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Prospect for Supramolecular Chemistry in High-Energy-Density Rechargeable Batteries

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Three high-energy-density electrode materials, namely silicon (Si) anodes, lithium (Li) metal anodes, and sulfur cathodes operating by alloying, electroplating, and electrochemical conversion, respectively, have gained discernable interest owing to their unparalleled theoretical capacity. Nevertheless, these electrode materials entail new intrinsic drawbacks, such as massive volume change for Si, uncontrollable lithium dendritic growth for Li metal, and the formation of soluble lithium polysulfides as well as their shuttling for sulfur cathodes. In this Perspective, we discuss how supramolecular chemistry and/or mechanically interlocked molecules and polymers, such as rotaxanes or entangled polymer networks, can play a pivotal role in addressing these challenges facing rechargeable batteries. We introduce the concepts of supramolecular chemistry and their working principles in high-energy-density electrode materials in Li-ion batteries.

Introduction

Rechargeable battery technology has been revolutionizing our daily life by powering portable electronic devices, electric vehicles (EVs), and grid-scale energy storage systems (EESs). Among various battery technologies (e.g., lead-acid, nickel-cadmium, nickel-metal hydride, and lithium [Li]-ion), Li-ion batteries based on reversible intercalation chemistry have become a main energy storage system by identifying proper electrode materials and their well-matched electrolytes.[1,2] However, the intercalation mechanism for anode (e.g., graphite, LiC_6) and cathode (Li metal oxide, $LiMO_2$, M=Co, Ni, Mn, etc.) materials inherently leads to a limited energy density, i.e., below 300 Wh kg^{-1} or 800 Wh L^{-1} at the cell level. Even though the energy density of these conventional battery cells has progressively increased, the emerging applications, mostly EVs, demand that the battery community explore different reaction mechanisms such as alloying, electrochemical conversion, and electrodeposition.

While the high specific capacities are feasible via new Li-insertion mechanisms, they result in drastic structural changes in the electrodes and thus generate numerous formidable challenges. For silicon (Si) anodes, Si repeatedly expands and contracts by up to ~300% during Li alloying and dealloying reactions ($Si + 4.4Li^+ + 4.4e^- \leftrightarrow Li_{4.4}Si$), leading to a fatal particle pulverization under the massive mechanical stress.[3,4] As for Li metal anodes ($Li^+ + e^- \leftrightarrow Li$), the Li metal is unevenly electroplated on the electrode, forming troublesome needle-like dendrites that trigger internal short circuits that lead to fire hazards and uncontrolled electrolyte decomposition.[5–7] In the case of sulfur cathodes ($S_8 + 16Li^+ + 16e^- \leftrightarrow 8Li_2S$), the dissolution and shuttling of intermediate high-order polysulfides (Li_2S_x, $4 \leq x \leq 8$) in organic electrolytes is the primary cause of capacity loss.[8–12] Given their significant structural changes during cycling with regard to volume, electrode morphology, and solubility, these emerging problems are quite nontrivial to be tackled with conventional

Context & Scale

The quest for new electrode materials for Li-ion batteries with high energy densities beyond conventional intercalation-based electrodes has gained significant attention due to the increasing demand for advanced portable devices and electric vehicles (EVs). Among various candidates, the most promising electrode materials along this direction are silicon and Li metal for anodes and sulfur for cathodes. While the intense research efforts in the past decade have resulted in rather promising results, we have yet to see substantial progress for all of these electrode materials. While their high theoretical capacities rely on different reaction mechanisms with Li ions compared to the current intercalation-based electrode materials, different reaction mechanisms present inherent drawbacks such as electrode swelling, uncontrollable Li dendrite growth, and generation of soluble redox reaction products. Considering the fact that these shortcomings are closely related to the interactions of electrode components, they offer a unique playground for various supramolecular interactions to address these daunting challenges. In general, the promise of supramolecular chemistry is the possibility of designing smart approaches. Therefore, a paradigm shift in electrode design is needed so that the electrode components can respond to these structural changes in a more active and effective manner.

molecules and polymers to carry out complex functions with high selectivity and reversibility by means of molecular recognition. The success of applying such opportunities to the emerging battery systems relies on identifying the right molecular recognition element and supramolecular interactions between the electrode components to make them adaptive, responding to the constantly changing local environment during cycling in the target electrode application; in this Perspective, we shed light on this aspect.

The inspiring model systems that exquisitely perform their own functions are exemplified by biological systems and machines (Figure 1). In biological systems, supramolecular chemistry and mechanostereochemistry[13] play a fundamental role in preserving the structural integrity and functions of biomolecules. Supramolecular chemistry deals with molecular entities held together by reversible "non-covalent interactions" (Figure 1A), which is in stark contrast to molecular chemistry concerning molecular entities connected by "covalent bonds". Mechanostereochemistry is the stereochemistry of mechanically interlocked molecules via "mechanical bonds and entanglements"— such as catenanes, rotaxanes, and knots (Figure 1A). For instance, supramolecular interactions (Figure 1A) are well known to stabilize the structural integrity of biomolecules, such as the DNA double helix via π-π stacking and hydrogen-bonding-based base pairing interactions, and protein folding/self-assembly forming primary, secondary, tertiary, and quaternary structures in the form of alpha helices, beta sheets, turns, and loops (Figure 1B). More recent studies validated that the mechanically interlocked structures of proteins, including rotaxanes, catenanes, and knots, significantly influence their biological functions.[13] Moreover, life-sustaining functions such as the self-healing of cells and antigen-antibody reactions can be realized by means of the supramolecular interactions. Because the structural integrity of electrodes, in common with biological systems, is critical for sustaining cycle life in battery systems, numerous valuable insights for addressing challenges associated with high-energy-density electrodes in Li-ion batteries can be adopted.

On the other hand, a variety of macroscopic machines are simply supposed to change the direction of force but can also simultaneously transmit and modify the force and torque, whereupon the output force can be amplified to much higher levels compared to the initial input force, namely mechanical advantage. As demonstrated by levers, pulleys, screws, and hydraulic jacks, many difficult tasks can be fulfilled by saving force. When these macroscopic machines are translated into molecular machines at the nanoscale while retaining their functions (Figure 1B), they could provide promising tools to address the chronic problems associated with high-energy-density batteries, such as the accumulation of mechanical stress (Figure 1C),[13–16] as corroborated by the recent research on molecular pulleys based on polyrotaxane binders for Si microparticle anodes.[16,17] Therefore, both supramolecular chemistry and mechanostereochemistry are expected to serve as key elements in the energy storage field.

In this Perspective, we highlight the concepts of supramolecular chemistry and mechanically interlocked molecules for their utilization in emerging battery systems, namely Si anodes, Li metal anodes, and sulfur cathodes. Although the phenomena occurring in these three electrodes are quite different, their underlying origin for capacity fading is commonly associated with the interactions between electrode components. For Si anodes, the mechanical stress and strain caused by massive Si volume change break the binder-binder and binder-Si interactions and thereby delaminate the electrode materials and lead to particle pulverization as well as uncontrolled growth of SEI layer, resulting in severe capacity fading. It is thus important to introduce a self-healing effect to restore the broken interactions, dissipate the mechanical stress, and keep the pulverized particles together, which can be largely realized by supramolecular chemistry and mechanostereochemistry. For Li metal anodes, the driving force for the dendrite growth is related to electrostatic interactions

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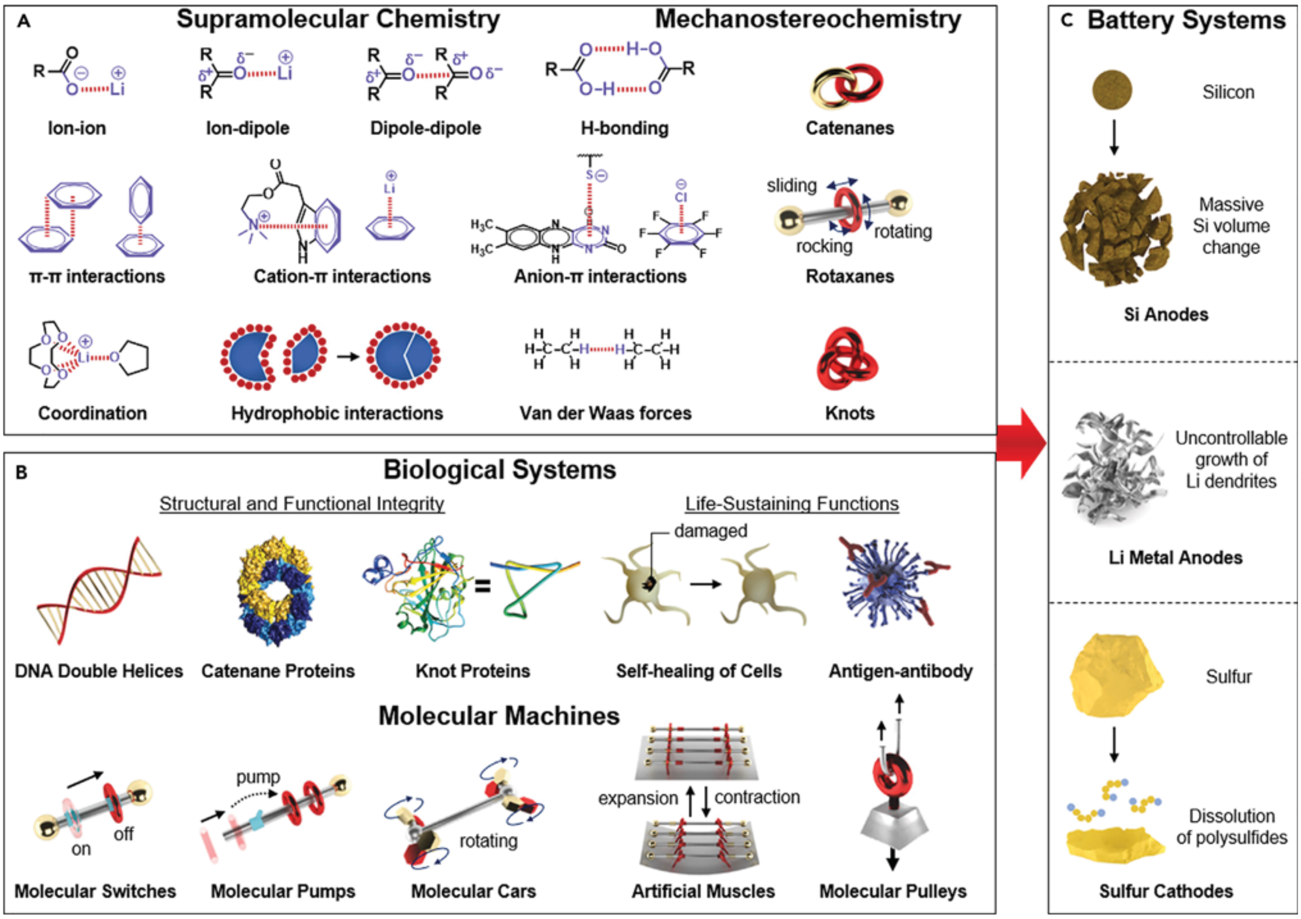

Figure 1. Concepts of Supramolecular Chemistry and Mechanostereochemistry

(A) Supramolecular interactions, mechanical bonds, and mechanical entanglements.

(B) Applications of supramolecular chemistry and mechanostereochemistry in nature and molecular machines. The catenane and knot proteins are adapted from Pieter et al.[13] with permission. Copyright 2016, Royal Society of Chemistry.

(C) Representative challenges of high-energy-density batteries—Si anodes, Li metal anodes, and sulfur cathodes.

between Li^+ ions and free electrons concentrated on the Li metal surface. This implies that numerous supramolecular interactions can be exploited to intervene with the interaction between Li^+ ions and free electrons to control the growth dynamics of Li metal. Accordingly, in the section of Li metal anodes, we introduced several supramolecular approaches in conjunction with the electrode structure design. Lastly, for sulfur cathodes, the dissolution of intermediate sulfur species into electrolytes, i.e., polysulfide shuttling, is a detrimental process leading to significant capacity fading. Hence, it is desirable to design electrode materials having strong interactions with polysulfides. We evaluated the potential of various materials for the mitigation of polysulfide shuttling in the context of the hard and soft acid and base (HSAB) theory as a guideline to screen strong interactions and also address the structural strategies related to the porosity of sulfur cathodes. In all of these electrode systems, while we discuss pioneering research efforts in the field, we also underline the possible impact of supramolecular chemistry.

Si Anodes

Si is regarded as one of the most promising anode materials owing to its high specific theoretical capacity (4,200 mAh g^{-1} for $Li_{4.4}Si$), low operating voltage

(~0.3 V versus Li/Li^+), abundant resources, and low cost. It should also be noted that the production of high-quality Si from raw materials is already at a mature stage in the semiconductor industry.[3,5] Nevertheless, the practical application of Si anodes has been impeded by the massive volume change (~300%) of Si upon lithiation and delithiation, which results in Si pulverization, unstable solid-electrolyte interphase (SEI) formation, and drastic morphology changes in the electrode. Simultaneously, a massive amount of mechanical stress is generated during cycling and transmitted along the polymeric binder backbones to their anchoring points on the Si surface. Therefore, it is quite challenging, yet important, to find strong interactions capable of preventing anchoring points from breakage under the external mechanical force. It has been confirmed[18] that when the strength of noncovalent interaction of anchoring points is tailored, the cycling performance can be improved substantially due to the self-healing effect originating from the dynamic nature of supramolecular interactions. Initially, polyvinylidene fluoride (PVDF), as the choice of binder for graphite-based anodes, has been investigated as a binder in Si anodes. However, severe capacity decay within the first few cycles demonstrates the inability of weak van der Waals interactions to sustain the structural integrity of the Si anodes. As an alternative, the strong covalent attachment to the Si surface also turned out to be deteriorated and broken due to their stiffness and irreversible bonding character, thus leading to a fast capacity decay.[18–21] It should be noted that battery cells with liquid electrolytes offer a myriad of opportunities owing to their relatively dynamic nature. During the lithiation of Si, the driving force for volume expansion is the formation of an alloy between Si and Li. During the delithiation, which is accompanied by a substantial volume shrinkage, the electrode matrix requires additional interactions to restore and maintain the electrode morphology. As noted above, these interactions cannot be either too weak (van der Waals forces) or too strong (covalent bonds) since there exists a trade-off between reversibility and strength of interactions.[3] In other words, the interactions must be strong, yet retain their dynamic nature. Therefore, it is essential to precisely control the strength of interactions between Si and other components (mainly binders) for good electrochemical performance in Si anodes. In this regard, we prospect that supramolecular chemistry and mechanically interlocked molecules can offer a molecular toolkit to tailor the strength of interactions by simply varying strength and extent of noncovalent interactions. Even though it was initially envisaged that the binder can only address the issues related to morphology change, it has been shown[16] to counteract the pulverization problem by keeping cracked Si particles coalesced and simultaneously mitigating uncontrolled SEI growth.

Self-Healing Effect via Supramolecular Interactions

Contrary to the initial consensus in the field that the strong bonding of binders results in better morphological control of electrodes,[3,19,22,23] supramolecular interactions (weaker strength) turned out to be more beneficial for long-term cycle life when compared to covalently crosslinked binders (higher strength) that do not possess any supramolecular interactions or dynamic components.[3,18] This discrepancy stems from the fact that supramolecular interactions can be reversibly broken and reformed (self-healing) under applied mechanical force, whereas covalent bonds cannot be recovered once they are broken (Figure 2A). Furthermore, silanol groups (Si-OH) of the native oxide layer on the Si surface can be readily utilized to form strong supramolecular interactions, such as hydrogen bonding and ion-dipole interactions. Therefore, the self-healing capability is regarded as the key factor for maintaining the structural integrity of Si nanoparticle anodes, and the self-healing property can be realized by means of supramolecular interactions.

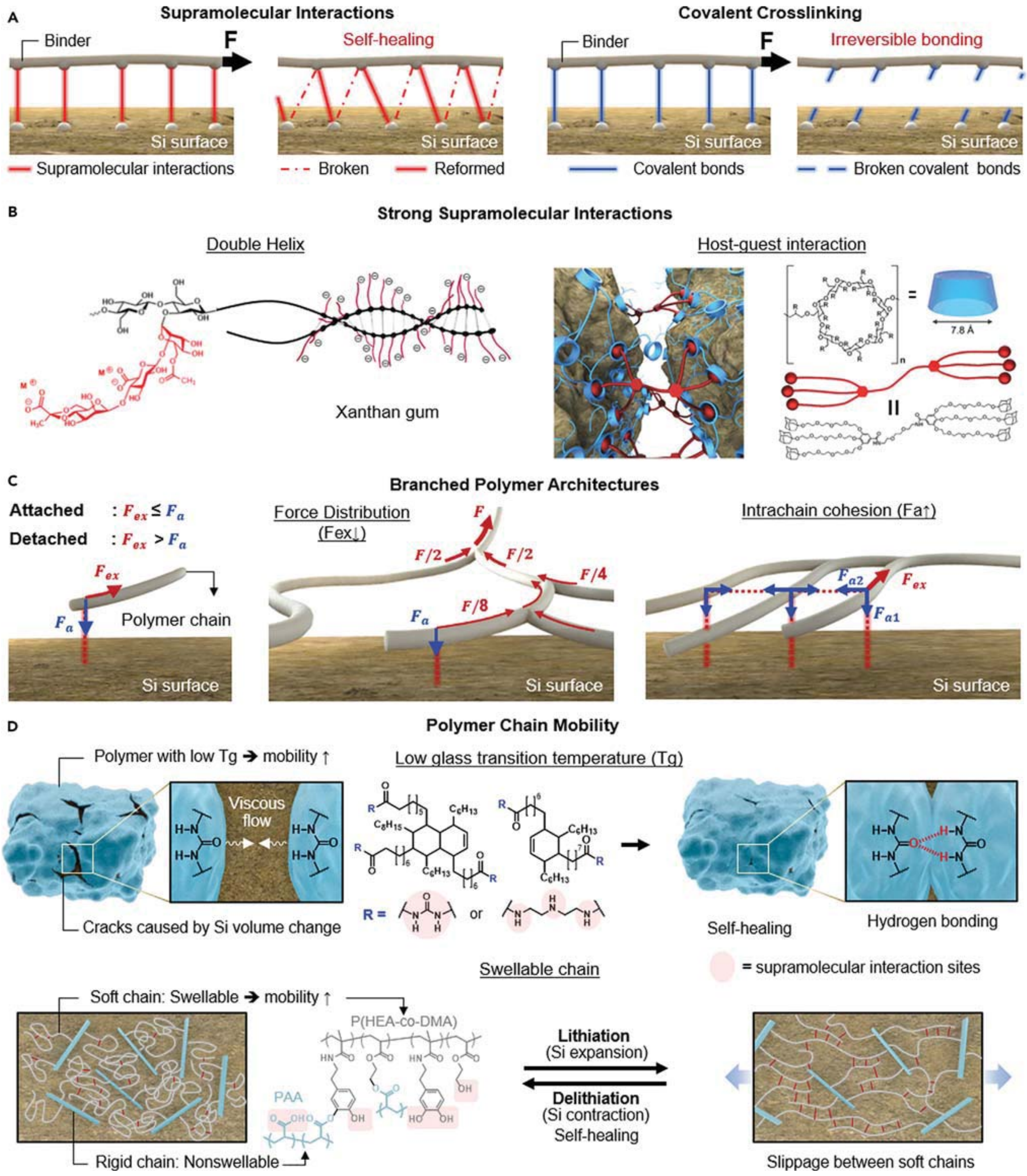

Figure 2. Design Parameters of Polymeric Binders for Improving Self-Healing Efficiency in Si Anodes

(A) Importance of supramolecular interactions in comparison to covalent crosslinking for the binder system.

(B) High structural integrity through strong supramolecular interactions (double helix and host-guest interactions) of binders. Adapted with permission from Kwon et al.[32] Copyright 2015, American Chemical Society.

(C) Force distribution and cooperative intrachain cohesion of branched polymeric binders in Si anodes.

(D) Self-healing process of polymeric binders facilitated by low T_g and swellable chains.

Self-healing efficiency (Figure 2) is found to be enhanced by tuning three parameters: (1) the bond strength of supramolecular interactions, (2) polymer architectures, and (3) the mobility of polymer chains.[3] First, the bond strength of supramolecular interactions essentially affects the self-healing efficiency in such a way that the strong bonding between the components favors the binding state (A + B → AB). In this regard, compared to conventional PVDF binders with weak van der Waals interactions, many polymers[24–27] (e.g., carboxymethyl cellulose, poly[acrylic acid], and alginate, etc.) engaging strong supramolecular interactions such as hydrogen bonding or ion-dipole interactions were reported to exhibit better cycling performance. Furthermore, higher binding affinities were also achieved through different kinds of supramolecular interactions, such as coordination bonds,[28–31] host-guest interactions,[32] and double-helix formation[33] (Figure 2B). Despite many promising results taking advantage of supramolecular interactions in Si anodes, there remains a number of unexplored supramolecular interactions, including numerous hydrogen bond motifs,[34] halogen bonding,[34,35] host-guest pairs,[36] charge-transfer interactions,[37] ionic bonds (e.g., ionomer-based self-healing polymers),[38] dynamic covalent bonds,[39] and mechanochemistry.[40,41] Therefore, related systematic studies will be needed to establish a more comprehensive relationship between supramolecular interactions and electrochemical performance.

It has been proposed that the mechanical stress caused by Si volume change can be largely controlled by polymer architectures such as branched structures[3] and mechanically interlocked structures[3,16] (see the next section, Mechanically Interlocked Molecules). From the mechanical point of view, polymer chains can provide strong adhesion to Si surface when the external mechanical force (F_{ex}) transmitted to the anchoring point is smaller than the adhesion force (F_a) ($F_{ex} \leq F_a$, left in Figure 2C), whereas detachment occurs under the opposite condition of $F_{ex} > F_a$. Hence, the key to high structural integrity lies in how these two forces are managed. Branched polymers, unlike linear polymers, have an effect on both F_{ex} and F_a. Branched polymeric architectures greatly reduce the force (F_{ex}) transmitted to each anchoring point by distributing the force to multiple side chains (middle in Figure 2C). Concurrently, the endurable force (F_a) of each anchoring point can be increased by cooperative intrachain cohesion with vicinal side chains (right in Figure 2C).[42] The force distribution and the intrachain cohesion mechanism can undermine the nonbinding state of anchoring pairs, leading to higher self-healing efficiency. Thus, the branched or network structures are advantageous for polymeric binders of Si anodes as demonstrated by several previous reports.[42–44]

Finally, the mobility of polymer chains (Figure 2D) has a crucial influence on self-healing efficiency[38] because it enhances the probability of dissociated polymer chains to be in contact again and facilitates the re-association of supramolecular interactions, aside from the recovery of their initial conformation and entanglement. This structural parameter is particularly important for Si microparticle anodes[31,45–47] because hoop stress and strain on the Si surface become more severe with an increase in the size of Si.[48] In this way, the polymer chains covered on the Si surface are subjected to massive mechanical stress and movement, leading to the fracture of the polymer layer.[45] This problem can be addressed by lowering the glass transition temperature (T_g) of polymeric binders below ambient temperature (~0°C), which helps to combine separated anchoring pairs at room temperature and increases self-healing efficiency (top in Figure 2D).[35–37] Another possible approach[31] for imparting chain movement is incorporating swellable soft chains (P[HEA-co-DMA]), which possess strong supramolecular interactions (e.g., the catechol group[49]), into a nonswellable rigid polymer chain (PAA) (bottom in Figure 2D).[31,50] Self-healing polymers[51] with

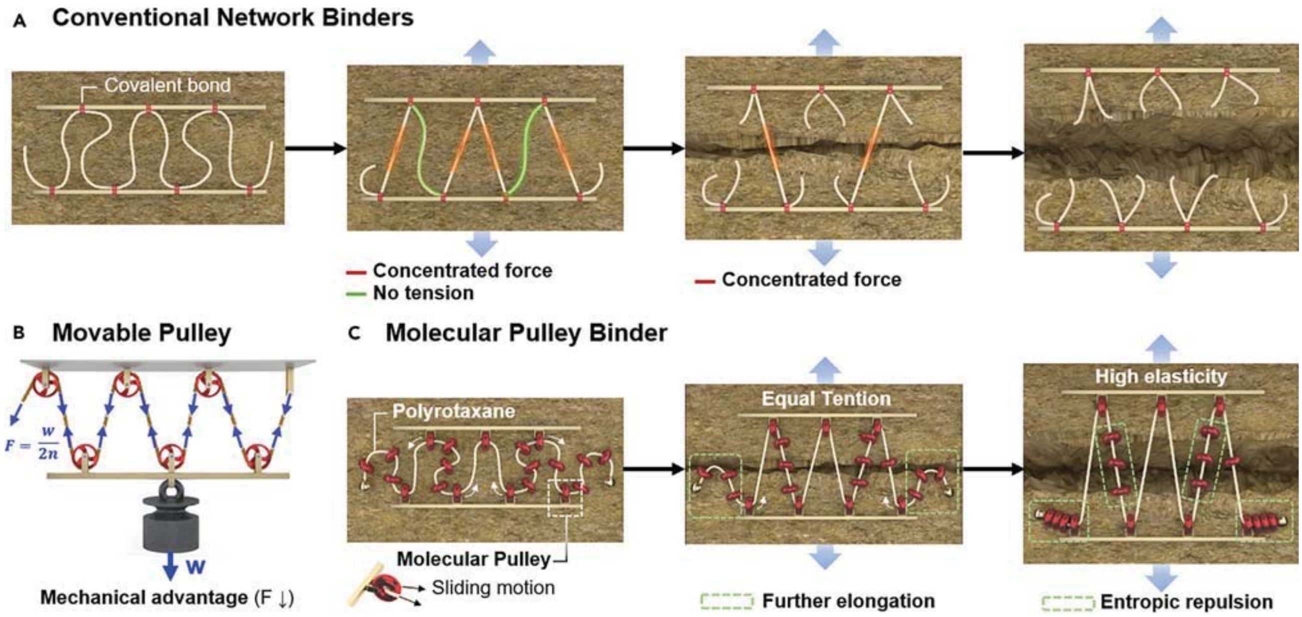

Figure 3. Application of Mechanostereochemistry to Si Anodes

(A) Operation mechanism and structural limitation of conventional branched and network binders.

(B) Operation mechanism and similarity of the movable pulleys and the molecular pulley binders for Si anodes.

hard-soft domains offer not only the high tensile modulus of the hard domains but also the reversible extension under stress of the soft domains. Accordingly, while the PAA-P(HEA-co-DMA) system has enough mechanical support from the nonswellable hard PAA, it can also buffer the strain caused by the volume change of Si particles because of the swellable soft P(HEA-co-DMA) component. Specifically, three monomer units of PAA, P(HEA), and P(DMA) have their own distinctive role for adhesion as the PAA-P(HEA-co-DMA) was superior to PAA, PAA-P(HEA), PAA-P(DMA), and P(HEA-co-DMA). The nonswellability of PAA in organic electrolytes is thought to play a critical role in strong adhesion because of minimal alterations in its mechanical properties between dry and wet states in organic electrolytes,[26] whereas swellable P(HEA-co-DMA) loses its interactions with the Si surface because of an increase in the interaction of the polymer chains with electrolyte. P(HEA) can endow the polymer network with elasticity, whereas P(DMA) mainly provides self-healing ability. Notably, the catechol groups of P(DMA) are reported to form exceptionally strong yet reversible bonds (coordination bonds) with the Si surface, which are approximately 10 times stronger than the hydrogen bonding between alginate and the Si surface.[3,29] The acidity of PAA is also expected to assist the bond formation between the catechol group and the SiO_2 layer on the Si surface.[52]

Mechanically Interlocked Molecules

As discussed in the previous section, the branched polymer structures can lower the external mechanical force (F_{ex} in Figure 2C) by force distribution and enhance the adhesion force (F_a in Figure 2C) by cooperative intrachain cohesion. However, conventional network polymers have a structural limitation in that mechanical force is locally concentrated on shorter chains as illustrated in Figure 3A, and polymer chains are successively broken while expanding. Especially in the case of highly expanding systems like Si microparticle anodes, the stretchability and elasticity of conventional polymeric binders is not sufficient to respond to volume changes effectively. For this reason, most research efforts on binders, with very few exceptions,[16,31,45] have focused on Si nanoparticle anodes. The study by Chen et al.[46] clearly shows how challenging it is to achieve good electrochemical performance when micrometer-sized particles are used as an active material. Despite the use of self-healing binder[45] with low glass transition temperature, cycling stability deteriorated with the increase in the size of the Si particle. For instance, 3.5-μm Si particles showed a sharp decrease in specific capacity (approaching 0 mAh g^{-1} within 100 cycles) while 800-nm Si particles exhibited good capacity retention of ~80% at the 500th cycle. Thus, for high-performance Si microparticle electrodes, the structural limitations of conventional network binders (i.e., the locally concentrated force and the low stretchability) should be addressed.

It has recently been demonstrated that mechanically interlocked molecules in the form of polyrotaxanes (see the structure of rotaxanes in Figure 1A and polyrotaxanes in Figure 3C), the so-called "molecular pulley binder," can be effective tools to realize the ideal force distribution with high elasticity for Si microparticle electrodes.[16] Notably, unlike previously reported binders, this binder system showed nonlinear stiffening behavior and high elasticity. In the macroscopic world, a movable pulley is a simple but powerful tool that can lift a heavy object using a reduced amount of force. Its working principle is based on the conservation of energy (work = force × distance), that the same amount of work can be done by applying a smaller force at the expense of a greater distance. In a pulley system rigged with n number of movable pulleys (Figure 3B), the force $\frac{w}{2n}$ over $2n$ times longer distance can lift up the object with a given weight of w. This system is perfectly suited for the binder system of Si anodes as demonstrated by the molecular pulley binder[16] realized by crosslinking poly(ethylene glycol)/α-CD polyrotaxane and poly(acrylic acid). The mechanical advantage of the movable pulley considerably decreases the mechanical tension applied to polymer chains (by a factor of $2n$) and consequently mitigates the polymer fracture. Simultaneously, the sliding motion (first in Figure 3C) of the molecular pulleys equalizes the mechanical tension (corresponding to $\frac{w}{2n}$ in the pulley system) of the all-polymer chains (the ideal force distribution), which eliminates the locally concentrated stress. Thus, the molecular pulley binder can elongate to a large extent without severe fracture.[16] Distinct from the macroscopic pulleys, the entropic repulsion (third scheme in Figure 3C) of free rings in the stretched state enables them to act like air springs and provide the driving force to return to their original distribution, whereupon the pulverized Si particles can be coalesced.[16] The resulting stable SEI layer and high electrode integrity play a crucial role in tackling the limitations of Si microparticle anodes (diameter = ~2.1 μm) and achieve a decent capacity retention (no obvious capacity decay within 150 cycles at 2.43 mAh cm^{-2}) and high Coulombic efficiencies (91.22% at the pre-cycle, 97.37% at the 1st cycle, and 99.82% at the 22nd cycle).[45,46] The high Coulombic efficiencies of this binder system also enabled a robust full-cell operation in pairing with a $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode. This particular study signifies the fact that properly designed binders can indeed help to address the shortcomings of Si microparticle anodes, and the effect of the binder goes beyond morphological control of the active material.

Li Metal Anodes

The Li metal anode is the "holy grail" of Li-ion battery technology because of its high theoretical capacity (3,861 mAh g^{-1}) and the lowest redox potential (−3.04 V versus SHE) under which Li metal is electroplated and stripped. Unfortunately, ever since the introduction of Li metal anodes in the 1970s, electrodeposition-based charging with Li metal foil has been considered unsuitable for rechargeable batteries because of its inherent dendrite growth.[53] The formation of Li dendrites was identified as the main cause of the uncontrolled formation and destabilization of the SEI layer due to its large surface area and massive volume change as well as the short circuits that may cause a fire hazard and explosion.[54–56] The dendritic growth mechanisms have been extensively studied under various conditions,[6,54,57–64] and they are heavily related to the inhomogeneous Li^+ flux in the electrolyte. The underlying reason was suggested to be the different strength of electric fields formed on the local surface of Li metal, where electrons are densely located at the sharp edges of conductors owing to the electrostatic repulsion between electrons, inducing a stronger electric field. With this in mind, several supramolecular interactions (e.g., ion-ion, ion-dipole, anion-π, cation-π, and coordination bonds as displayed in Figure 1A) can possibly intervene in interactions between Li^+ ions and free electrons concentrated on the dendrites so that Li^+ ions are repelled from the dendrites. The distribution of free electrons on the surface can also be controlled by electrode designs such as micropatterns and electrically conducting scaffolds, which change the local electric fields and control the movement of Li ions. In addition, the local Li-ion flux can be increased from the holes and cracks in the SEI layers (so-called ''hot spots'') generated by the Li metal volume change.[55,65–67] Therefore, it is essential to control the growth dynamics of Li metal to suppress the dendrites.

Electrostatic Shielding Mechanism

An electrostatic shielding mechanism[68] was proposed to suppress the Li dendritic growth and form smooth Li metal films by taking advantage of repulsive ion-ion interactions. When the protruding dendrite grows from the Li metal surface, a stronger electric field is formed around the dendrite. This means that more electric field lines are focused toward the dendrite as illustrated in Figure 4A. Because Li ions move along the electric field lines, more Li ions reach the dendrite and the growth of the dendrite is accelerated. It has been shown that when the surface of the protruding dendrite is protected by foreign metal cations (top in Figure 4A), Li ions are repelled from the protrusion of Li metal to a smooth surface via electrostatic repulsion between Li^+ ions and foreign metal cations. The preferential deposition on a smooth surface lasts until the prominent Li tips disappear. One technical problem of this concept is finding suitable shielding metal cations with lower reduction potentials than that of Li^+ to achieve efficient surface adsorption and prevent the reduction of the shielding metal cations on the surface of Li dendrites. This task is actually nontrivial in that Li is the most electropositive metal. Skillfully, Cs^+ and Rb^+ were chosen as shielding metal cations for the supramolecular coating of the prominent Li tips because their reduction potentials (−3.026 and −2.980 V versus SHE, respectively) are slightly higher than that of Li^+ (−3.040 V versus SHE). Then, the reduction potentials of Cs^+ and Rb^+ were lowered below that of Li^+ by using the principle of the Nernst equation $E_{Red} = E^{\varnothing}_{Red} - \frac{RT}{zF}\ln\frac{\alpha_{Red}}{\alpha_{Ox}}$, wherein the effective reduction potential (E_{Red}) can be adjusted by controlling the activity (concentration) of oxidants (α_{Ox}) such as Cs^+ and Rb^+. At 0.05 M of Cs^+ and Rb^+ in the electrolyte, their effective reduction potentials were found to be −3.103 and −3.057 V versus SHE, respectively, which are lower than the reduction potential (−3.040 V versus SHE) of 1.0 M of Li^+. Accordingly, smooth dendrite-free Li metal surface was achieved at a current density of 0.1 mA cm^{-2}.

Despite the facile modification of the reduction potential based on this concept, there are still several points to be addressed to advance the concept to be practically viable. For example, the process is inherently limited because of the inevitable rise in the reduction potentials of shielding cations with an increase in their concentration along with their poor solubility in organic electrolytes. The available shielding ions are also limited to rare alkali metal ions such as Rb^+ and Cs^+. In addition, the small

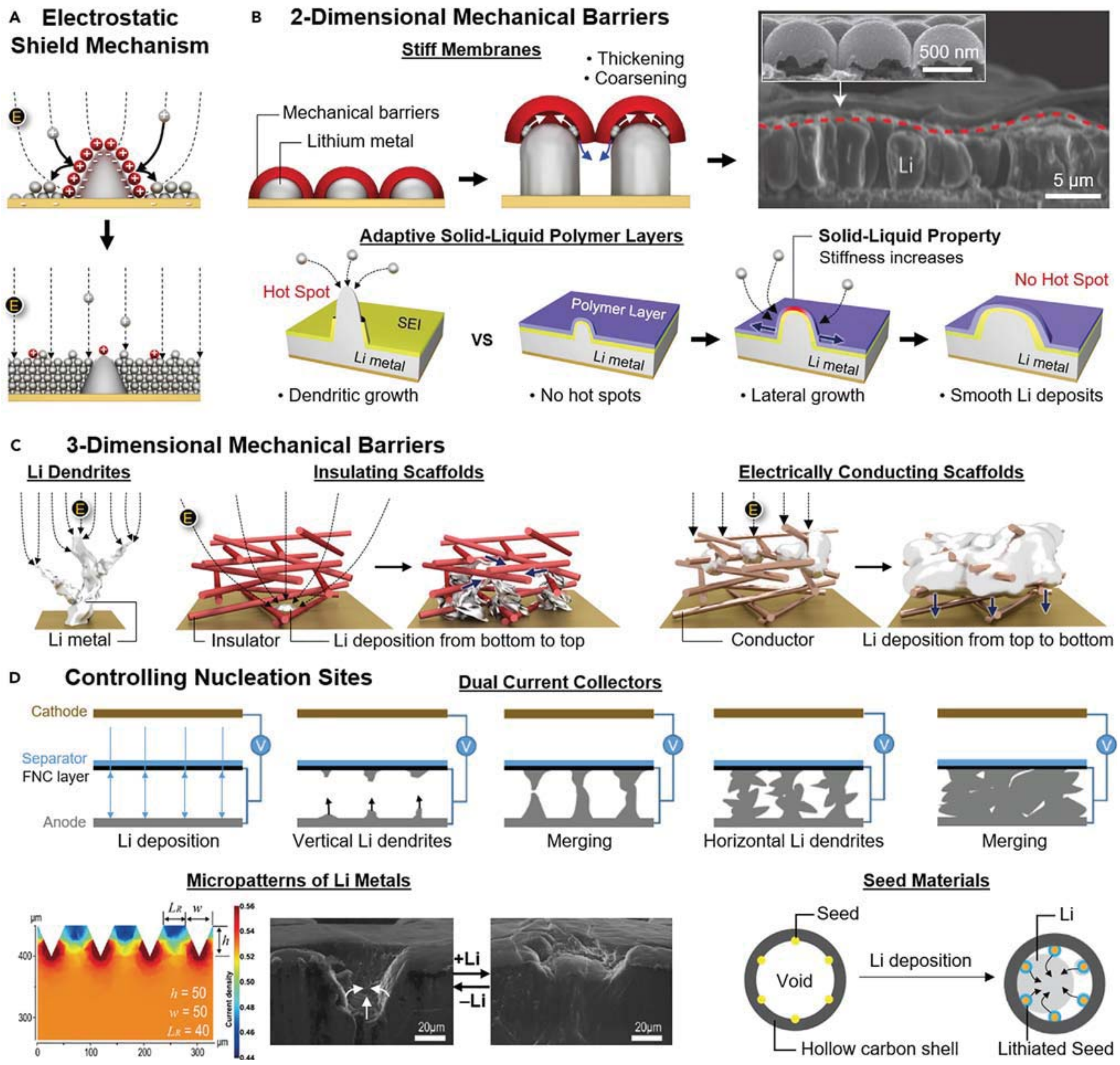

Figure 4. Approaches to Control the Li Dendritic Growth for Li Metal Anodes

(A) Graphic representation of the electrostatic shielding mechanism.

(B) Working principle of 2D mechanical barriers.

(C) Working principle of 3D mechanical barriers.

(D) Concepts of controlling dendrites via nucleation sites. The figure of the FNC layer is adapted from Liu et al.[7] with permission. Copyright 2017, Nature Publishing Group. The images of the micropatterns of Li metals are adapted from Park et al.[90] with permission. Copyright 2016, Wiley-VCH Verlag GmbH & Co. The image of the seed materials is adapted from Yan et al.[91] with permission. Copyright 2016, Nature Publishing Group.

difference in the reduction potentials between shielding ions and Li metal would be problematic at high current densities, impairing the shielding effect. Energy level engineering of shielding cations would be necessary to modulate their redox potentials below that of Li metal probably using counterions and chelating ligands, for which supramolecular chemistry can offer a myriad of host-guest complexes. In the context of electrostatic shielding approach, it would certainly be interesting to explore π-electron-deficient, charged organic molecules as coating layers to benefit from supramolecular interactions such as ion-ion, ion-dipole, and anion-π interactions (Figure 1A).

Mechanical Barriers

The utilization of mechanical barriers is the most direct method to control the growth of Li dendrites because they mechanically enforce the direction of Li dendritic growth to change and merge them. It was reported that the materials with a high Young's modulus (higher than ~6 GPa) can suppress the penetration of Li dendrites,[69,70] and the growth of Li metal can be guided toward a more desirable morphology (crystallographic orientation) or confined by well-designed mechanical barriers and electrolyte additives.[71] The concave shape of two-dimensional (2D) stiff mechanical barriers (top in Figure 4B) can rectify the Li dendritic growth by blocking the straight growth and directing Li^+ along the curvature, forming smooth dome-shaped Li metal tips. Li metal further grows by Li insertion at its tips and bases by lifting the mechanical barriers up, and the columnar morphology is eventually achieved via the thickening and coarsening process.[70] The merits of the Li metal rods lie in their structural stability during cycling. Rather than the branched growth from the Li tips, the adjacent Li tips are merged into rounded and smooth granules due to the increased Li-ion flux between them, even without the coverage of the mechanical barriers.[65]

In addition, well-designed SEI layers, which can be controlled by electrolyte additives[71,72] and artificial coating,[73–76] can also serve as a mechanical barrier and affect the morphology of Li metal. A superior SEI layer needs to meet several requirements, including electrochemical stability, Li-ion conductivity, and high surface energy. In particular, SEI layers with high surface energies were shown to be more resistant to the formation of dendrites.[77] Among several inorganic components, LiF has been identified as one of the good SEI components to suppress the dendrite growth and form dense and uniform Li deposits,[78–80] which is derived from its high electrochemical stability, higher surface energy,[77] and lower diffusion energy barrier[78] for Li-ion diffusion compared to other SEI components such as LiOH, Li_2CO_3, and Li_2O. Another interesting SEI additive is $CsPF_6$. The electrolyte additive $CsPF_6$ serves a dual purpose by forming a concave-shaped SEI layer via the Cs^+-mediated reduction of PF_6- (2.05 V versus Li/Li^+) as well as by engaging the Cs^+-assisted electrostatic shielding mechanism.[72,81] Given that PF_6- bound to Cs^+ is more susceptible to reduction due to its low lowest unoccupied molecular orbital (LUMO) level, the selective adsorption of Cs^+ on the protruding Li metal through the electrostatic shielding mechanism would enable the formation of a concave-shaped SEI layer. Accordingly, the morphology of the deposited Li metal is more rounded and smoothened. This study clearly shows the positive impact of counterions, and it could be further extended to different counter-anions as well as coordinating ligands in order to further improve electrochemical performance, yet another aspect that can benefit from supramolecular chemistry.

2D adaptive polymeric layers (bottom, Figure 4B) based on reversible supramolecular interactions[66] and dynamic covalent bonds[82] were also applied to Li metal electrodes as interfacial protective layers. In contrast to the stiff mechanical barriers, these polymers do not have a high Young's modulus to suppress the Li dendritic growth. Instead, they can viscously flow on the Li metal surface and keep covering the protruding Li deposits, which can inhibit the formation of cracks and pinholes on the SEI layer, the so-called "hotspots" where locally surging Li-ion conductivity accelerates the Li dendritic growth (bottom, Figure 4B). The "solid-liquid" property,[82] in which the polymers are flowable at a lower strain rate but become stiffer at a higher strain rate, enables the polymer layer to act as a dynamic constraining layer. When Li ions begin to be deposited outward from the Li metal, the polymeric layer on the Li surface becomes stiffer and suppresses additional central growth (bottom, Figure 4B). The access of Li ions is allowed through the sides of the Li protrusion, leading to the lateral growth and the relatively smooth morphology of the Li deposits.

Three-dimensional (3D) mechanical barriers can not only suppress the dendritic growth but also provide a defined volume space for Li deposition, thus alleviating the electrode volume change during striping and plating.[55,83–88] For 3D nonmetallic scaffolds (Figure 3C),[55,85] Li metal is nucleated on a current collector at the beginning stage, but not on the insulating scaffolds. In that the insulating scaffold does not interfere with the formation of electric fields (see the electric field lines of insulating scaffolds in Figure 4C), Li ions are still selectively deposited on the tip of Li metal forming Li dendrites. However, the growth direction of the Li dendrites is diversified by the mechanical barriers, whereupon the dendrites are merged together and smooth morphology is achieved within the 3D scaffold.

On the other hand, 3D electrically conducting scaffolds can interfere with electric fields due to the existence of free electrons throughout the network and can act as an electromagnetic shield.[83,84,86,87] Through this effect, Li-ion flux is more evenly formed and the dendritic growth can be suppressed (see the parallel electric field lines of the electrically conducting scaffolds in Figure 4C). However, there is a concern that Li dendrites would grow directly from the top surface of the conducting scaffold toward the counter cathode electrode because the plating of Li metal can also occur on the conducting scaffolds, unlike their insulating counterparts. Interestingly, when the scaffold reacts more rapidly with Li ions compared to the Li metal, it was found that Li metal can grow along the scaffold surface from top to bottom as opposed to the formation of Li dendrites on the Li metal surface (right, Figure 4C); for instance, copper nanowire network with 5.11 times higher electric conductivity than that of Li metal demonstrated such a growing tendency of Li metal.[83]

THE CONTROL OF NUCLEATION SITES

The strategies introduced in this section induce Li dendrites to collide and merge with each other by controlling the Li metal nucleation sites rather than mechanical suppression. To this end, three methods have been proposed: (1) using multiple current collectors, (2) patterning Li metal, and (3) using Li metal seed materials. A simple way to achieve collision of Li dendrites is to set two current collectors confronting one another. In this concept, functionalized nanocarbon (FNC) was reported as a second current collector, which was coated on the separator and electrically connected to the copper current collector (Figure 4D).[7] Li metal can be deposited onto both the current collector and the FNC layer, and the dendrites grow toward each another. Once they collide, the electrochemically sensitive tips of Li metal dendrites merge and disappear. After that, although dendritic growth in a horizontal direction is initiated again, the dendrites are eventually merged with Li metal (top, Figure 4D). In this way, Li-dendrite microshorting and the formation of dead Li metal can be avoided, thus resulting in an improved long-term cyclability. As demonstrated by this study,[7] the second current collector must be well designed for the success of this approach; it needs to possess a high porosity for facile transport of Li ions between cathode and anode when the second current collector is attached on the separator. Moreover, the authors argued that special treatments such as Li doping would be necessary for Li metal to grow directly on the second current collector.[7] Besides, Li doping can help the transport of Li ions through the carbon layer by changing the hydrophobic surface of carbon materials to a hydrophilic one. Most carbon materials are not lithiophilic, meaning that Li diffusion into the carbon materials is not a favorable process.[87] In addition, the authors were also concerned about the possibility of dendritic growth from the secondary current collector through the separator, although no dendritic growth was observed on the back side of the FNC in their work.[7]

Surface templating of Li metal by employing micropatterns was also investigated to electroplate Li metal on selected regions.[89,90] Analogous to the principle of the dendrite growth, Li ions are preferentially reduced at the sharp edges of micropatterns on the Li metal surface. The optimized structure of the micropattern was identified from the theoretical calculations (lower left, Figure 4D).[90] The pyramidal pit with a height of 50 μm, width of 50 μm, and ridge length of 40 μm showed the highest contrast of current density between the ridge and valley region. Li deposition started from the pointed valleys and filled the whole space of the pits in the charging cycle. In the subsequent discharge, the Li metal in the filled pits was preferentially stripped and recovered the original valley shape. This approach is quite interesting because Li ions are directed spontaneously to migrate to a specific area along the enhanced electric field of the micropattern, and Li deposits are stripped preferentially from these areas compared to the Li metal template. Nevertheless, further investigation is necessary to corroborate more on the mechanism of the change in the current density according to the patterns[90] and reversible stripping of Li deposits. The limited volume of pits for Li plating and the consequent limited areal capacity are among the critical problems to be resolved for practical application.

Li metal seed materials such as Au, Ag, Zn, and Mg were also proposed and used to drive Li metal deposition onto a selected area.[91] The common feature of these metals is that pure Li metal phase exists in their Li metal binary phase diagrams as opposed to other metals forming only alloy phases with Li along the entire Li metal relative compositions. This means that Li metal nucleation (Li metal phase) is viable upon lithiation of these metals, with small nucleation energy. Subsequently, Li metal growth is guided to preferentially initiate from these nucleation sites on the seed materials. This approach greatly enhances the controllability of Li metal growth. If the seed materials are placed in a Li metal host (such as hollow carbon spheres), Li metal can be reversibly plated and stripped within these structures (lower right, Figure 4D), resulting in excellent electrochemical stability. It is noteworthy that the structure of Li metal hosts is a critical parameter to control the efficiency of Li dendrite suppression. In particular, achieving uniform dimensions of hosts is crucial, as irregular pore sizes could lead to dendrite growth on their outer surface.

Sulfur Cathodes

The conversion mechanism of sulfur, which is based on the sequential reduction and chemical transformation following $S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4 \rightarrow Li_2S_2 \rightarrow Li_2S$, endows Li-S batteries with approximately five times higher theoretical capacity (1,672 mAh g^{-1}) compared to those of $LiCoO_2$ and $LiFePO_4$ cathodes based on intercalation chemistry.[92] The formation of various sulfur species in the electrolyte along with the differences in their solubilities presents significant problems in Li-S batteries. In fact, sulfur electrode can be regarded as an electrochemically active polysulfide catholyte in that its reaction with Li ions involves solid-liquid phase transition. While S_8 and the short-chain polysulfides (Li_2S_2 and Li_2S) can remain insoluble in the electrolyte, the intermediate polysulfides (Li_2S_x, $4 \leq x \leq 8$) can be readily dissolved and can shuttle between both electrodes. Ironically, the dissolution of sulfur species is essential to achieve the near-theoretical capacity of the sulfur cathode. This shuttling phenomenon, however, limits the electrochemical activation of the short-chain polysulfides (Li_2S_2 and Li_2S) that account for a high portion of the specific capacity (1,255 mAh g^{-1}, corresponding to 75% of the theoretical capacity).[11] The mobile soluble polysulfides in the electrolyte can be reduced and deposited in the form of Li_2S_2 and Li_2S on the surface of the Li metal counter electrode and the cathode, resulting in poor ionic and electric conductivity, high resistance, and severe active material loss.[8,9,93] Hence, it is essential to develop materials with high affinities toward the soluble polysulfides such that the polysulfides can be effectively trapped in the cathode during cycling.

Supramolecular Interactions with Li Polysulfides

There are three possible binding sites for Li polysulfides (Li_2S_x): Li^+, terminal sulfide (S^-), and bridging sulfur (–S–) chain. Given that strong supramolecular interactions are generally based on the strong electrostatic forces such as ion-ion/ion-dipole interactions, it would be more desirable to target at Li^+ or S^- as a binding site rather than the indistinctive bridging sulfur chains. Several supramolecular interactions such as ion-ion, ion-dipole, coordination, cation-π, and anion-π interactions (Figure 1A) can possibly be exploited for the confinement of the polysulfides.

Li^+ is a representative hard Lewis acid that can form strong and stable coordination complexes with hard Lewis bases containing O, N, F, and Cl according to the HSAB theory (Figure 5A).[94] Numerous biological molecules and synthetic ionophores demonstrate that Li^+ can commonly form 4-, 5-, 6-, 7-, and 8-fold coordinative complexes with various hard Lewis basic ligands due to the lack of direction in the ion-dipole interactions.[95,96] Thus, Li^+ can be simultaneously held from multiple directions while it is bound to the polysulfides via ionic bonding so that the soluble polysulfides can be trapped in the cathode (Figure 5B). Many functional groups containing hard Lewis basic oxygen and nitrogen atoms are expected to have strong interactions with Li^+ bound to the soluble polysulfides. Carboxylate ($–COO^-$) is one of the strongest ligands for Li^+ via the strong ion-ion interactions and coordination bonds between Li^+ and the carboxylate oxygen (hard Lewis base). The amine group ($–NH_2$) is also expected to form strong interactions with Li^+ via ion-dipole interaction between Li^+ and the hard Lewis basic nitrogen atom. Ester (–COO–), amide ($–CONH_2$), and ketone (–(C=O)–) moieties can have ion-dipole interactions between Li^+ and their carbonyl oxygens (hard Lewis bases) (Figure 5B).[97] However, for amides, it is noted that the nitrogen atom of amide bonds cannot directly interact with the Lewis acids (Li^+), as it loses its basicity owing to the delocalization of lone pair electrons to the partial π-bond between nitrogen and carbonyl carbon.[98,99] Instead, the dipole moment of carbonyl oxygen can be increased by the substitution of an electronegative nitrogen atom. The strength of interaction between carbonyl oxygen and Li^+ is increased going from primary to tertiary amides.[95] In addition, ether, imine, alcohol, and phosphate groups also incorporate the hard Lewis basic oxygen and nitrogen atoms. Generally, the bond strength decreases in the order of coordination bonds, ion-ion interaction, and ion-dipole interaction. As for the common functional groups,[97,100–107] their interaction strengths with LiS and Li_2S were investigated through *ab initio* simulations[11,97] and were found to decrease in the order of amine, ester, amide, ketone, imine, ether, disulfide, thiol, nitrile, sulfide, fluoroalkane, chloroalkane, bromoalkene, and alkane.

In line with the HSAB theory, the shuttling of polysulfides can be restrained by the coordination bonds and/or ion-ion/ion-dipole interactions with the terminal sulfur

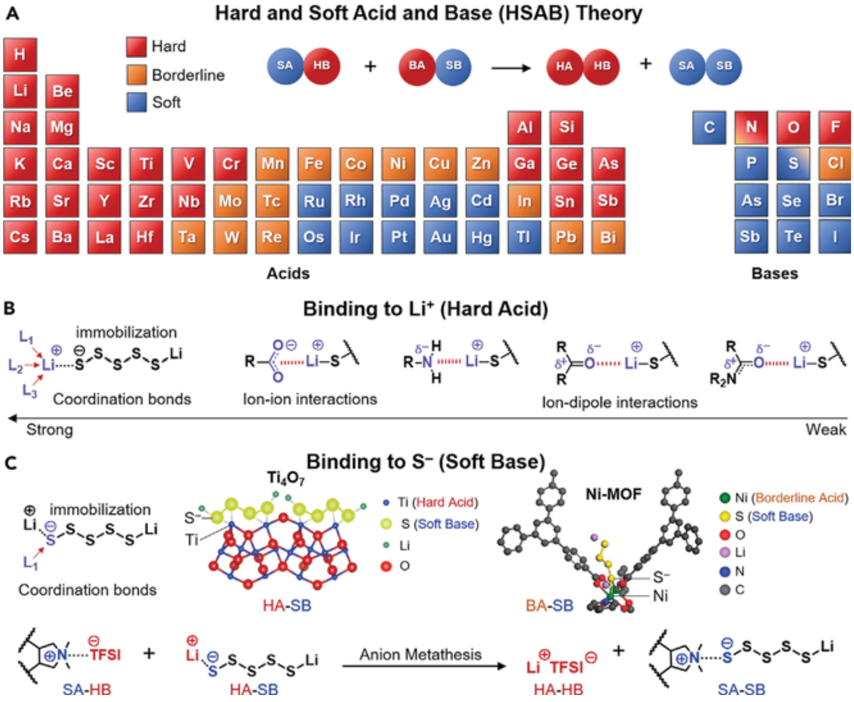

Figure 5. Approaches for Strong Binding to Li Polysulfides for Sulfur Cathodes

(A) Principle of hard and soft acid and base theory.

(B) Concepts for binding to Li^+ of Li polysulfides.

(C) Concepts for binding to S^- of Li polysulfides. Ti_4O_7 is adapted from Pang et al.[109] with permission. Copyright 2014, Nature Publishing Group. Ni-MOF is adapted from Zheng et al.[110] with permission. Copyright 2014, American Chemical Society.

(S^-) anion of the polysulfides (Figure 5C). S^- is a soft Lewis base that forms strong coordination complexes with soft Lewis acids. Fortunately, the mismatch of the "soft" base (S^-) with the "hard" acid (Li^+) offers a very good opportunity to immobilize the polysulfides by using "soft" Lewis acidic materials. Although Cr-MOF[108] and Ti_4O_7[109] exhibited improved binding affinity toward sulfide anion (S^{2-}), the selective binding would be limited because of the fact that Cr^{3+}, Cr^{6+}, Ti^{3+}, and Ti^{4+} are hard Lewis acids (Figure 5C). Ni-MOF[110] incorporating the borderline Lewis acidic atom (Ni) was also examined and found to prevent the fast leaking of soluble species from the cathode. Poly[(*N*,*N*-diallyl-*N*,*N*-dimethylammonium) bis(trifluoromethanesulfonyl)imide] (PEB-TFSI)[111] was also investigated as an adsorbent binder for sulfur cathodes. This particular study can also be reinterpreted by the HSAB theory. PEB-TFSI consists of soft acid (ammonium ion[112] of PEB) and hard base (N^- of TFSI), whereas Li polysulfide (LiS_x) contains hard acid (Li^+) and soft base (S^-) as noted above. The mismatch between acid-base pairs enables anion metathesis; that is, soft base polysulfides prefer binding with a soft acid PEB^+ while hard acid Li^+ ions prefer binding to a hard base TFSI, leading to the immobilization of polysulfides in the cathode.

Porous Materials

Infiltration of sulfur into highly porous materials can slow down the dissolution of polysulfides through kinetic inhibition. Porous materials should possess high electric conductivity to keep insulating sulfur moieties electrochemically active. For this reason, porous carbonaceous materials[113–118] attracted a great deal of attention in early studies, and the hydrophobicity of their pores enabled the facile infiltration of hydrophobic sulfur simply by the melt-diffusion method.[115] However, hydrophilic Li polysulfides can readily diffuse out from hydrophobic pores, which decreases the confinement efficiency of these materials. Hence, carbonaceous porous materials were coated with hydrophilic polymers[106,115] and inorganic materials[119,120] and doped with heteroatoms.[105,107] Moreover, porous materials containing nitrogen and oxygen atoms, i.e., covalent organic frameworks (COFs),[121] metal organic frameworks (MOFs),[108,110,122] and covalent triazine frameworks (CTFs),[123,124] were also investigated. The supramolecular structure of cucurbit[6]uril is also a good case in point.[104] Cucurbit[6]uril consists of six glycouril ($=C_4H_2N_4O_2=$) monomers linked by methylene bridges. The dipole moments of its 12 carbonyl oxygens would be enhanced by tertiary nitrogens as mentioned in the previous section, which facilitates the coordination with Li^+ ions. Besides, cucurbit[6]uril moieties are self-assembled into a honeycomb-like porous structure via $C-H\cdots O$ hydrogen bonds,[125] which increases the surface area and fully exposes the binding sites to soluble polysulfides in the electrolyte. Furthermore, the one-dimensional channel of the hydrogen-bonded supramolecular framework is shown to be dynamically stretchable, which allows it to accommodate larger polysulfides.[104] This study clearly shows that supramolecular design can help to retain structural and functional integrity by closely interacting with reaction products generated during the charge-discharge process, which would otherwise dissolve into electrolyte and impair the cell performance.

Summary and Outlook

High-energy-density electrode materials are gaining significant attention from the entire battery community as the EV market expects exploding growth in the near future. Recent studies[3] employing supramolecular chemistry and mechanostereochemistry demonstrated their unique role in resolving the chronic issues of Si anodes arising from immense volume expansion of Si up to 300% upon lithiation. Supramolecular chemistry and mechanostereochemistry can offer unique tools to maintain the interparticle interaction even during the significant volume change of Si. In particular, the strong supramolecular interactions are more beneficial over covalent bonds due to the self-healing effect originating from the reversibility of noncovalent interactions. The effectiveness of the self-healing effect can be tuned by adjusting the strength of supramolecular interactions, thus providing an invaluable tool to control the electrochemical outcome at a molecular level. Importantly, the binder superstructure, i.e., double helix, and binder-binder interactions, have also been shown to have a significant impact on the electrochemical outcome. Branched polymer structures also affect the self-healing capability in such a way that they decrease the force transmission to the anchoring points and increase the endurable force at the anchoring points via cooperative intrachain cohesion. The enhanced mobility of polymer chains can be achieved by decreasing T_g for high self-healing efficiency; however, these systems require high binder contents (∼35 wt %). In addition, a highly elastic polymeric binder incorporating polyrotaxanes was shown to withstand mechanical stress in Si anodes and enable the coalescence of pulverized Si particles. By virtue of stress dissipation, force distribution, elasticity, and entropic repulsion of the polyrotaxane binder, the structural integrity of Si electrodes was substantially improved even for Si microparticles with commercial-level areal capacities.

Li metal anode technology is faced with a significant challenge associated with Li dendrite growth. In an attempt to control the Li plating dynamics, some supramolecular approaches have been proposed. Shielding cations attached to protruding Li dendrites electrostatically repels Li^+ ions to the surroundings, which eventually remove the Li dendrites. Mechanical barriers can change the growth direction of Li deposition and merge them by mechanical blockage. Thus, given that the shape of mechanical barriers is critical for the morphology of Li deposition, the well-designed SEI layers are also expected to play a crucial role, just like mechanical barriers. Supramolecular polymer layers enable the dynamic control for the desirable Li metal morphology. For example, adaptive supramolecular polymers with low glass transition temperatures can serve as responsive protection and dynamic constraining layers. While these polymers keep covering the Li metal surface via viscous flow in response to the change in Li metal morphology, the interplay between liquid state and solid-like stiffness in these adaptive layers helps to suppress Li dendrite growth by redirecting the Li^+-ion flux, thus leading to a smooth Li metal morphology. Three-dimensional scaffolds can confine the Li deposition as well as mitigate the volume change of the electrode. Besides, metallic scaffolds offer the additional advantage of electromagnetic shielding, which can alleviate the inhomogeneous electric field around Li deposition. In order to collide and merge with each other, Li dendrites were guided to grow from face-to-face nucleation sites by using dual current collectors, patterning Li metal surfaces, and using seed materials.

Sulfur cathodes suffer from a severe shuttling problem of intermediate soluble polysulfides. This shuttling problem can be mitigated to a certain extent by using porous carbonaceous materials as structural hosts. Li polysulfides can be targeted via hydrophobic short sulfur chains as well as ionic sites such as Li^+ and S^-. Considering the strength of ion-ion interactions and acid-base properties, targeting ionic sites would be more desirable. In fact, numerous studies have demonstrated that this strategy can be used effectively to mitigate polysulfide shuttling. As it is commonly utilized in supramolecular chemistry, one can look into adapting cooperative noncovalent interactions in order to target multiple binding sites simultaneously. It might, however, be necessary for these systems to find the ideal binding strength in order to address the trade-off between strong binding and good reversibility. There are also still unexplored supramolecular interactions such as cation/anion-π interactions (Figure 1A) and the effect of preorganization (chelating and macrocyclic effect) for coordination bonds in the context of sulfur cathodes. It should also be noted that the proposed approaches should be considered by taking Li metal anode into account, as the reaction products in the sulfur cathode can diffuse and affect the interfacial stability of the Li metal anode. Besides, more systematic investigations are required in the context of the HSAB theory; various soft acids remain uninvestigated to bind the soft base S^- of polysulfides. Therefore, there is plenty of room for improvement from the viewpoint of supramolecular chemistry.

As is nicely demonstrated in numerous pioneering studies, the challenges of high-energy-density electrodes can be addressed by supramolecular chemistry and mechanostereochemistry. Despite their excellent improvement with regard to electrochemical performance, the application of these chemistries to battery systems is still in its infancy. We believe that supramolecular chemistry and mechanically interlocked molecules will offer invaluable opportunities for the challenges associated with high-energy-density electrodes because a vast amount of knowledge is already present in the literature on designing highly selective hosts for anions and cations as well as supramolecular systems for the stabilization of surfaces and nanomaterials facilitated by various noncovalent interactions. The main advantage of these systems will be their adaptive nature to respond to substantial changes in the electrodes during cycling in an efficient manner. It is clear that high-energy-density electrode materials will be the new playground for supramolecular chemistry and mechanically interlocked molecules alike.

AUTHOR CONTRIBUTIONS

All authors contributed equally to the writing of the manuscript.

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