battery could reach 149 W h L^{-1} (133 W h kg^{-1}), which is ~ 5 times that of the vanadium redox battery (Figure 7d).

7. CONCLUSIONS

In this Account, we have surveyed the recent nanotechnology-based design principles to address the challenges for next-generation battery chemistries. Approaches such as nanostructuring, surface protection, and nanoconfinement have been demonstrated to be effective in stabilizing advanced electrode materials that normally undergo drastic volumetric changes. Incorporating nanofillers with fast-conduction surfaces into polymer solid electrolytes can significantly enhance the Li-ion conductivity. Moreover, nanomaterials design can also play a crucial role in improving battery safety as well as the stability and capacity of grid-scale energy storage systems. In all, the future is bright with nanotechnology, and more efforts are needed to accelerate the large-scale applications of nanomaterials in batteries by means of environmentally friendly and low-cost fabrications.

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