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# Self-Healing: An Emerging Technology for Next-Generation Smart Batteries

Rekha Narayan, Christel Laberty-Robert, Juan Pelta, Jean-Marie Tarascon, and Robert Dominko\*

Complex battery degradation is an interplay of different processes correlated to the thermodynamic, chemical, and mechanical instability of materials. Their degradation kinetics and mechanisms are functions of several intrinsic and environmental conditions. The degradation of the battery cell can be minimized by using preventive steps, like artificial interphases, coatings, additives, or materials that operate within the thermodynamic stability voltage window. Like in most systems/applications degradation processes/aging cannot be avoided since battery cells operate in different environments. Self-healing functionalities have been proved in different areas of material science and they can significantly improve the performance of battery cells. Some of them have been demonstrated on the laboratory scale, while other degradation processes have been tackled only by the development of preventive approaches. Since self-healing functionalities add additional weight and cost to the battery cell, directions of development should be focused on modification of nonactive materials, preferably based on biosourced materials to lower environmental impact. Important issues include detection of degradation using sensors and the vectorization of self-healing components and their controlled release. In addition to this, a triggering process of extrinsic self-healing components together with manufacturability and recyclability should be considered from the early stages of the development phase.

## 1. Introduction

The ability of the living nature to prevent or cure damages has developed various intrinsic defense and healing mechanisms. Defense (preventive) mechanisms are helping living organisms to survive in different environments while the healing mechanisms are a survival mode once the damage is done. Both directions of nature evolution enabled beautiful and rich biodiversity that are witness today.<sup>[1]</sup> Self-healing processes appear in nature with different kinetics, such as stop bleeding in minutes, skin wound healing in days, and healing of broken bone in weeks. The kinetics is limited with the ability to deliver material or energy to the site of the damage<sup>[1]</sup> and this is extensively studied in the multidisciplinary field in the medical science called “regenerative engineering.”<sup>[2]</sup> In general, self-healing can be divided into autonomous (intrinsic), where there is no need for any intentional healing stimulus and nonautonomous (extrinsic) self-healing,

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where additional external stimulus is required.<sup>[3]</sup> The former is inherent to organisms or the material selection and the latter is based on vectorization of drugs or on self-healing functionalities that are triggered by external stimulus.<sup>[4]</sup> Learning from nature, where most of the self-healing approaches rely on the use of sacrificial weak bonds, material scientists have developed different approaches such as self-healing fiber-reinforced polymer composites, self-healing coatings, self-healing cementitious materials, self-healing ceramics, self-healing organic dyes, self-healing concrete molecules, and many others.<sup>[5–8]</sup>

Batteries are gaining high importance in the transition toward carbon neutrality and their acceptability will highly rely on the improved quality, reliability, lifetime, and safety (QRLS).<sup>[9–11]</sup> Their cell components and interfaces are based on highly reactive materials which, under certain internal and/or external conditions, result in copious parasitic reactions compromising their functionality and acceptance. Use of the preventive steps with properly designed interfaces can enable improved properties however a preventive approach cannot completely stop chemical and/or physical damages that are compromising the acceptability and safety of the battery cells. Moreover, the battery cells are operating in different conditions, and their chemical and electrochemical reactions as well as physical and mechanical processes occurring during the multiple charge–discharge cycles, contribute to the overall aging that determines the lifetime, their safety issues, and thus overall quality and reliability. Like in other fields, self-healing functionalities in batteries can significantly improve performance and contribute to their sustainability, lower environmental impact over the lifetime and better acceptability. Some self-healing functionalities have been proofed on the laboratory level, others still need to be designed to meet the requirements of a highly reactive environment in the battery cells. Among them, the use of microcapsules hosting healing species, self-healing materials based on bioinspired mechanisms and biology still need to be explored to a large extent to prove their functionality in intrinsic or extrinsic self-healing processes.

Implementing self-healing features into batteries by now is a flourishing research field following the biomimetic approach. Nonetheless, considering the wide breadth of self-healing knowledge available outside batteries, still there are innumerable possibilities by which these strategies may be employed to tackle unattended decay roots. Importantly, self-healing approaches to battery systems should be developed for different parts of the battery cell and their functionalities should be synchronized with battery chemistry. Different nonactive components like separators, binders, current collectors can act as a self-healing battery part enabling an intrinsic approach while the same battery components could be a storage place for extrinsic self-healing functionalities.

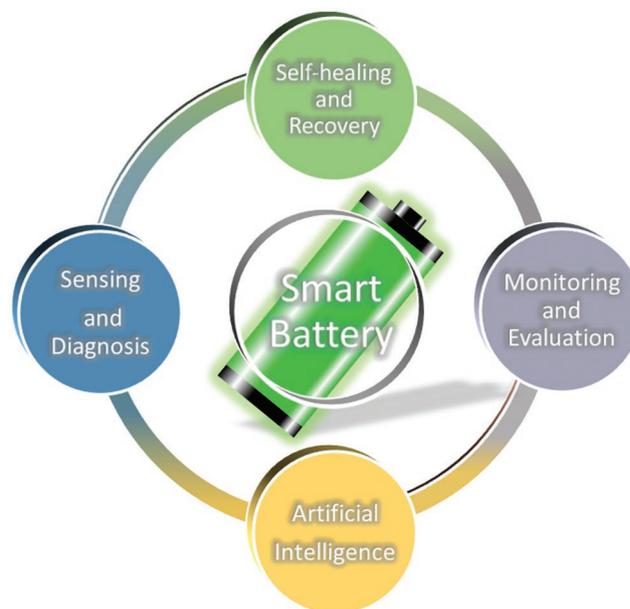
In this paper, we give a brief introduction to the degradation processes in batteries and we review known approaches of self-healing applications in batteries. On this basis we discuss challenges and we give a perspective as stated in the Battery 2030+ roadmap.<sup>[12,13]</sup>

## 2. General Self-Healing Approaches

Self-healing materials are part of the functional materials or additives in the composites that can recover/reestablish

functionality of the device after mechanical damage, chemical deterioration, or change in physical/chemical properties. Batteries as energy storage devices undergo different degradation processes during continuous operation. Their aging can be divided into chemical and electrochemical aging. Degradation processes responsible for battery aging are divided into two larger categories. The major degradation processes for Li-ion batteries, which are described in the next section are: i) particle cracking and loss of electrical connectivity, which are considered as mechanical degradation, and ii) chemical and electrochemical degradation with degradation processes as solid electrolyte interface (SEI) growth and decomposition, gas evolution, dissolution of transition metals, current collector corrosion, and dendrite formation among others. From the above stated it is obvious that due to the diversity of degradation processes, different self-healing approaches should be considered in battery cells. A plethora of different degradation mechanisms, which are unique for each battery chemistry calls for the targeted design of self-healing functionalities for either intrinsic or extrinsic self-healing processes. Intrinsic or autonomous design should enable their activity continuously during chemical and electrochemical aging while extrinsic or nonautonomous design should be released upon external stimulus.

Battery cells can contain several self-healing functionalities, however, the main importance is that additives or new functional materials are stable over the lifespan of a battery cell, they should have a capacity to repair the damage with acceptable kinetics which needs to be adjusted to the degradation process. Importantly, added self-healing functionalities should not affect to the large extend the overall performance of the battery cells (energy density and power), while their cost should be economically viable enabling a higher quality and reliability with improved safety, and prolonged lifetime (QRLS). Another important aspect is their manufacturability and possibility to incorporate them into the manufacturing process. Finally, even that self-healing functionalities would enable a prolonged



**Figure 1.** Key concepts toward developing smart batteries.

lifetime, their design (intrinsic functionalities) or amount of stored chemicals/additives (extrinsic functionalities) will undoubtedly have a limited period of usage and research community should be aware of possible recycling procedures.

A key concept required for the development of smart batteries is presented in Figure 1. It is based on the advanced sensing approach with incorporated sensors as a part of battery cells. Based on the algorithms and advocate diagnostics, different self-healing functionalities can be used or triggered, once cell performance is degraded to a certain level. After the treatment, a cell is monitored and its performance is evaluated with a diagnostic build in the BMS. Finally, the battery cell having improved QRLS can be further used in the battery pack.

### 3. Selected Degradation Processes and Related Self-Healing Approaches

Recently, many comprehensive reviews,<sup>[14,15]</sup> providing a general summary of the self-healing advancements in batteries have been reported mainly from the point of view of the materials design and healing strategy, but a systematic correlation analysis with the fundamental degradations has yet to be realized. In this Perspective, we rewind some of the main degradation pathways in batteries and extend to survey the self-healing approaches

explored so far to mitigate the corresponding categories of damage. We also critically re-examine the intrinsic and practical problems related to each degradation route from different perspectives to highlight the hidden opportunities for the development of unorthodox self-healing innovations in batteries. An overview of the degradation mechanisms associated with Li-ion batteries represented in Figure 2 implies the complexity of the interplay between individual components and close interrelation among the aging processes of chemical, electrochemical, and mechanical origins. Depending on the nature of the damage, we have broadly subdivided the different degradations in Li-ion batteries into two main categories. For each class, the underlying reasons for the particular degradation which requires restorative treatment are discussed first, followed by the remedial research approaches in a conjunction with special attention paid to self-healing prospects and recommendations for the future.

#### 3.1. Mechanical Degradation Mechanisms and Related Self-Healing Functionalities

##### 3.1.1. Electrode Cracking

One of the major challenges for the next-generation Li-ion batteries with high-energy density and high power is the

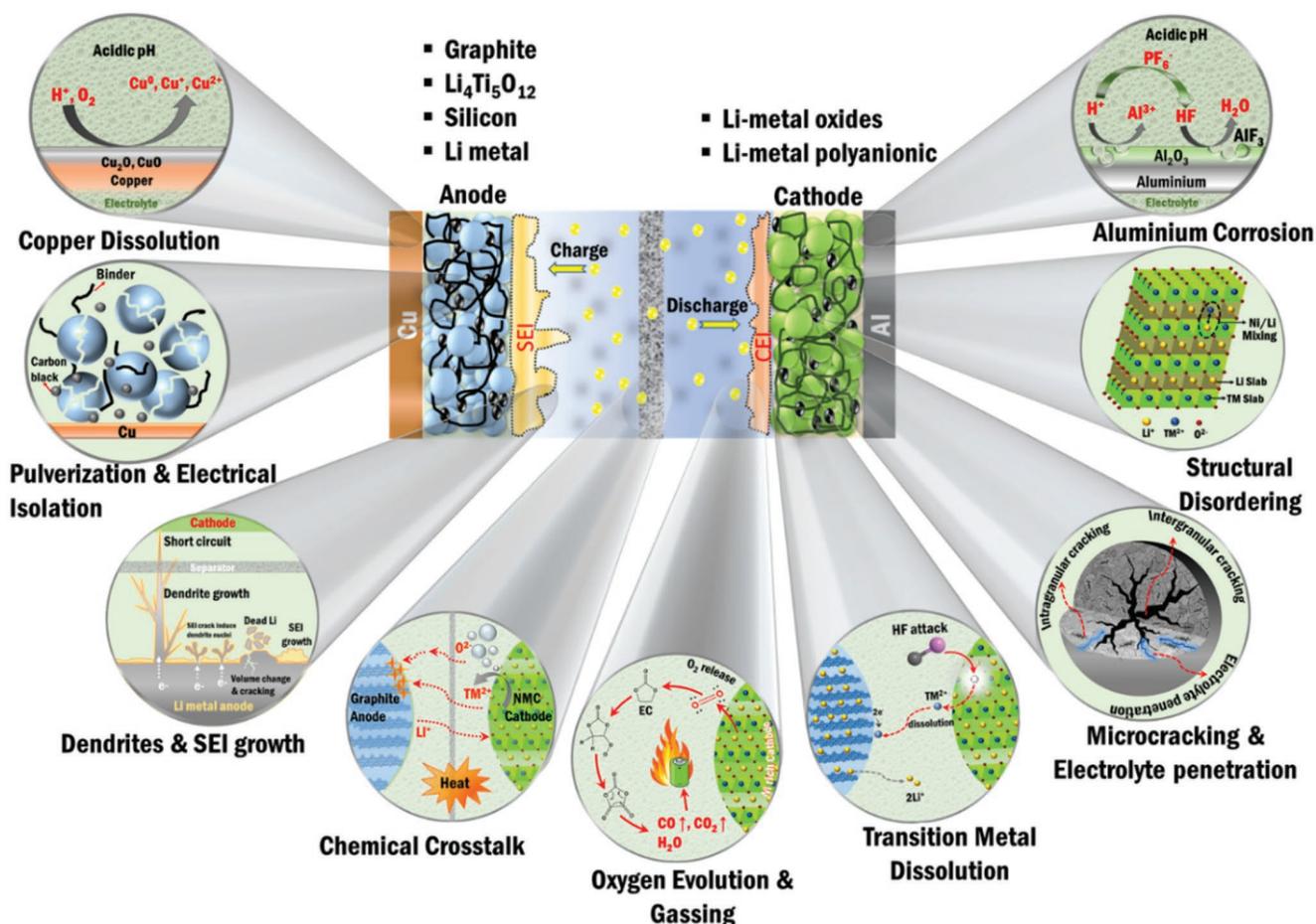


Figure 2. Overview of the major degradation mechanisms in Li-ion batteries.

mechanical fracture triggered by a large volume change occurring in electrode materials.<sup>[16–18]</sup> For example, the layered cathode materials  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$  (NMC,  $x + y + z = 1$ ), which is one of the most important cathode materials for the next-generation lithium Li-ion batteries, suffers from a rapid capacity degradation during cycling. Literature reports point out that its degradation mechanism is strongly dependent on the cut-off voltage during charge, the nickel content and the state of charge. The degradation mechanisms include cation migration and dissolution, formation of an undesirable surface film, and mechanical stresses. These stresses are accompanied by volume changes in electrode particles during the charge and discharge process,<sup>[19]</sup> which cause particle cracking and disintegration.<sup>[20]</sup> As a result, the formed cathode electrolyte interphase (CEI) is disrupted and then rebuilt by consuming active lithium and electrolyte. Any loss of active lithium would enhance the layered oxides degradation.<sup>[21]</sup> The higher the nickel content,<sup>[22]</sup> the more severe the bulk structural changes originating from  $\text{Ni}^{3+/4+}\text{-O}^{2-}$  instability generating anisotropic forces that accelerate the formation of microcracks. It has been found that the intergranular cracking of the secondary particles in the “meat ball” structure of the layered oxide materials is more damaging than the intragranular cracks formed in primary particles because the former breaks the electronic and ionic connectivity between particles bringing an uneven state of charge. In general, bearing both chemical and structural constraints, the strategies<sup>[23]</sup> to mitigate the microcrack generation in Ni-rich cathodes have been based on bulk structure/surface modifications and microstructure design engineering.

So far improved stability of layered oxide cathodes has been obtained through preventive steps as heteroatom doping<sup>[24]</sup> or by using organic conductive polymer coatings that offer better elasticity and adhesion properties. Representative examples include networks based on graphene,<sup>[25]</sup> conductive polymers like poly-3,4-ethylenedioxythiophene,<sup>[26]</sup> polyaniline,<sup>[27]</sup> polypyrrole,<sup>[28]</sup> etc. Additionally, microstructure engineering of the cathode by core-shell<sup>[29]</sup> and concentration gradient designs<sup>[30]</sup> has also been explored to realize a microcrack-free cathode. Though not solving the problem fundamentally, surface coating is another preventive strategy, which can provide a multifunctional protective layer over the primary and secondary cathode particles to relieve the stress by inhibiting side reactions with electrolyte, scavenging HF, electron/ion conductive media as well as the removal of surface lithium residues.<sup>[31]</sup> To achieve the desired efficiency of the coating, it is critically important to balance the thickness and homogeneity which can be done by using the atomic layer deposition technique.<sup>[32]</sup>

Strangely, keeping aside the preventive approaches mentioned above, no significant restorative methods are traversed so far to address the cathode disintegration. For instance, despite the well-recognized benefits of binders with robust mechanical and adhesive properties, hardly any research has been reported employing self-healable binders to resolve the cracking in high voltage transition metal oxide cathodes. It is widely known that the adhesive properties of the most prevalent polyvinylidene fluoride (PVDF) binder used for cathodes are not sufficiently high enough to buffer the internal stress generated during the high voltage operation.<sup>[33]</sup> Replacing the conventional binder interacting through weak van der

Waals forces, with highly viscoelastic and branched polymeric binders integrating stronger supramolecular interactions<sup>[34]</sup> like hydrogen bonding, ionic cross-linking, etc. is highly desirable not only for accommodating the volume change by equally distributing the stress upon each polymer branch but also for spontaneous self-healing of the bonds broken by cracking and to stabilize the cathode electrolyte interface.

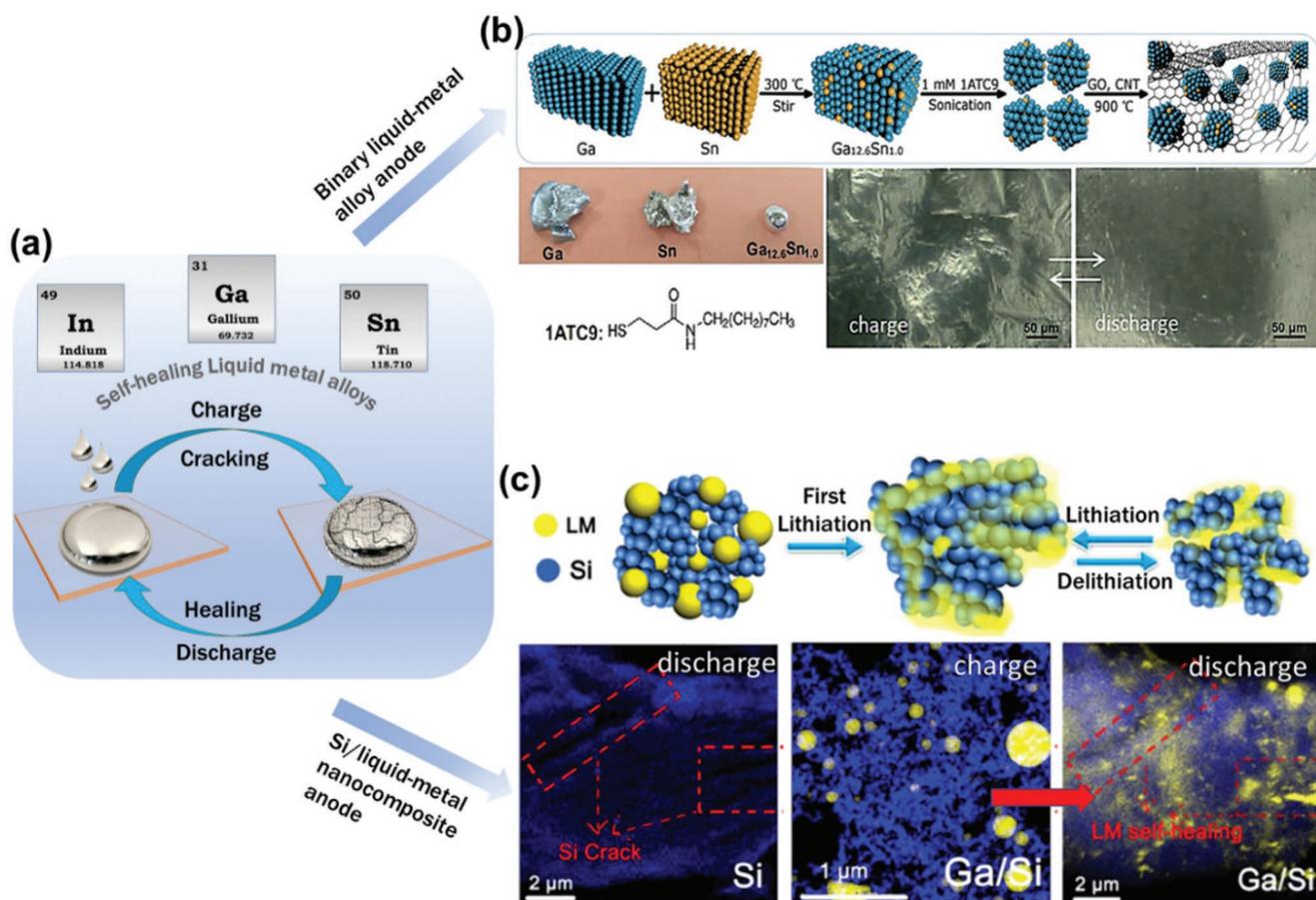
### 3.1.2. Silicon Anode Degradation

Comparable phenomena (mechanical failure) have been also identified during lithium alloying with silicon (Si) electrodes. Large volume expansion ( $\approx 300\%$ ) causes a series of electrode fading problems,<sup>[35]</sup> including Si pulverization, active materials shedding, continuous SEI layer forming. Consequently, the Si anodes show a fast capacity loss, low Coulombic efficiency, and electrode deterioration upon cycling. These defects are particularly evident in the thick and high mass-loading of Si electrodes.

Regeneration of cracked silicon particles suffering from massive volume change during repeated cycling is a key challenge to mitigate the capacity fading issue. The structure fracture loosens particle-to-particle contacts, loss of electrical connectivity, and subsequent capacity fading. Embracing self-healing functionalities in material design seem imperative to create electrodes which can endure the mechanical stress or make the cracks disappear magically. To circumvent silicon particles pulverization, so far two major self-healing approaches have been explored: i) the use of low melting point liquid metal alloy anodes and ii) the addition of self-healing binders.

Self-healing applications are best implemented when materials can be used in liquid form owing to the favorable fluidity and surface tension. The concept of self-healing metallic alloy anodes using low melting liquid metals was first developed by Deshpande et al., where metallic gallium (Ga m. p. 29.8 °C) alloyed with lithium ( $\text{Li}_2\text{Ga}$ ) was demonstrated to achieve spontaneous microcrack healing in LIBs.<sup>[36]</sup> The reversible liquid–solid–liquid transition of the liquid metal alloy marked the key to self-repair of anode cracking during lithiation/delithiation cycles, though heating up to 40 °C was necessary due to the melting point of Ga, which is slightly higher than room temperature. However, for practical applications, the low melting temperature of the liquid metal electrodes is critically important. Among the many low-melting elements in the periodic table, the post-transition metals especially Ga, In and Sn are the most extensively studied in LIBs due to their relatively high stability in air/moisture and nominal toxicity compared to the alkali metals which are easily oxidized and flammable under ambient conditions (Figure 3a).

Though limited by material selection possibilities, the approach of liquid metal alloy electrodes is a viable method if the melting temperature can be lowered to facilitate self-healing at or near room temperature as is shown in Figure 3b.<sup>[39,37]</sup> Compared to pure liquid metal, binary or ternary fusible alloys provide rich phase diagrams with several phases having different melting points. Studies show that even the notoriously huge particle cracking in Si anodes caused by volume expansion could be addressed to some extent using the liquid metal alloys as mechanical reinforcement support through their intrinsic self-healing strategy.<sup>[38,40,41]</sup> Hydroxylated Si particles coated with Ga–Sn room



**Figure 3.** Self-healing approaches employing low-melting liquid metal alloy anodes explored for LIBs. a) Reversible liquid–solid–liquid transition-based healing mechanism. b) Binary alloy anode approach: room temperature self-healing Ga–Sn alloy with RGO/CNT framework support for Li-ion anode with visible surface roughness change observed during charge/discharge cycles. Reproduced with permission.<sup>[37]</sup> Copyright 2017, Royal Society of Chemistry. c) Nanocomposite anode approach: conductive-additive free liquid metal/Si nanocomposite anode for LIBs with STEM images showing the spontaneous repairing of cracks by liquid Ga versus no healing in bare Si anode. Reproduced with permission.<sup>[38]</sup> Copyright 2018, Elsevier.

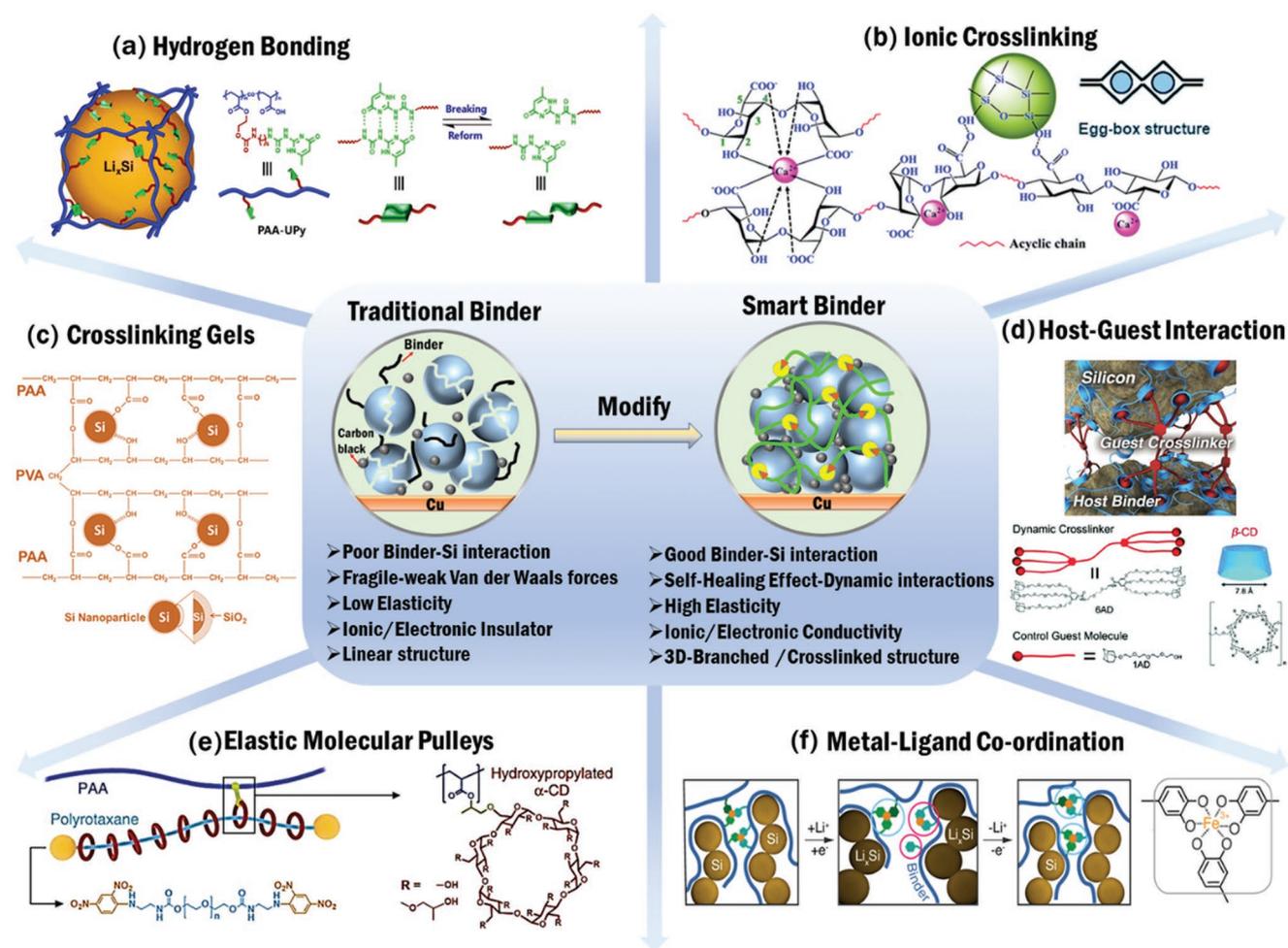
temperature liquid metal alloy were reported to remarkably alleviate the electrode pulverization which helped to achieve excellent cyclability and rate performance.<sup>[40]</sup> Besides coating, liquid metal nanoparticles have also proved a robust electric network in nanocomposite anode prepared by mixing gallium–indium–tin (GaInSn or Galinstan) liquid alloy with Si particles (Figure 3c).<sup>[38]</sup>

Despite good self-healing efficiencies with the liquid metals, unstable SEI remains a problem. Robust room temperature self-healing CuGa<sub>2</sub>S<sub>2</sub> nanoplatelet anodes working in a wide temperature range (243–328 K) were realized by Song et al.<sup>[42]</sup> in Li/Na ion batteries. Though the mechanism is not clear, the synergistic combination of high conductivity copper and self-healing Ga demonstrated stabilized SEI that is beneficial for electrochemical stability. Lastly, a better stabilization of SEI and reversible lithium insertion/extraction compared with silicon anode was reported via a combination of liquid metal Ga–Sn alloy anode together with the PEO solid electrolyte.<sup>[43]</sup>

Self-healing binders with a strong chemical bonding with active materials are another promising direction to alleviate the pulverization of silicon. So far, beyond conventional PVDF, various functional binders such as sodium carboxyl methylcellulose,<sup>[44,45]</sup> poly(acrylic acid) (PAA),<sup>[46,47]</sup> polyethylene

glycol (PEG),<sup>[48]</sup> polyamide imide,<sup>[49]</sup> guar gum,<sup>[50]</sup> and sodium alginate<sup>[51]</sup> have been comprehensively investigated. These binders show enhanced cohesive capability with Si particles via hydrogen bonds and/or covalent bonds. In this strategy, the Si particle size appears to be an important parameter to consider. The cycling stability of nano-Si has been improved by using carboxyl methylcellulose (CMC) as it can bond to oxygen on the Si surface.<sup>[48]</sup> However, CMC is not effective for micrometer-sized Si because it cannot bond to the cracked Si because of the lack of oxygen on the fresh pulverized Si surface. Similar issues have been found with other natural polymers.<sup>[50]</sup>

Some new concepts such as cross-linking gel polymers,<sup>[52–54]</sup> metal–ligand coordination bonds,<sup>[55]</sup> ionic cross-linking,<sup>[56,57]</sup> host–guest interaction,<sup>[58]</sup> ion/electron coconducted,<sup>[59]</sup> viscoelastic multiple hydrogen-bonded cross-linking,<sup>[60–63]</sup> boronic ester (B–O)-based dynamic covalent bonds,<sup>[64]</sup> and highly elastic pulley systems<sup>[65]</sup> have been explored to enhance the structural stability of Si anodes (Figure 4). Similar to the case of the self-healing liquid metal alloys, self-healing binders are typically used with the low Si loading (<1 mg cm<sup>-2</sup>). Improving the performance of Si anode under a high loading with high areal capacity (>4 mAh cm<sup>-2</sup>) and excellent cycling stability becomes a critical direction



**Figure 4.** Design considerations and application of smart binder versus traditional for mitigating pulverization in Si anodes: examples of self-healing approaches explored. a) Multiple hydrogen bonded cross-linking. Reproduced with permission.<sup>[60]</sup> Copyright 2018, Wiley-VCH. b) Ionic cross-linking. Reproduced with permission.<sup>[56]</sup> Copyright 2014, Royal Society of Chemistry. c) Polymeric cross-linked gel binders. Reproduced with permission.<sup>[52]</sup> Copyright 2014, Wiley-VCH. d) Host-guest interaction based dynamic cross-linking. Reproduced with permission.<sup>[58]</sup> Copyright 2015, American Chemical Society. e) Highly elastic molecular pulley binder. Reproduced with permission.<sup>[65]</sup> Copyright 2017, American Association for the Advancement of Science. f) Metal-ligand coordination bonded cross-linking. Reproduced with permission.<sup>[67]</sup> Copyright 2019, American Chemical Society.

of binder development. In this direction, an elastic self-healing CA-PAA binder has been designed for silicon anode with high loading to implement long-term stable cycling.<sup>[35]</sup> The multiple hydrogen bonds formed by in situ cross-linking of water-soluble CA and PAA establish a reversible network for silicon particles. The CA molecule not only serves as the protecting buffer layer to release the inner stress and stabilize the SEI, but it also connects with PAA to form an “inner flexibility and outer rigidity” spatial topology. Still, the lab-scale evaluation of most of these Si-binders use >10 wt% and tests are done in half-cell configuration with excess Li and electrolyte, hence not a true validation of their practical applicability. Therefore, the successful commercialization of self-healing binders requires more realistic testing and characterizations in terms of binder content, slurry compatibility, mechanical properties, swelling in a liquid electrolyte, electrochemical stability, etc. Furthermore, the future smart binders should also invest in dual interaction handles for Si/graphite composite anodes which would be more practically useful in current commercial LIBs, though some studies are already initiated.<sup>[66]</sup>

### 3.1.3. Electrical Contact Loss

A widely invoked degradation mechanism in electrodes is loss of internal electrical connectivity.<sup>[68]</sup> The loss of connectivity has been directly observed by Kosteci and McLarnon by Raman spectroscopy mapping and current-sensing atomic force microscopy. They have shown an evolution of surface composition ratio between  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  and carbon in the composite cathode<sup>[69]</sup> and a poor residual electronic contact between sub-micrometer primary particles within agglomerates during cycling. These phenomena are attributed to the movement of conductive carbon. But the loss of internal electrical connectivity has also been attributed to particle fracture.<sup>[70–72]</sup> Itou and Ukyo have investigated the mechanism of the resistance increase of LIBs using  $\text{Li}(\text{Ni},\text{Co})\text{O}_2$ -based materials. They demonstrated that the morphological and local structure changes of positive materials cause an increase of resistance.<sup>[72]</sup> The loss of internal electrical connectivity has been also linked to precipitation of thick SEI<sup>[73,74]</sup> and gas generation.<sup>[75]</sup> For example, particles in

graphite electrodes can be electrically isolated from the current collector due to coverage by SEI.

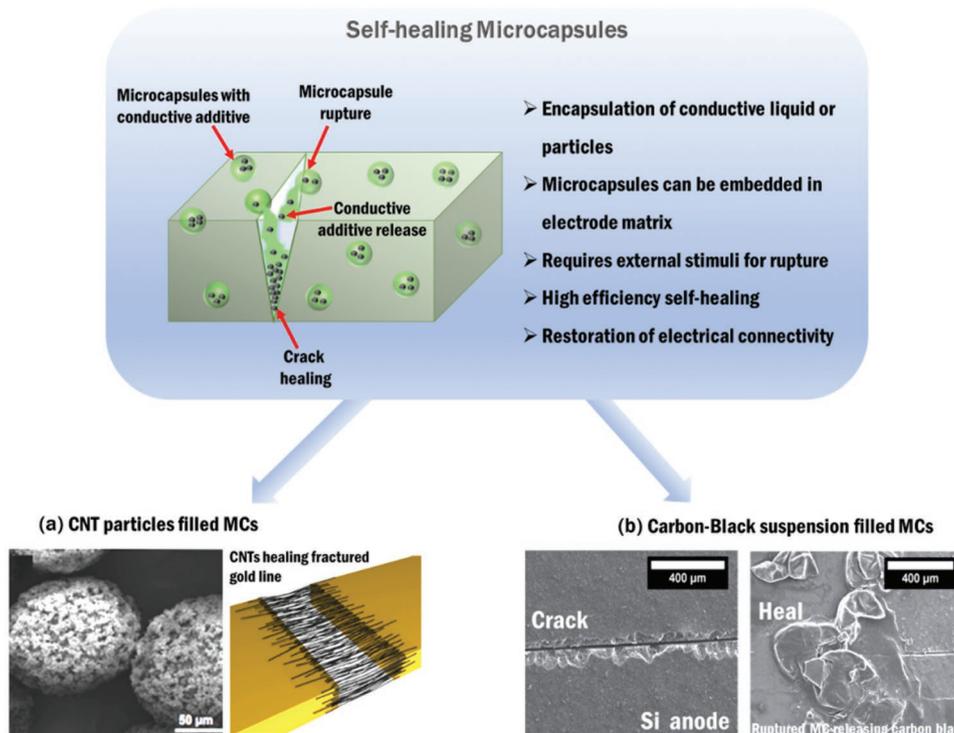
Controlled release of additives<sup>[76,77]</sup> is a promising strategy for solving many anticipatory degradation mechanisms in batteries for overall improvement in terms of performance, safety, and reliability. Robust microcapsules compatible with different electrochemical systems can be used to deliver additives (Figure 5) upon external stimuli such as time, heat, chemical triggers, or mechanical damage. Upon the mechanical crack damage such as crushing releases the conductive reagents, which infiltrate the damaged area and self-heal the broken circuit. Loss of electrical contact induced by particle cracking, binder degradation, and delamination from the current collector can be recovered with high efficiency using this approach. Nevertheless, self-restoration of electrical connectivity in electrodes based on intrinsic functionality has not yet been demonstrated inside LIBs.

### 3.2. Chemical and Electrochemical Degradation Mechanisms

#### 3.2.1. Electrolyte Degradation/Formation of SEI

It has been generally recognized that the cycling stability and safety of lithium-ion batteries are closely associated with liquid organic electrolytes.<sup>[78,79]</sup> Electrolytes used in Li-ion batteries are typically thermodynamically metastable and this results in the formation of the SEI at the negative electrode and the formation

of CEI at the positive electrode. The composition of the SEI is still under debate, however, it is well accepted that it is composed of degradation products from solvents and salts. Passivation enables long-term cyclability and introduces additional resistance which is increasing and changing during battery aging (e.g., dynamic nature of the SEI). Namely, the stability of SEI can be catalyzed by degradation products from the cathode and consequently become soluble or unstable. A common consensus is that the SEI is mainly composed of lithiated ethylene dicarbonate and LiF. The organic part of SEI is decomposed during the battery aging into salts which together with other inorganic degradation products form a compact layer on the surface of active particles. Due to this continuous process, the SEI grows albeit at lower rates compared to the formation cycles. The continuous growth of SEI leads to the impedance rise as well as irreversible consumption of lithium and electrolyte components resulting in the overall consumption of up to 10 at% of lithium in the cell.<sup>[80]</sup> Similarly, for silicon and metallic lithium anodes, the deposited SEI layer is inhomogeneous and brittle with the freshly exposed surfaces being the source of further electrolyte decomposition. For stable cycling, it is ideal to have a morphological and compositional homogeneous SEI film with uniform ionic conductivity. Furthermore, it should be flexible enough to accommodate the volume changes and electronically insulating to suppress electrolyte degradation.<sup>[81]</sup> Such SEI figures of merits can be obtained using preventive steps with miniature amounts of preselected additives in the electrolyte. SEI engineering strategies have been the subject of



**Figure 5.** Self-healing microcapsules approach for restoration of electrical conductivity after electrode cracking. a) Microcapsules containing carbon nanotube particles demonstrated for autonomous restoration of electrical conductivity in fractured gold line. Reproduced with permission.<sup>[76]</sup> Copyright 2012, American Institute of Physics Publishing. b) Line crack in a Si nanoparticle anode self-healed by ruptured microcapsules releasing carbon black suspension. Reproduced with permission.<sup>[77]</sup> Copyright 2014, Wiley-VCH.

many recent reviews considering the vast amount of research spent in this area, but achieving an ideal SEI design remains a challenge, mainly because of diverse combinations of electrolytes and active materials.<sup>[81]</sup>

For safer batteries, replacing the liquid electrolytes with solid-state electrolytes has been actively researched. In general, solid-state electrolytes based on polymers are advantageous over inorganic materials owing to their rich tunability of physical and electrochemical properties, plus their soft nature enabling conformal contact with electrodes leading to comparatively lower interfacial resistance.<sup>[82]</sup> To achieve improved battery performance, an ideal polymer electrolyte (PE) is desired to simultaneously meet the performance requirements of i) high room temperature ionic conductivity close enough to liquid electrolytes ( $>10^{-4}$ – $10^{-3}$  S cm<sup>-1</sup>) but poor electronic conductivity ( $<10^{-6}$  S cm<sup>-1</sup>), ii) high Li<sup>+</sup>-ion transference number as close as possible to unity, iii) wide electrochemical stability window preferably  $\geq 4.5$  V versus Li/Li<sup>+</sup>, iv) low interfacial resistance, and v) excellent mechanical and thermal stabilities. High ionic conductivity and cation transference number decrease the concentration polarization and improve the rate performance<sup>[83]</sup> whereas wide electrochemical stability facilitates the application of high-voltage cathodes. High thermal stability ( $>150$  °C) of the polymer host ensures stable cycling under extreme conditions and strong mechanical modulus ( $>1$  GPa) are important to withstand the volume changes and resist dendrite growth.<sup>[84]</sup> Nevertheless, practically maximizing all these desirables in a single polymer electrolyte is still an arduous task. Moreover, the solid polymer electrolytes are also prone to cracking or damage during the charge/discharge cycles, hence adding autonomous self-healing properties to these electrolytes significantly enhance reliability of the batteries. Self-healing electrolytes with high ionic conductivity, high flexibility, thermal stability and ability to recover from structural damages have been extensively investigated.<sup>[85]</sup> Work can be divided into three different directions: gel polymer electrolytes (GPEs), composite polymer electrolytes (CPEs), and solid-state polymer electrolytes (SPEs). In all the strategies, the self-healing properties are brought by the presence of dynamic covalent bond interactions (mostly hydrogen bonding) and nondynamic covalent bond interactions.<sup>[86,87]</sup> In polymer electrolytes, the ion transport occurs freely in the amorphous regions above the glass transition temperature ( $T_g$ ), so polymers with low  $T_g$  present better ion transport properties.<sup>[88]</sup> To increase the amorphous phase or reduce the crystallinity or  $T_g$ , different strategies are employed such as polymer matrix modification via copolymerizations, blending or cross-linking, mixing with inorganic fillers to form CPES or addition of liquid plasticizers to form GPEs. However, it has been found that the chemical nature, surface chemistry, particle size as well as particle concentration of the additives or fillers significantly influences the ionic conductivity, electrochemical and mechanical properties of the PEs.<sup>[89–92]</sup> In GPE electrolytes, the self-healing functionalities are provided by the polymer matrix, while the additive, lithium salts, and liquid solvent ensure ionic conductivity. In this context, ionic liquids have been selected as plasticizers (Figure 6a)<sup>[93]</sup> due to their ability to be incorporated into covalently cross-linked polymer networks.<sup>[94,95]</sup> But, the use of plasticizer despite its merits to electrochemical performance usually deteriorates the mechanical robustness and reduces

the transference number  $t_{Li^+}$  of the lithium cation below 0.5 which affects the long-term cycling stability of the battery. A way to increase the lithium-ion transference number is to develop single-ion conducting (SIC) electrolytes.<sup>[96,97]</sup> But, most of these SIC electrolytes suffer from cracks during the electrochemical process. Therefore, adding a self-healing function to these SIC electrolytes would be an effective strategy to heal cracks and restore their original property. Self-healing single-ion conducting polymer electrolytes using RAFT copolymerization of the monomer of poly(ethylene glycol) methyl ether methacrylate, ureido pyrimidinone methacrylate (UPyMA), and lithium 4-styrenesulfonyl(phenylsulfonyl)imide (Figure 6b) have been investigated without the introduction of any lithium salts.<sup>[98]</sup>

Dealing with CPEs, ureidopyrimidinone (UPy) unit which exhibits good “dynamic hydrogen bonding” has been grafted on SiO<sub>2</sub> and the (UPy)-functionalized SiO<sub>2</sub> (SiO<sub>2</sub>-UPy) was integrated into the polymer matrix containing UPy units (Figure 6c) to form supramolecular networks with the polymer via the interactions of quadruple hydrogen bonding.<sup>[85]</sup> The existence of the UPy functions onto SiO<sub>2</sub> aids to uniformly disperse the fillers and improves the interphase between SiO<sub>2</sub> and the polymer matrix providing a fast conduction channel for lithium ions.

Turning to SPEs, Zhou et al. developed a polymer electrolyte formed by a physically cross-linked network via UPy containing brush-like poly(ethylene glycol) chains.<sup>[100]</sup> This polymer electrolyte is flexible and able to provide fast intrinsic self-healability and high stretchability. To further improve the healing efficiency and healing times of SPE, disulfide metathesis was used to fabricate SPE through RAFT polymerization of poly(ethylene glycol) methyl ether acrylate and 1,2-Bis(ureidoethylenemethacrylate) di-sulfide (cross-linker). The combination of hydrogen and disulfide bonds improved the self-healing characteristics of the self-healing SPE (Figure 6d).<sup>[99]</sup>

Furthermore, the dynamic hydrogen bonding provided by amino terminated poly(ethylene glycol) was used by Wu et al.<sup>[101]</sup> as a framework to fabricate rapid SPE with a high polarity of the framework responsible for high ionic conductivity. In the SPEs approach, polymer networks with dynamic covalent cross-links have been recently investigated as an electrolyte to self-heal the conductivity and rheological properties following damage.<sup>[102]</sup> These polymer networks act as solids at room temperature but can flow at high temperatures.<sup>[102]</sup> Interestingly, they can also be dissolved in water to recover the starting monomers; this property can be used for recyclable, healable electrolytes in Li-ion batteries. Synthesis of PEO networks containing dynamic boronic ester cross-links was performed by adding lithium bis-trifluoromethyl sulfonyl imide (LiTFSI). Obtained ionic conductivity exceeds  $10^{-4}$  S cm<sup>-1</sup> and it is a function of Li:EO ratio (salt concentration). The system possesses a vitrimer like behavior with a transition from Arrhenius stress relaxation times, to non-Arrhenius behavior during dissociation. The polymer network shows self-healing properties and restoration of conductivity upon the damage.

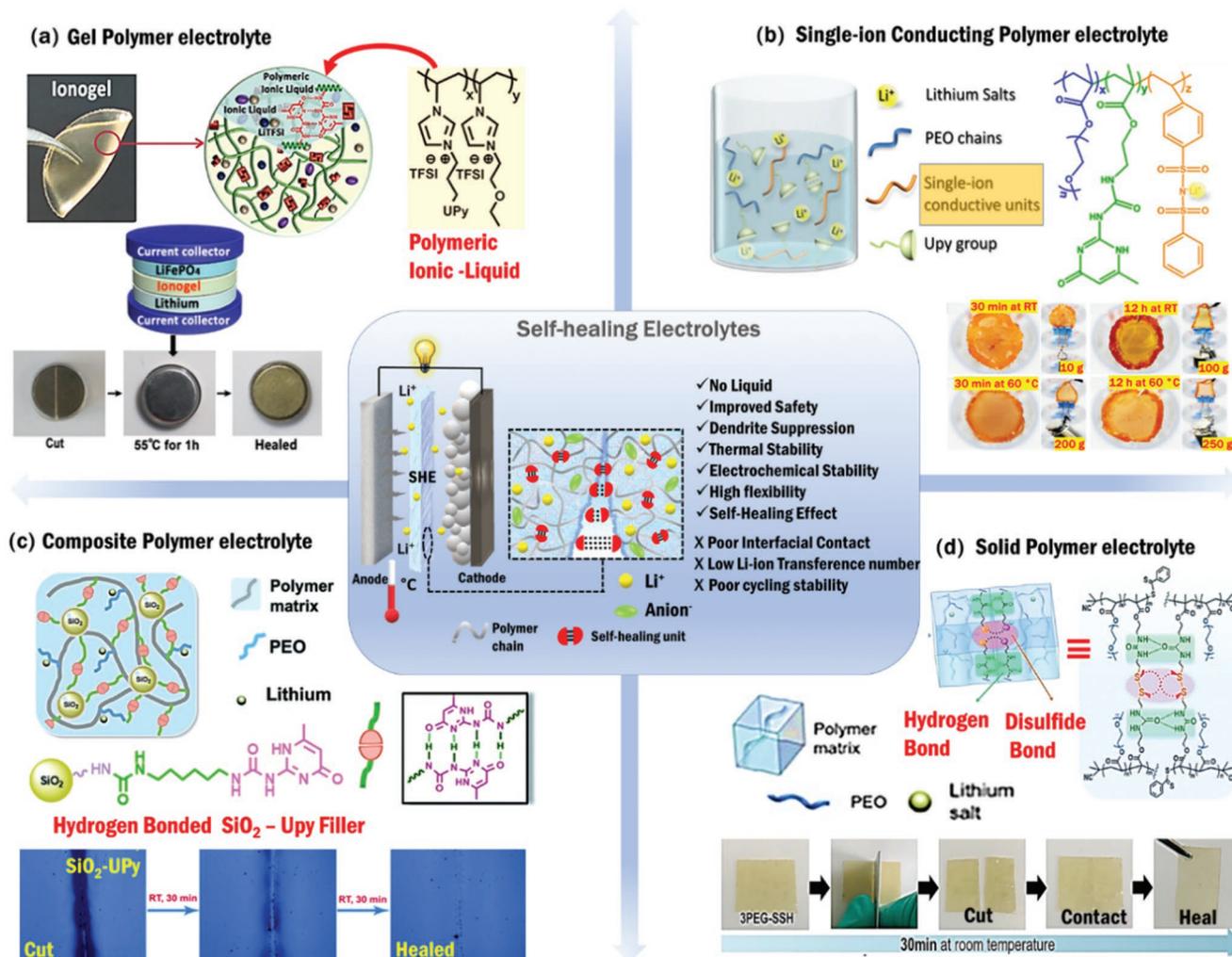
Altogether, in polymer electrolytes, the most difficult part in incorporating self-healing functionalities is to afford excellent electrochemical performance and high healing efficiency without the need of external stimuli. Up to now, there are no

relevant studies on self-healing PEs with high self-healing efficiency, the capability of conducting lithium ions and excellent electrochemical performance in LIBs. There is still a lot of room to develop this strategy.

### 3.2.2. Lithium Plating/Dendrite Formation

Lithium plating/dendrite formation in Li-ion batteries is caused by high charging current density, low charging temperature ( $-20\text{ }^{\circ}\text{C}$  coupled with a high charge rate), overcharge, improper cell balance (uneven electrode casting), and it is a function of electrolyte selection.<sup>[103,104]</sup> When the charging rate exceeds the rate of lithium-ion diffusion into graphite, lithium plating results in the formation of moss-like deposits including

dendrites. Although metallic lithium is not considered as a negative electrode in Li-ion batteries, studies performed by using Li metal provide solutions for the Li-ion cells as well as for novel generations of batteries with metal or anodeless electrodes.<sup>[105]</sup> We should emphasise that the dendrite formation is even more problematic in the cells with metallic lithium. There the formation of dendrites is governed by the mass transport of Li ions in the electrolyte phase and by diffusion, convection, electromigration, and the morphological instability of the lithium metal anode.<sup>[106]</sup> The local variation in the mass transfer rate creates a concentration gradient near the electrode surface causing uneven Li plating.<sup>[107]</sup> This is additionally enhanced with volumetric changes and formation of cracks or delamination of SEI during cycling that exposes a fresh surface to the electrolyte on which an additional SEI grows depleting the electrolyte.



**Figure 6.** Pros and cons self-healing polymer electrolytes for safer Li-ion batteries: examples of different categories explored. a) Gel polymer electrolytes using an ionic liquid plasticizer showing good flexibility and self-healing behavior of the ionogel membrane based on hydrogen bonded supramolecular copolymer network when cut and placed inside a Li/LiFePO<sub>4</sub> button cell. Reproduced with permission.<sup>[93]</sup> Copyright 2019, American Chemical Society. b) Single ion conductive polymer electrolyte combining lithium 4-styrenesulfonyl(phenylsulfonyl)imide (SSPSiLi) unit for high Li-ion transference number and quadrupole hydrogen bonding UPyMA unit for self-healing under different thermal and mechanical conditions as shown in the optical images. Reproduced with permission.<sup>[98]</sup> Copyright 2021, American Chemical Society. c) Supramolecular composite polymer electrolyte prepared incorporating UPy-functionalized SiO<sub>2</sub> filler into PEG-UPy polymer matrix enhancing the filler dispersity and healing properties. Reproduced with permission.<sup>[85]</sup> Copyright 2019, Royal Society of Chemistry. d) Solid polymer electrolyte with self-healing capabilities enabled by dynamic disulfide and hydrogen bonded polymer cross-links. Reproduced with permission.<sup>[99]</sup> Copyright 2020, American Chemical Society.

The tandem occurrence of dendrites and electrolyte loss causes upon cycling the growth of dead mossy Li that blocks the ion transport leading to capacity fading and low Coulombic efficiencies.

In general, the most common solution to achieve dendrite free deposition and long cycle life is the formation of stable, uniform SEI.<sup>[108]</sup> The stable SEI besides suppression of dendrites should possess self-healing properties to spontaneously repair the unpredictable damages without losing effectiveness during cycling. We should emphasise that lithium metal anode has been attempted in the commercial batteries by several companies, out of them Blue Solution technology shows long term cyclability without entering into safety issues because of the use of a specific company coating. Their technology is based on PEO-based polymer electrolytes suffering kinetic issues at low temperatures and low oxidative stability. That calls for further development of innovative solutions in surface engineering.

Many different solutions have been proposed in the last decade to suppress and control the growth of Li-dendrites such as electrolyte engineering (using additives<sup>[109,110]</sup> or modifying salt concentrations<sup>[111,112]</sup>), separator modifications,<sup>[113]</sup> nanostructuring Li metal anode or guiding Li deposition using 3D stable hosts or current collectors,<sup>[114–117]</sup> protective artificial interlayers/coatings including the self-healing viscoelastic polymers for stabilizing Li metal/electrolyte interface based on supramolecular hydrogen bonds, transient B–O dynamic bonds,<sup>[118–123]</sup> etc., but most of them showing the cycling stability only for few tens or hundredth cycles in symmetric cell design. Moreover, the studies are generally conducted with thicker Li metal anode (>250  $\mu\text{m}$ ) which represents large excess of Li reservoir and the cycle life does not correlate with Li consumption. It may also be noted that the symmetric Li//Li cycling test fails to differentiate internally shorted cells. Though challenging, for real practical applicability it is necessary to achieve stable cycling over several hundredth of cycles using thin ( $\leq 50 \mu\text{m}$ ) Li anode with practical areal capacity, to claim the high energy density of the Li metal. In full cells, when there is excess Li, the Coulombic efficiency (CE) corresponds to the cathode reversibility and once the excess Li is consumed the capacity decay becomes faster reflecting the Li anode efficiency. Therefore, a limited amount of Li and/or lean electrolyte conditions are imperative for demonstrating obvious advantages of protective measures against dendritic growths and unstable SEI. An evaluation of the recent studies reporting the reversible stripping/deposition of lithium in asymmetric cell configurations under practical testing conditions shows positive advancements with the CE values steadily improving, thanks to the latest developments especially polymer/inorganic composite coatings. For instance, a molecular layer deposited ultrathin organic/inorganic hybrid alucone coating on lithium metal yielded a steady CE of 99.5% over 160 cycles for the Li–Cu cells cycled at  $0.4 \text{ mA cm}^{-2}$ , whereas the uncoated Li/Cu cell failed at  $\approx 60$  cycles.<sup>[124]</sup> Further at the current density of  $1.0 \text{ mA cm}^{-2}$ , alucone-coated Li survived >130 cycles with stabilized CE at 98.5%. The highly cross-linked aluminum cation bridged PEO hybrid structure of alucone formed by alternate exposures of ethylene glycol and trimethyl aluminum precursors bestowed superior mechanical properties to the protective coating that enabled uniform denser lithium deposition and stable SEI layer. A combination

of polymer–inorganic composite protective coatings with 3D current collector scaffolds reported by Wang et al. demonstrated 99.1% CE of Li plating and stripping on a coated 3D carbon host at high current density ( $2 \text{ mA cm}^{-2}$ ) and high capacity ( $4 \text{ mAh cm}^{-2}$ ).<sup>[125]</sup> The coating comprised of a poly(sulfonate-dioxolane) (SF-DOL) copolymer mixed with graphene oxide (GO) nanosheets together named as reactive polymer coating (RPC), which in situ reacts at the interface forming SEI containing lithium fluoride nanoparticles from the reduction of SF group along with polymeric lithium salt and GO providing excellent passivation, homogeneity and mechanical strength. A high average CE of 99.3% was achieved for plating/stripping of this RPC-stabilized Li on flat stainless-steel electrode at  $1 \text{ mA cm}^{-2}$  and  $1 \text{ mAh cm}^{-2}$  in carbonate electrolyte ( $1 \text{ M LiPF}_6 + 2\% \text{ LiBOB} + \text{EC/EMC}$ ). Strikingly, the RPC-stabilized Li@3D host//NCM 523 full-cell retained 90% of the initial capacity over 200 cycles under lean electrolyte ( $7 \mu\text{L mAh}^{-1}$ ), limited Li amount (1.9-fold Li-excess), and high areal capacity ( $3.4 \text{ mAh cm}^{-2}$ ) conditions.

Several other parallel studies are reported where stable long term cycling under high current densities with CE values for Li/Cu asymmetric cells  $\geq 97\%$  have been achieved using different approaches such as grafting of polydimethyl siloxane macromolecules on oxidic Li surface,<sup>[126]</sup> multifunctional high  $\text{Li}^+$  single-ion conducting polymeric network based on Al(OR)<sub>4</sub>-dynamic cross-links,<sup>[127]</sup> SPEEK-Li/POSS ionomer membrane coatings comprised of lithium-exchanged sulfonated polyether ether ketone embedded with polyhedral oligosilsesquioxane units,<sup>[128]</sup> lithophilic  $\text{CuSO}_4$ -doped polydopamine coatings on Cu foil,<sup>[129]</sup> hybrid organic–inorganic polyurea-Zn based gradient coatings,<sup>[130]</sup> etc. Uniquely, in a different approach, Wang et al. have recently demonstrated a strategy involving asymmetrical bidirectional current mode of charging, where the already formed dendrites could be self-healed by timely correction via reverse current without the requirement of any chemical/physical modification of the anode.<sup>[131]</sup> Having discussed the progressive achievements made to address the dendritic growths and associated issues, there is still a need for significant improvements especially in terms of gravimetric and volumetric energy densities, practical form-factor scalability, and manufacture cost, in order to facilitate uncomplicated safer use of Li metal anodes in emerging commercial battery technologies.

### 3.2.3. Gas Evolution

Gas evolution is generally correlated to the SEI formation occurring in the formation cycles and to the cell aging due to reconstruction of SEI. Additional gassing is formed on the cathode surface, particularly on nickel-rich NMC materials ( $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$  ( $x > 0.6$ ,  $x + y + z = 1$ )) in the connection with electrolyte oxidation on the surface and potential oxygen release from the structure at high potentials.<sup>[132]</sup> Latter is a known process which proceeds at a high state of charge, where the layered materials undergo thermodynamic phase transition initiated by preferential migration of transition metal ion to Li slabs (known as cation mixing) accompanied by the release of a large amount of highly reactive molecular oxygen. Higher the nickel content, lower is the onset decomposition temperature<sup>[133]</sup> and

this is a reason why commercial cells using pure LiNiO<sub>2</sub> as cathode material are not in the market, although LiNiO<sub>2</sub> was considered as a potential positive electrode long time ago.<sup>[134]</sup> Some gaseous products released during cell aging are soluble in the electrolyte and can be consumed within parasitic reactions. Impurities, for instance water or Li<sub>2</sub>CO<sub>3</sub> film on the cathodes, are another source of potential gas evolution, and formed gasses have an impact on the stability of passivation layers on both electrodes. The stability of passivation layers is greatly influenced by increased temperature which can be a result of internal (heat generated at high current densities, overcharging or internal/external short circuits) or external (environmental) processes. With an increased temperature, the SEIs undergo decomposition. Studies show that SEI decomposition could be initiated at temperatures fairly low as 69 °C and the exothermic decomposition of metastable organic degradation products release gases like CO<sub>2</sub>, ethylene, etc.<sup>[135]</sup> Broken SEI layer triggers the exothermic reaction of exposed Li with carbonate electrolyte generating flammable hydrocarbon gases, which in turn raises the cell pressure. The damage is heightened to cell burning if there is oxygen evolution from the cathode side.

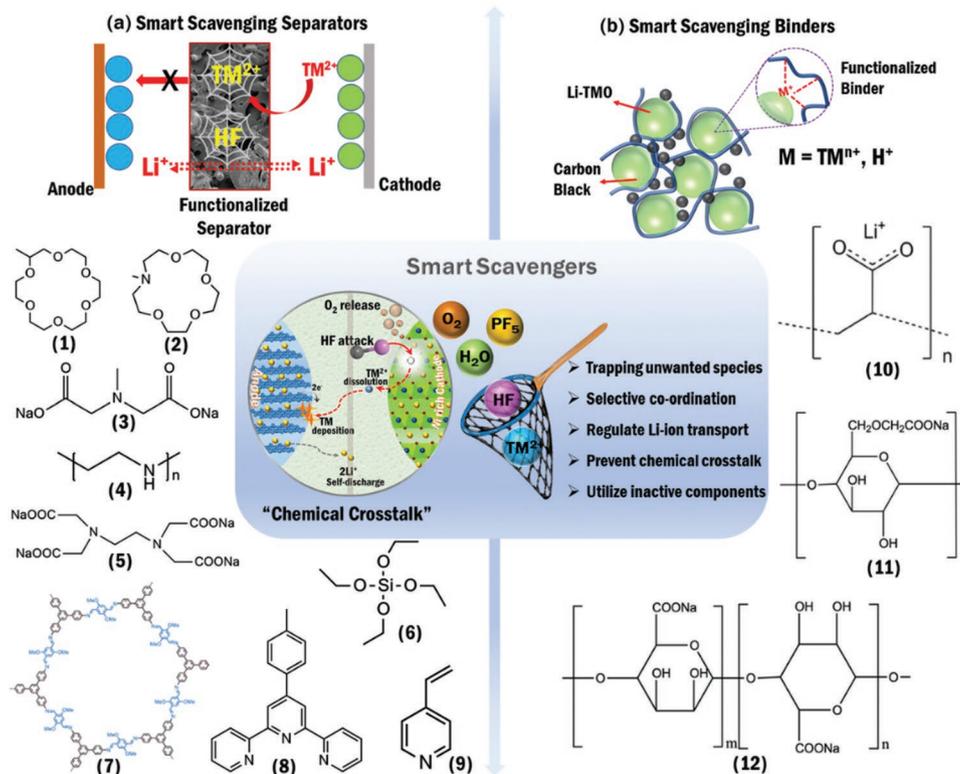
#### 3.2.4. Metal Dissolution

Metal dissolution is typically accompanied with gas evolution on the cathode. Manganese dissolution is the most severe problem and several studies were devoted to the understanding dissolution of manganese from different structures and in different environments (electrolytes, potentials). A recent review paper provides a detailed overview of mechanisms of dissolution.<sup>[136]</sup> Paper discusses reasons of capacity fade in a cell containing cathode materials with manganese in the divalent or trivalent oxidation states. The most known process of Mn dissolution from cathode materials occurs in LiMn<sub>2</sub>O<sub>4</sub>.<sup>[137,138]</sup> It is well accepted today that divalent and trivalent oxidation states are prone to be soluble, while tetravalent Mn is the most stable.<sup>[136,139]</sup> Apart from the disproportionation reaction, Mn dissolution is caused by phase transformations, and chemical lithiation.<sup>[140,141]</sup> Phase transformation is also a reason for Co dissolution from LiCoO<sub>2</sub>, while Ni is the most stable among Mn, Co, and Ni cations.<sup>[136]</sup> The process of dissolution is faster at elevated temperatures and when impurities are present in the electrolyte (i.e., traces of water). Interestingly dissolution of Mn from the cathode material is responsible for only 20–33% capacity drop,<sup>[142]</sup> additional capacity fading is caused by deposition of Mn on the anode inducing increased polarization. The dissolved transition metal cations leach into the electrolyte and migrate to the negative electrode, react with SEI by an exchange reaction with Li<sup>+</sup> ions to form resistive surface films. These reactions globally termed “dissolution–migration–deposition–catalytic reactions” mechanism hinder the lithium diffusion channels, thereby increasing the impedance, decreasing the reversible capacity and shortening the battery life. Polarization increases also due to electrolyte consumption due to the re-passivation process. Dissolution of iron from LiFePO<sub>4</sub> was detected however on a much lower extend and it highly depends on the synthesis procedure used for LiFePO<sub>4</sub>.<sup>[136]</sup> The source of cations during the aging process is also rooted in the current collectors

which are prone to corrosion reactions at high oxidation potential or chemical attacks driven by salts or their degradation products.<sup>[143,144]</sup>

Self-healing solutions for gas evolution and metal ion dissolution are related to the unavoidable atomic-level structural changes including irreversible phase transitions in Li, Ni, Mn-rich oxides. No wonder, none of the preventive approaches addressing this fundamental structure instability issues have thus far achieved total success to the level required for commercial application in LIBs.<sup>[145]</sup> Consequently, complementary curative research strategies inclined toward stabilizing the CEI or scavenging the undesired species are employed to alleviate the problem altogether. Since the TM dissolution is interlinked with concomitant oxygen release and aggravated by HF attack, scavenging these parasitic species can not only control the metal dissolution but also prevent oxidation of the electrolyte solvents and inhibit the chemical crosstalk with the anode. Ideally a thin homogeneous CEI passivation layer should be able to protect the cathode surface from corrosion and hinder the TM dissolution, but unfortunately the naturally formed CEI found to consist of Li<sub>2</sub>CO<sub>3</sub>, LiF, R–O–Li, ROCO<sub>2</sub>–Li, etc. is usually brittle and uneven.<sup>[146]</sup> Functional electrolyte additives capable of in situ constructing robust CEI layer with simultaneous selective scavenging of obnoxious reactive substances including HF, PF<sub>5</sub>, water traces, gaseous oxygen species, etc. are widely experimented methods, and the progress has been thoroughly reviewed recently.<sup>[147]</sup> However, some major disadvantages of the approach like premature consumption of the additives during cycling, poor control over CEI thickness and the inability of a single additive to meet multiple scavenging functions warrant further research toward other radical self-sustainable strategies. One such smart direction involves the functionalized use of electrochemically inactive battery components like separators (Figure 7a) and binders (Figure 7b) as supplementary tools preventing or at least impeding the chemical crosstalk.<sup>[148]</sup>

Many studies have been reported mainly for lithium manganese oxide (LMO) cathodes, proposing the application of chemically functionalized smart separators immobilized with TM ion (particularly Mn<sup>2+</sup>) chelating agents like crown ethers (18-crown-6,<sup>[149]</sup> aza-15-crown-5,<sup>[150]</sup> disodium iminodiacetate,<sup>[151]</sup> polyethyleneimine or tetrasodium edetate (Na<sub>4</sub>EDTA),<sup>[152]</sup> covalent organic frameworks with polar (–C=N–) groups,<sup>[153]</sup> etc. Effective trapping of the dissolved Mn ions by these separators demonstrated excellent control over the chemical crosstalk leading to stable SEI on the graphite anode and improved capacity retention in the LMO–graphite cells. In addition multifunctional separators which can not only trap dissolved TM ions but also scavenge acidic species like HF from the electrolyte solution are studied where functional moieties such as tetraethyl orthosilicate,<sup>[154]</sup> poly(4-vinyl pyridine),<sup>[155]</sup> terpyridine/polyvinylpyrrolidone,<sup>[156]</sup> dilithium maleate,<sup>[157]</sup> are used to reduce the acid attack. Controlled transport between two electrodes can be obtained with the use of the track-etched polymer membranes. Different types of polymers can be used for track-etched membranes as a function of medium or solvent conditions. It is now possible to design a single pore membrane to a high pore density membrane containing up to 10<sup>10</sup> pore cm<sup>–2</sup>. The pore diameter can be sub-nanometric to micrometric, and the thickness of the membrane ranging from 6 to



**Figure 7.** Smart scavenger design considerations for trapping the parasitic species and mitigating the chemical crosstalk in Li-ion batteries. a) Multifunctional smart scavenging separators: chemical structures of the active functional groups used to modify the separators for trapping dissolved transition metal ions and acidic species. (1) 18-crown-6, (2) aza-15-crown-5, (3) disodium iminodiacetate, (4) polyethyleneimine, (5) tetrasodium edate ( $\text{Na}_4\text{EDTA}$ ), (6) tetraethyl orthosilicate (TEOS), (7) covalent organic frameworks with polar ( $-\text{C}=\text{N}-$ ) groups, (8) 4-vinyl pyridine, (9) terpyridine. b) Smart scavenging binders with active metal carboxylate functionalization for transition metal ion and HF trapping, (10) lithium polyacrylate, (11) carboxymethyl cellulose, and (12) sodium alginate.

$50\ \mu\text{m}$ .<sup>[158]</sup> The fabrication method of track-etched nanopores<sup>[159]</sup> is based on high-energy ion beams from an accelerator, typically leading to the fabrication of small surface area separators. Their application has been demonstrated on the case of the track-etched polymer membranes in polyethylene terephthalate (PET), which were used as separators in Li-S cells.<sup>[160]</sup>

Besides separators, binders with active functionalization such as metal carboxylate groups are also demonstrated to scavenge HF by exchanging metal cations on the binder with acidic protons and thereby suppressing the unfavorable side reactions at the cathode.<sup>[161,162]</sup> Considering the encouraging results, the prospects of advanced smart binders with optimized trapping and scavenging functions extended toward immobilizing dissolved metal ions and removing impurities like water, reactive oxygen species, etc. deserve much more research attention as the binders are in intimate contact with the active material facilitating fast and easy modulations to tackle electrode degradation.

### 3.2.5. Degradation of Inactive Components

The inactive battery components including binder, current collectors, conductive additives, and separators are also susceptible to degradation. Primarily, the contact loss between

the electrode and the inactive components increases the cell impedance. In addition, at elevated temperatures and voltages, binder materials tend to decompose generating unwanted side products and disintegration of active materials.<sup>[80,163]</sup> Hence, it would be highly beneficial to develop high voltage advanced binders which are not only able to prevent the crumbling of active particles by self-recovering from the cracks, but also exhibit excellent heat resistance with decomposition temperatures at least above  $200\ ^\circ\text{C}$ . Studies show that electrode performance can also be affected by the degradation of electronically conductive additives in the composite.<sup>[164]</sup> Occasionally, anion intercalations at significantly lower potentials can initiate the structural degradation and particle breakage of carbon black additives in organic carbonate electrolytes, leading to gradual delamination from the composite.<sup>[165]</sup> Further, at high voltages, surface layers of electrolyte oxidation products are formed on the carbon black surface, decreasing the electronic conductivity and consequently accelerating the cathode degradation.<sup>[166]</sup> Corrosion of current collectors upon contact with electrolyte can reduce their conductivity resulting in power limitations. Dissolution of copper current collector at anode side is triggered during overdischarge and sufficient residues in the electrolyte promote Cu-dendrite, which shortens battery life due to occurrence of short circuits.<sup>[167]</sup> Recently the dissolution mechanism of copper anode current collector detected  $\text{Cu}^{2+}$  as the main

dissolved species in electrolyte alongside traces of  $\text{Cu}^+$ .<sup>[168]</sup> Accordingly, the proposed mechanism associates the acidic electrolyte decomposition product, HF to trigger the dissolution of the passivating oxide layer ( $\text{Cu}_2\text{O}$  ad  $\text{CuO}$ ) generating  $\text{Cu}^+$  species which can either undergo disproportionation to  $\text{Cu}^0$  and  $\text{Cu}^{2+}$  or oxidized by  $\text{O}_2$  to  $\text{Cu}^{2+}$ . Unlike copper, corrosion of aluminum cathode current collector is less severe but leads to impedance rise. Severe corrosion of Al has been reported with electrolytes containing hygroscopic lithium salts such as LiTFSI<sup>[169]</sup> or those which lack fluorine like  $\text{LiClO}_4$ .<sup>[170]</sup>

Compared to binders and current collectors, the degradation of separators deserves higher significance because it is a critical component preventing loss of electronic contact and ensures  $\text{Li}^+$  ion transport between electrodes. Separators are prone to mechanical damage from excessive dendrite growth leading to internal short circuits, which can occur also under thermal abuse conditions if their melting points are not high enough.<sup>[171]</sup> Besides few preventive approaches which can minimize the degradation of inactive components, curative actions were not proposed in the literature, although corrosion or extensive passivation of current collectors, stability of separators and conductive additives will be of special importance if we want to extend the cycle life of batteries.

#### 4. Challenges and Perspectives

The Battery 2030+ roadmap<sup>[12,13]</sup> aims to design and manufacture the battery of the future to answer the electrical energy storage societal challenge and contribute to sustainable development. One of the challenges for the sustainable battery design is integration of smart functionalities for their diagnosis by sensing<sup>[172]</sup> and treatment of degradation processes by self-healing functionalities. A summary of the various self-healing strategies explored so far for mitigating the degradations in LIBs and their practical limitations are provided in **Table 1**. The objectives are to increase the quality, reliability, cycle life, and safety of batteries and decrease the environmental footprint. Another challenge is the coupling sensing and self-healing functions.<sup>[173]</sup>

The complexity of different degradation processes requires a multilevel approach addressing several degradation processes with vectorization of the extrinsic self-healing additives/chemicals and intrinsic self-healing functionalities developed for specific battery chemistries. Many nonactive battery components like the separator or the binder could be designed as storage place for additives/chemicals. The sustainability of the batteries can be improved with the introduction of biomimetic materials, which should be developed together with self-healing functionalities. Finally, the extrinsic self-healing needs triggering acts which are based on continuous monitoring using sensors built in the battery cell. Above mentioned directions are described next.

##### 4.1. Vectorization: How to Apply This Strategy in Batteries

In the 1990s started the concept of nonviral gene therapy, with different lipids vectors designed to cure or limit human

**Table 1.** Summary of general self-healing solutions explored so far to mitigate the degradations in LIBs along with their practical limitations to overcome before commercialization.

Degradation pathway (battery part)	Self-healing solutions	Practical limitations
Electrode particle cracking (anode)	Self-healing binders	<ul style="list-style-type: none"> <li>High binder contents (&gt;10 wt%) used incomparable to current industrial conditions</li> <li>Low active material loading (&lt;1 mg cm<sup>-2</sup>)</li> <li>Binder application demonstrated only in half-cells</li> <li>Binding affinity majorly limited to silicon anodes</li> </ul>
	Liquid metal alloys	<ul style="list-style-type: none"> <li>Complicated interfacial chemistry with electrolyte due to coexistence of multiple cations</li> <li>Limited choices of low temperature fusible alloys</li> <li>Higher material cost including metallurgical processing</li> </ul>
Loss of electrical connectivity (anode, cathode)	Microcapsules encasing conductive additives	<ul style="list-style-type: none"> <li>External stimuli required for triggering the self-healing</li> <li>Poor control over the amount and release profile of additives</li> <li>Restoration of electrical contact using stimuli responsive microcapsules not yet realized inside LIBs</li> <li>Chemical and electrochemical stability of microcapsules under battery electrolyte conditions not fully studied</li> <li>Influence of used up microcapsule residues on battery performance unknown</li> </ul>
Electrolyte degradation & unstable SEI (electrolyte)	Self-healing polymer electrolytes (solid, gel, and composites)	<ul style="list-style-type: none"> <li>Still challenging to achieve solvent free electrolytes with room temperature ionic conductivity &gt;10<sup>-3</sup> S cm<sup>-1</sup></li> <li>Poor interfacial contact with high resistances</li> <li>Low Li-ion transference number</li> <li>Moderate electrochemical performance</li> <li>Electrochemical stability window not wide enough for high voltage cathodes</li> <li>High synthesis technique costs and complex processes</li> </ul>
Lithium plating/dendrite formation (anode)	Self-healing artificial SEIs	<ul style="list-style-type: none"> <li>Rare reports have tested the protective strategies up to the mark of practical standards</li> <li>Sustainability of protective coatings not always tested under high current density or high-capacity conditions</li> <li>Large Li excess often used (&gt;250 μm thick anodes) not feasible for high energy density</li> <li>Lean electrolyte conditions not maintained (typically used electrolyte-to-capacity ratio &gt; 40 μL mAh<sup>-1</sup>)</li> </ul>
Transition metal dissolution and gas evolution (cathode)	Smart scavenger separators and binders	<ul style="list-style-type: none"> <li>Scavenging functionalities are majorly explored for dissolved transition metal ions and HF</li> <li>Scavengers with strong affinities toward O<sub>2</sub> and reactive oxygen species are lacking</li> <li>Abuse tolerance and quality of functionalized separators/binders not tested in comparison with existing commercial ones</li> <li>Low-cost manufacturability and scalable fabrication techniques yet to be demonstrated</li> </ul>

diseases development.<sup>[174]</sup> The principle is to deliver with a vector (a vehicle function), a therapeutic gene in the cell's nucleus to treat the loss of function of the deficient mutated gene. The release of the molecule is activated either by an environmental stimulus inside the human body, such as the pH, chemical redox, temperature, or enzymatic activity. The stimulus can also be external, such as optical, electrical, or magnetic. New organic or inorganic vectors/particles have been designed with progress in material science and nanotechnology.<sup>[175]</sup> Vectors must have precise control of size, porosity, shape, mechanical properties, with the possibility of functional groups for the target cell or tissue without cytotoxicity. The drug release can be controlled in space and in time. The application domains are not limited to nonviral gene therapy. Vectors are also tools for cancer diagnostic and therapy using cancer cell imaging and optical properties (photoactivation)<sup>[176]</sup> or the release of antitumor agents to treat a tumor.<sup>[177]</sup> Other applications concern tissue engineering to repair tissues or an organ. A 3D scaffold can be designed to engineer complex tissues or deliver cells to the specific failure zone in the body to regenerate damaged tissues or organs,<sup>[178]</sup> but also for vaccines and nutrient delivery.

How the concept of self-healing could be applied to the energy storage using the vectorization of self-healing components and their controlled release to prevent multiple degradation processes in the battery cell. The challenge is to design self-healing functionalities that will target a specific degradation process (major degradation processes for Li-ion cells are described in Section 3). In an ideal case, self-healing functionalities should prevent cross-communication between electrodes, which can be achieved with active separators or binders. Separators or binders are also ideal places to act as a storage place for microcapsules filled with sacrificial salt or additive which can substitute lost lithium or dissolve resistive passive film, etc. Capsules could be sensitive to temperature, volume, or pressure increase. This physical behavior has been observed using an optical sensor (fiber Bragg grating, FBG) to monitor in operando the SEI formation.<sup>[179]</sup> The proof of concept has been recently shown using an activatable self-healing gel for electrode protection against mechanical stress.<sup>[180]</sup> It was done by encapsulating a conducting gel-like polymer with a polymer gel through a coaxial flow into a microfluidic set-up—the droplet sizes being precisely controlled. The microcapsules are then embedded into a sulfur cathode. A force of around 20 N is sufficient to break the microcapsules and release the self-healing material.

#### 4.2. Self-Healing Biosourced Materials for Batteries

Biosourced polymers can be divided into three major groups according to their chemical structure: a) proteins, b) polysaccharides, and c) polyesters. Polysaccharides, their derivatives and blends with other polymers offer enormous possibilities for modification to achieve properties desirable for batteries. They are typically extracted from renewable sources, such as lignin, cellulose, polylactide, and others.<sup>[181–184]</sup> This family of polymers is applied as a binder or it is copolymerized together with plasticizers into gel polymer electrolyte. Examples include a cross-linked polymer prepared from cellulose and epichlorohydrin or solid polymer electrolyte from pectin using ethylene

carbonate as a plasticizer.<sup>[181]</sup> Natural polymers offer substantial possibilities for modification and many of their properties can be adjusted. For instance, natural polymers can be modified to support battery self-healing functionalities, including controlled transport of cations, maintenance of electrode integrity and the possibility to capture degradation products by using scavenger or chelating molecules. Further exchange of OH groups with silane groups enables to tune the hydrophobic nature of cellulose, and with that its affinity to water. A fully silylated cellulose layer with suitable salts deposited on the metallic lithium can serve as an artificial SEI and it enables a much longer cycling life in the full cell configuration.<sup>[185]</sup>

The next large family of natural polymers is based on proteins. Nature has created soft, flexible and highly selective membranes, protecting the cell interior from its environment. Biological membranes are made of lipids, sterols, and proteins, which are selective and specific barriers to the transport of ions, molecules, or biomolecules in aqueous medium. Biological channels, composed either with the same protein in a multimetric form or with different proteins, are inserted into the membrane. These channels could be hardly used in nonaqueous mediums. Some of these protein channels may assist in the movement of ions by facilitating diffusion down their concentration gradient or active transport with energy against their gradient of concentration, acting as gates. Such channels govern the cationic concentration inside the cell, mimicking somewhat into a battery. The protein assembly controls the porosity of these channels, and their diameter is between few angstroms to few nanometers. These channels or protein nanopores have been successfully used as a single-molecule technique with an electrical detection to answer societal challenges for health and biotechnology. Several applications concern ultrafast sequencing of DNA/RNA,<sup>[186]</sup> biomarkers,<sup>[187,188]</sup> and pathogenic agents detection,<sup>[189]</sup> the high-resolution size discrimination of biomolecules<sup>[190,191]</sup> the twenty amino acids identification and chemical modifications detection paving the way to protein sequencing.<sup>[192]</sup> Some of the biological pores possess adequate stability in the harsh environment of contemporary batteries and can be exploited as building units for a highly selective separator.<sup>[193]</sup> Lysin, which forms a mushroom-shaped pore, can be used as a model biological pore. The laboratory-isolated pore exhibits remarkable temperature and chemical stability. The inner diameter of the channel measures up to 2.5 nm,<sup>[194,195]</sup> which in addition to its negatively charged surface results in the pore being preferentially permeable to cations, making it an interesting candidate for use in ion-selective membranes. Pores can be modified by changing the amino acid sequence, which determines the shape and function of the protein. Modification of proteins can be performed in optimized bacteria cells, into which a gene of interest is introduced via standard molecular techniques. The resulting protein can be readily isolated via many biotechnological techniques.<sup>[196]</sup> Since bacteria are easy to handle and cheap to grow, these biofactories allow for effective engineering exploration and large-scale production of proteins needed.

One challenge will consist in mimicking biological membranes in terms of barrier selectivity to improve battery aging. Another one will be to follow, inside the battery, the stability of the electrolyte, with a highly sensitive and selective sensor

on the biomimetic separator using an electrical detection. The smart biomimetic separator design will prevent parasite species diffusion during redox shuttles and/or metal dissolution diffusion toward the Li anode and allow lithium transport across the membrane in the battery cell. It could also be used to sense the real-time formation of redox species electrically. Several functionalized separators as trapping sieves used up to now have been described in the interlayer part but cannot yet recreate the properties of biological membranes. One of the most challenging strategies will be to design a hybrid membrane that consists of a polymeric<sup>[197]</sup> or solid-state membrane with protein nanopores.<sup>[198,199]</sup> A possible solution would be the use of protein pores and block copolymer to form lamellar multilayered membranes on the top of the support (i.e., separator).<sup>[200]</sup> Two key milestones will be to engineer a recombinant protein nanopore highly resistant to organic solvent than the selectivity could be controlled as well as the sensitivity. By adjusting the membrane's pore density we, could optimized battery performance in terms of capacity and Coulombic efficiency, although kinetic issues concerning the transport still need to be checked.

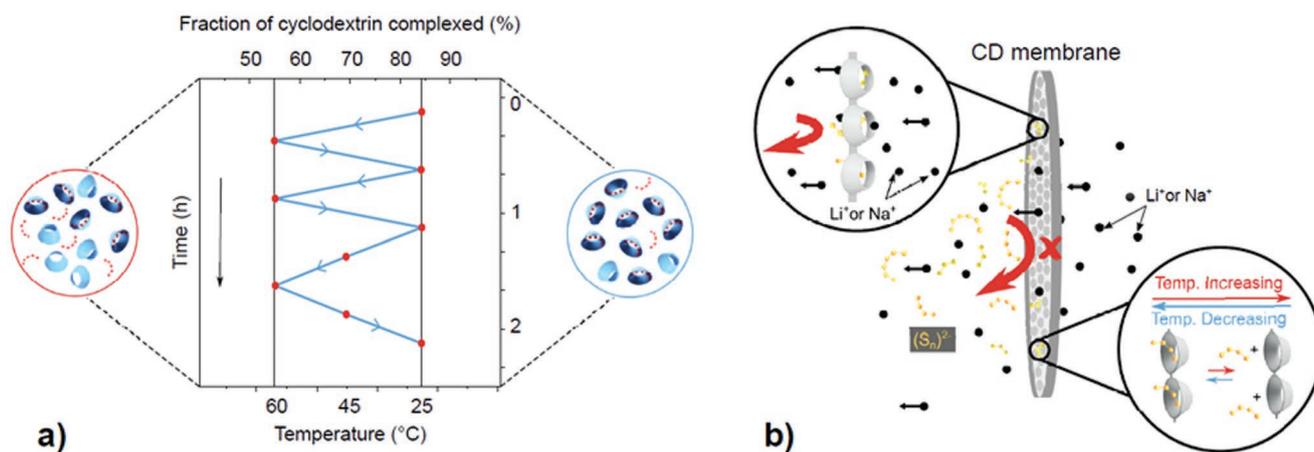
Another strategy is the functionalization of macrocycle cages, such as cyclodextrins or calixarene, on the PET membrane separators or similar supports. This strategy could improve the capture of parasite redox species. These molecules turn out to be very promising because of their high solubility, their lipophilic inner cavities, and hydrophilic outer surfaces. Furthermore, they are bioavailable, and they have a specific recognition ability toward small guest molecules/cations, enabling them to form inclusion complexes. They have been mainly used for cyclodextrins in pharmaceutical or soil decontamination.<sup>[201,202]</sup> Recently, host-guest interactions between different chain-length polysulfides and cyclodextrins have been investigated.<sup>[203]</sup> Additionally, they show that a temperature stimulus could control the polysulfide/cyclodextrin complex equilibrium. They show a fast kinetic over a narrow temperature range and in a neatly reversible way. This stimuli temperature response on the capture and release of polysulfides by cage molecules could offer opportunities in the future. For example, it would be interesting to synthesise stimuli-responsive cyclodextrin materials to develop novel regenerative separators (see **Figure 8**). In

this approach, the diffusion of polysulfides species toward the Li anode would be prevented while letting them participate in the redox process by thermal regeneration of the membrane.

#### 4.3. Monitoring, Sensing, and Triggering

The best option to monitor the success (or failure) of a given self-healing functionalities are electrochemical tests. Classical electrochemical tests provide estimation of improved QRLS, while understating of the fundamental reasons of improved QRLS require the use of advanced analytical tools or sensors. The envisioned self-healing functionalities are predominantly active at the interface separating the electrode from the electrolyte. As shown in Section 3, the identification of degradation mechanism represents a huge technical challenge as interfaces are notoriously difficult to access, particularly under operating conditions, mainly because of their nanometric multicomponent structure, complex evolution kinetics (depending intimately on the composition of the electrode and electrolyte), and their extreme sensitivity. The development of advanced characterization techniques is needed in several different directions.

- Multiscale characterization: Side-reactions as well as self-healing reactions occur and affect battery performance at multiple sites/areas on different length scales. The specific actions of self-healing components and agents need to be gauged at several possible sites to ensure self-healing action at the intended site and scale while limiting the effects elsewhere in the battery.
- Multicomponent characterization: Both the desired reaction products and the undesired side-products are typically found in solid, liquid, and gaseous forms. Experimental techniques are generally limited to probing a specific state/phase of matter and a range of complementary techniques is necessary.
- Trace element (or process) detection: Ageing and capacity loss occur at a very small magnitude (<300 ppm in a commercial Li-ion cell) if the extent of side-reactions is normalized to all reactions in the cell.
- Multitude of timescales: Both the ageing as well as the remedying self-healing process occur in the running cell on timescales



**Figure 8.** a) Temperature-sensitive host-guest interaction between cyclodextrins and polysulfides and b) conceptual illustration of a thermoresponsive cyclodextrin material as an efficient regenerative Li-S battery separator. Reproduced with permission.<sup>[203]</sup> Copyright 2020, Nature.

of single chemical reactions (fs) up to a year. Suitable characterization techniques may need operando probing capturing fast reaction dynamics (including intermediary reaction steps).

Thus, there is a need to develop appropriate tools to diagnose battery failures either at the laboratory scale or as part of a system in real work conditions. This will call for different analytical techniques. Researchers have been extremely successful in the development of sophisticated diagnostic tools (such as X-ray<sup>[204]</sup> and Neutron diffraction<sup>[205]</sup> or radiography,<sup>[206]</sup> nuclear magnetic resonance,<sup>[207]</sup> electron paramagnetic resonance<sup>[208]</sup> or transmission electron microscopy,<sup>[209]</sup> which can ideally operate in situ as the battery is cycled, hence giving insights of the various materials function cooperatively. Although quite spectacular, these analytical advances have relied on specific equipment and cells that cannot be transferred for analyzing commercial cells except combined in situ XRD and Neutron tomography studies performed on commercial 18650 cells at large-scale facilities. Such a battery diagnosis at the system level under specific working conditions is truly missing. It results that battery packs are often conservatively overengineered to minimize the risk of premature or catastrophic failure on the expense of sacrificing cell performances.

Although battery monitoring in real field conditions had been less prolific, it had witnessed several interesting developments relying for many decades on the use of hydrometers or even optical prisms to determine the state of charge of Pb-acid batteries. Other sensors like thermocouples, thermistors, pressure gauges, acoustic sensors positioned mainly on the cell housing rather than on its interior have also been widely used. Besides, AC impedance spectroscopy is a well-established passive characterization technique that has been used in many battery systems including Pb-acid, Ni–Cd, Ni–MH, and Li-ion. It enables to study a global evolution of the cell impedance, associated to the contact and charge transfer resistances at the electrode–electrolyte interface that can vary over time and/or during cell operation. Thus, monitoring the impedance growth on a battery upon cycling and ageing is of great help to follow its state of health. Whatever, all these sensing techniques have led to limitations in designing BMS systems stemming from ill-defined parameters. Today's disruptive innovation to outplay such a limitation adopts injecting smart functionalities into the battery mainly through the development and integration of ingenious sensing technologies that enable smooth information transfer in and out of the cell. Smart sensors with spatially resolved monitoring (at various locations/components within the cell) are obligatory besides the prerequisites of high sensitivity and resolution changes in multiple parameters, such as chemical composition, strain, temperature, and pressure.

Such demands have triggered increased interest for innovative operando and nondestructive approaches with the ingress of optical sensing to the field of batteries. Specifically, pertinent to batteries, optical fibers offer several positives such as minimal invasiveness due to their tiny dimensions ( $\varnothing < 200 \mu\text{m}$ ), corrosion resistance while being an electronic insulator as well as immunity to electromagnetic waves. Among the various optical sensors, fiber Bragg grating sensors are widely used in various application domains. Since the basic FBG operation involves simple correlations between the wavelength of the

reflected optical signal with local temperature ( $T$ ), pressure ( $P$ ), and strain ( $\epsilon$ ), they were pioneered in the battery community by Pinto et al.<sup>[210]</sup> Additionally, correlations were also established between these parameters and battery events such as short-circuit, state of charge, and state of health. Recently, the feasibility to estimate the SEI heat of formation as an additional metric has been demonstrated by simple mathematical conversion of thermal events into heat, thereby throwing light into the cascade reactions associated with the SEI formation during charging process. Besides, the development of optical microcalorimetry has enabled access to additional thermodynamic metrics such as entropy and enthalpy that are kings to monitor battery state of health. However, FBGs remain largely unsuccessful particularly in terms of determining any electrolyte composition changes or tracing the nature of parasitic organic species underlying the side reactions.<sup>[179]</sup>

These limitations have recently been removed by the development of versatile fiber optic sensors based on tilted fiber Bragg grating that exploited evanescent waves. Such sensors facilitate the tracing of both Li inventory and electrolyte concentration via monitoring the refractive index variation of the surrounding electrolyte medium, which is a function of the salt concentration. Besides, it enables for operando monitoring battery electrolyte's chemistry and turbidity, hence enabling to decipher the reaction pathways pertaining to battery degradation. Altogether this type of sensing offers exciting opportunities for a “lab-on-fiber” platform to collect all the observables in a single fiber. Based on the same principle of evanescent waves, IR optical sensing is getting momentum to the stage it is nearly possible to identify the nature and composition of chemical species in electrolytes. Direct contact between the fiber core and electrode has intensively promoted plasmonic detection via the deposition of a gold nanometric layer on either a tilted Bragg grating or on unshathed fibers to trace Li inventory into electrolyte or Li content into the active electrode material. Importantly, it is worth further mentioning that compared to silica, polymeric fibers offer extended advantages for pressure detection and pH sensing albeit more adapted to aqueous batteries.

Altogether, optical sensing offering humongous opportunities to follow novel metrics (inside cell temperature, heat, Li contents, materials stresses, cell pressure build-up, SEI growth, etc.) hence providing the necessary diagnostic to trigger on the demand the self-healing functionalities injected into the batteries. However, for the development of smart batteries based on sensing and self-healing functionalities that will enhance, their QRLS, we need to master the communication of the sensors with BMS systems. Thus, injecting such a colossal amount of information in advanced battery management systems is another indispensable aspect to consider that will benefit from tremendous progress in the field of machine learning and artificial intelligence.

## 5. Conclusion

Li-ion battery cells are prone to different degradation processes that can be divided into two large categories. Mechanical degradation is related mainly to the mechanical loss of ionic or electronic contacts between active particles and additives

(carbon additives and current collectors). Certain self-healing functionalities have been developed mainly addressing problems related to the silicon anode, while pulverization of the cathode materials has been addressed mainly through the preventive approaches. Another important part of degradation processes is related to chemical and electrochemical degradation processes. Among different processes, the most important are electrolyte decomposition and formation of passive films, then lithium plating/dendrite formation, transition metal dissolution, and gas evolution and degradation of inactive components. This shows the complexity of degradation processes which are very often interconnected. For instance, mechanical degradation of some cathode materials is followed by transition metal dissolution and the potential release of gasses. Dissolved transition metals migrate to an anode where they are reduced. That leads to changes in the passive film structure and the need for additional passivation. Such a complex mechanism requires a vectorization of several intrinsic or extrinsic self-healing functionalities which are triggered based on the external stimulus. Even though some self-healing functionalities have been developed, the field is still in the infancy period. A new approach where inactive components (separators, binders, carbon additives) are replaced with more sustainable and environmentally available materials needs to be developed and coupled in the battery cell with sensing. Such a smart battery cell when coupled with an adapted battery management system will have high quality, improved safety, high reliability, and long cycle life. Thus, an exciting research at the crossover of many disciplines (materials/surface science, inorganic/organic/polymer chemistry, biology, etc.) is waiting for us. Success will depend upon our efficacy to enthusiastically bring together talented scientists from all of these disciplines.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

degradation, Li-ion batteries, self-healing functionalities, triggering, vectorization

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