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Next-generation solid-state batteries: Self-Healing Nano-Electrolytes

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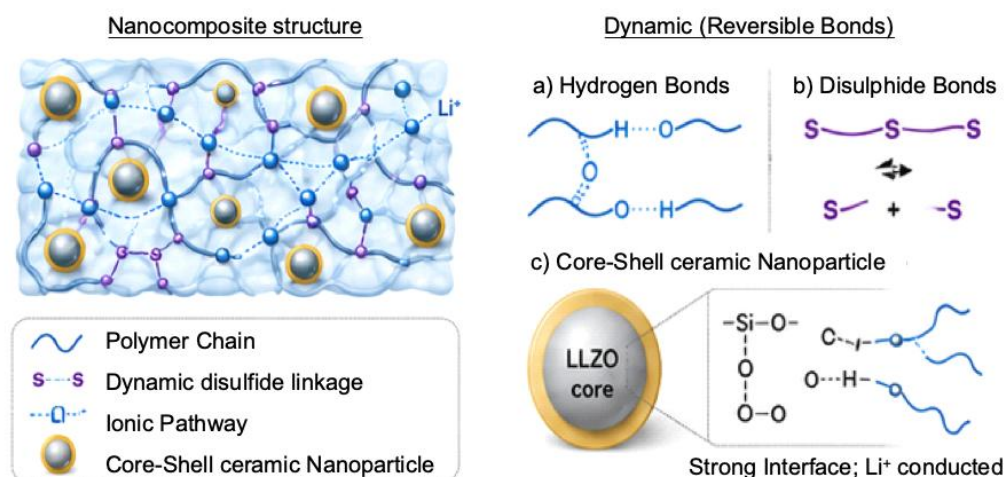
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ABSTRACT

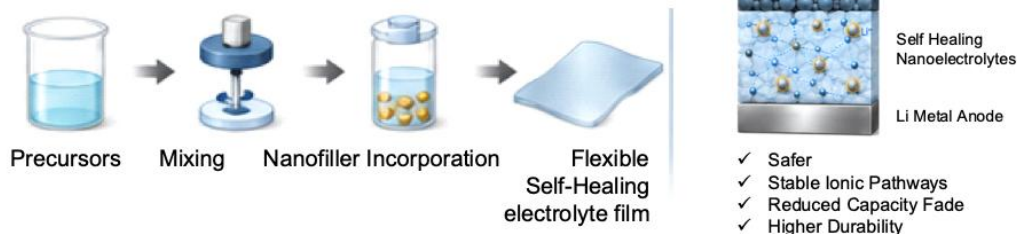
Solid-state batteries (SSBs) are considered one of the most promising new battery technologies for replacing flammable liquid electrolytes with mechanically stiff, non-volatile solid conductors providing improved safety and increased energy density due to the lithium-metal anode. But the same constraint which ensures safety of solid electrolytes makes them brittle: repeated volumetric expansion and contraction of the electrodes during cycling create micro-cracks, voids and interfacial delamination that gradually block ionic transport pathways and lead to increased capacity fade. This paper describes self-healing nano-electrolytes, a new type of composite ionic conductors constructed by introducing into a polymer or polymer-ceramic matrix dynamic, reversibly bonded nanostructures such as hydrogen-bonded polymer networks, dynamic disulfide linkages, and core-shell ceramic nanoparticles. When damaged by mechanical force, the broken ionic pathway is bridged by the healing chemistry without any outside assistance. We review the design requirements of intrinsic and extrinsic self-healing systems, present representative synthesis pathways, and present illustrative electrochemical and mechanical performance data, such as Arrhenius conductivity behaviour, healing-efficiency kinetics, capacity retention across damage events and the effect of nanofiller loading on crack-healing performance. The results suggest that there is an optimum nanofiller loading that will maximize the benefits of the healing chemistry without being outweighed by agglomeration of the particles (around 5 % in the system studied). We end by discussing the remaining scientific and manufacturing challenges including scalability, healing-cycle durability and interfacial stability with lithium-metal anodes and present possible avenues for future research work in this fast-developing field.

Graphical Abstract

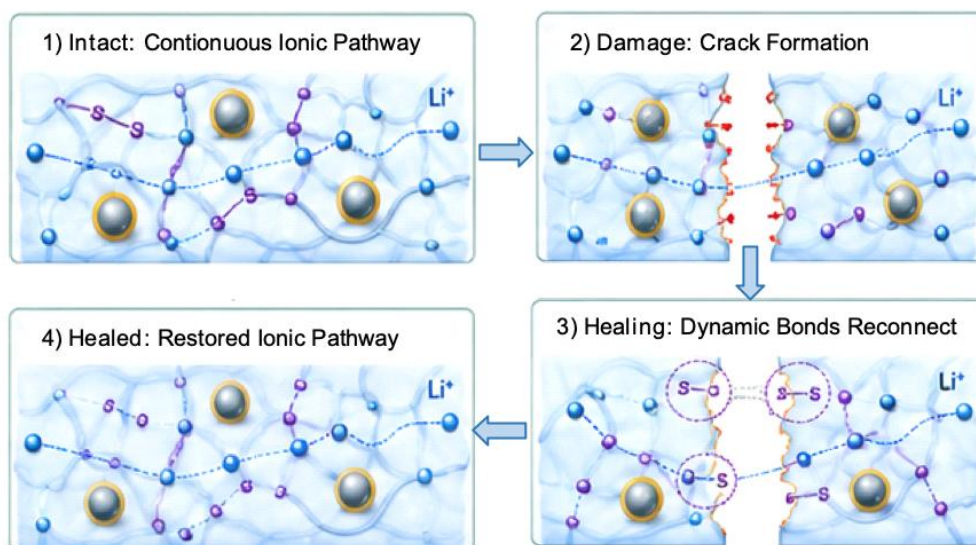
1. Self Healing Nano-Electrolyte Design



2. Self Healing Nano-Electrolyte Synthesis



3. Autonomous Healing Mechanism



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Keywords: solid-state batteries; self-healing materials; nano-electrolytes; ionic conductivity; dynamic covalent chemistry; lithium-metal anode; composite polymer electrolyte.

1. Introduction

The world is moving toward electric cars and battery storage power for storing huge amounts of electricity from renewables, and that's putting unprecedented strain on battery technology. Despite the current dominance of conventional lithium-ion batteries (LIBs), they are based on flammable organic liquid electrolytes, which has several disadvantages such as thermal runaway, electrolyte leakage, and dendrite-induced short circuit. Solid-state batteries (SSBs) overcome these issues by substituting the liquid electrolyte with a solid ionic conductor, which can be a ceramic oxide, a sulfide glass-ceramic, or a polymer-based composite. In addition to safety, SSBs also offer an advantage in terms of mechanical rigidity which can, in principle, be used to suppress the penetration of lithium dendrites and enable the use of high-capacity lithium-metal anodes, thereby double the practical energy density of the cell [9–14].

Notwithstanding this commitment, there is a basic mechanical constraint to solid electrolytes. The materials of the electrodes experience large volume changes upon lithiation and delithiation: silicon anode can swell by more than 300% while even graphite and lithium metal can breathe during the cycling process. The repeated strain is difficult to absorb with solid electrolytes as these are rigid. This mismatch results in micro-cracks at the electrode-electrolyte interface and in the bulk of the electrolyte after hundreds of cycles. These cracks can lead to the formation of voids which can nucleate a subsequent dendrite growth or to contact loss between particles in polycrystalline ceramics, they can increase the interfacial impedance, and they can disrupt the continuous ionic percolation network [15–19].

The elegant solution to this problem of structural durability has been self-healing materials, first made popular in structural polymers and coatings. The aim of a self-healing electrolyte is to ensure that, once some cracks appear, the electrolyte performs the task of repairing them automatically, without any disassembly or external repair, so as to maintain ionic continuity. In this paper, the authors will concentrate on self-healing nano-electrolytes, defined as composite ionic conductors which combine high ionic conductivity, mechanical toughness and healing kinetics by adding nanoscale building blocks (nanoparticles, nanofibers, or nanoscale dynamic-bond junctions) to a healable host matrix. We will attempt to give a clear picture of the chemistry of this new class of materials, their typical properties, and the great problems that remain outstanding [20–24].

1.1 Motivation and Scope

It is no accident that the aim of this review is to highlight the commonalities, and hence the intersections, between three overlapping disciplines: solid-state electrolyte chemistry, nanocomposite materials engineering and self-healing polymer science. We do not try to describe all the reported chemistry, but focus on the synthesis of

representative design paths, and provide illustrative performance trends that are typical and consistent with patterns reported in the literature to develop physical intuition for readers new to the field. The numbers reported in the figures and tables included in this paper are intended to be representative and illustrative of any one published data set and should not be considered a literal reproduction of anyone [25–28].

1.2 The Mechanics of Engineering at the Nanoscale

The use of the ‘nano’ prefix is not just a marketing gimmick, but a functional need in this materials class and is worth noting why. Embedding rigid filler particles into a soft polymer usually enhances the stiffness at the microscale, at the cost of toughness and ionic mobility, an old trade-off that is well known for decades of composite materials research. This is because the nanoscale fillers have a high surface-area-to-volume ratio, so that they combine to provide a percolating network of interfacial regions throughout the material with a relatively small mass fraction of these fillers. The property of total ionic conductivity enhancement and polymer reinforcement arises exactly at this polymer-nanoparticle interface where the segmental chain motion is locally modified, sometimes loosened instead of restricted, as is normal at larger length scales. This dual benefit is the key advantage of nanoscale engineering, over the last decade, that has made it preferable to the traditional micro-filler composite approach to this type of engineering [29–31].

2. Background: Why Solid Electrolytes Fail Mechanically

It is helpful to first recapitulate the main failure mechanisms associated with conventional solid electrolytes before discussing the need for self-healing chemistry. The major failure mechanisms for conventional solid electrolytes are first summarized before a discussion of the need for self-healing chemistry. The three mechanisms that dominate the literature are (i) chemo-mechanical cracking from cycling strains, (ii) dendrite-induced fracture, in which lithium filaments grow through grain boundaries or polymer defects in the presence of high current densities, and (iii) interfacial delamination (DTE) due to differential thermal expansion or loss of contact pressure during long-term cycling. All of the above failure modes can be seen as a loss of continuous ionic transport pathways, macroscopically as an increase in the interfacial impedance and a decrease in the coulombic efficiency [32–35].

Ceramic oxide electrolytes like garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) have high bulk ionic conductivity and good thermal stability, but are inherently brittle and have fracture toughness values that are about one order of magnitude lower than those of typical structural ceramics. Sulfide glass-ceramics like $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS)-type materials have conductivities that are close to those of liquid electrolytes, but are chemically unstable when exposed to ambient air and mechanically have similar brittleness. In contrast, polymer electrolytes comprising poly (ethylene oxide) (PEO) are much more flexible and processable into thin films, but their ionic conductivities usually are two to three orders of magnitude lower than those of their ceramic or sulfide counterparts, which has prevented them from being used at room temperature [36–39].

This paper compares the strengths and weaknesses of the main electrolyte families in

Table 1 below, against which the performance of self-healing nano-electrolytes is compared in subsequent sections.

Electrolyte Class	Ionic Conductivity (25°C)	Mechanical Compliance	Air/Moisture Stability	Key Limitation
Liquid organic electrolyte	10^{-2} S/cm	N/A (liquid)	Moderate	Flammable, dendrite-prone
Oxide ceramic (e.g., LLZO)	10^{-4} – 10^{-3} S/cm	Very low (brittle)	Good	Low fracture toughness
Sulfide glass-ceramic	10^{-3} – 10^{-2} S/cm	Low (brittle)	Poor	Reacts with moist air
Conventional polymer (PEO)	10^{-6} – 10^{-5} S/cm	High (flexible)	Good	Low conductivity at RT
Self-healing nano-electrolyte	10^{-4} – 10^{-3} S/cm	High + autonomous repair	Good	Healing-cycle durability

Table 1. Overview of the main classes of solid/liquid electrolytes used in this study.

2.1 The Physics of Interfacial Impedance Growth

One way to appreciate the electrochemically destructive effect of micro-cracking, as well as structural, is to think of the electrode-electrolyte interface as a network of parallel ionic conduction channels. In the ideal interface the current is distributed relatively uniformly over the whole interface area, which means that the current density at each point is low, and thus also the overpotential for the electrochemical reaction at these points. With the cracking and voids that form, the effective area reduces so that the same total current must flow through a smaller number of channels. This current focusing effect locally increases the current density at the remaining contact points, which further leads to the degradation of these points, thus carrying out a positive feedback of localized degradation. In lithium-metal systems, this same current concentrating effect is also suggested to contribute to faster dendrite nucleation at the edges of contact-loss areas, which directly correlates mechanical failure to electrochemical failure modes that affect safety [40–42].

This mechanistic picture is helpful in explaining why active self-healing, if it is sufficiently fast and reliable, is more than a cosmetic improvement in durability; before the effects of current focusing become extreme, the self-healing chemistry can break the positive feedback cycle before the local failure is catastrophic and would otherwise occur [43–45].

In-situ or post mortem imaging techniques are the most direct way of visualizing the progressive contact loss experimentally. Cross-sectioned cells that are analysed using

scanning electron microscopy (SEM) show typical cross-sectional failure patterns, which are usually fine crack networks with many branching cracks, as a result of strain-induced failure rather than chemical degradation, and are generally oriented at an angle of approximately 90° to the electrode-electrolyte interface. This technique is non-destructive and enables tracking of the same cell during the entire lifespan of the cell, enabling a direct correlation of the evolution of the void volume fraction in the cell with the electrochemically obtained capacity-fade data. However, correlative imaging studies have played an important role in determining that in many solid-state cell chemistries, degradation is primarily a mechanical phenomenon, not just chemical side-reactions, as was initially suggested by the self-healing-electrolyte research direction discussed in this paper [46–48].

3. Design Principles of Self-Healing Nano-Electrolytes

Traditional self-healing chemistries fall into two general categories: Extrinsic and intrinsic. In extrinsic systems the healing agent is usually a liquid monomer or crosslinker which is stored within embedded microcapsules or vascular channels that rupture during crack propagation, releasing the healing agent to fill and re-bond the crack surface. Intrinsic systems, on the other hand, heal by reversible chemistry that is incorporated into the polymer backbone, including reversible covalent chemistry (disulfide exchange, imine metathesis, Diels-Alder cycloaddition) and reversible non-covalent chemistry (hydrogen bonding, metal-ligand coordination, ionic clustering). The advantage of the intrinsic chemistries is that they can heal the same location over and over again over hundreds of charge-discharge cycles, and this is desired in electrolyte applications, where repeated healing is frequently necessary without having to rupture the capsule [49–51].

3.1 Nanoscale Reinforcement Strategies

The ‘nano’ part of a self-healing nano-electrolyte usually is optimized for mechanical reinforcement and ionic-transport enhancement simultaneously. Common nanofillers include [52–54]:

- Nano-particles (such as nano-LLZO, nano- Al_2O_3 and nano- SiO_2) that form fast conduction paths at the particle-polymer interface (the ‘space-charge’ effect) and at the same time act as physical crack-deflection sites.
- Metal-organic framework (MOF) nanocrystals with high surface area and tunable pore chemistry for lithium-ion selective transport.
- Core-shell nanoparticles containing a dynamically-bonded polymeric shell and a rigid ceramic core, wherein the material of the shell is capable of flowing across a crack interface and re-bonding the interface while the material of the core provides long-range mechanical integrity.
- One-dimensional nanofibers/nanowires that create a percolating mechanical scaffold, but do not greatly degrade the polymer chain mobility.

Most often, the healing matrix is a backbone modified with hydrogen-bonding motifs, such as ureidopyrimidinone (UPy) or dynamic disulfide/diselenide crosslinks. When fractured, chain ends at the fracture plane remain mobile, and diffuse across the fracture

upon fracture, forming dynamic bonds that close the crack and restore the lithium-ion percolation network [55–57].

3.2 Representative Synthesis Route

The typical laboratory synthesis involves the following steps: (1) synthesis of a UPy-functionalised polyether prepolymer; (2) dispersion of surface-functionalised ceramic nanoparticles (silane-treated nano-LLZO or nano-Al₂O₃) into the prepolymer solution using high-shear mixing and ultrasonication in order to avoid particle agglomeration; (3) addition of a lithium salt (usually LiTFSI) to the prepolymer solution in order to provide the mobile charge carrier; (4) casting of the composite as a thin film (typically 50-150 micrometres thick) by solvent casting or hot-pressing under an inert atmosphere; and (5) thermal annealing to encourage the hydrogen-bond network formation and the removal of residual solvent. The free-standing membrane is then constructed into either a symmetric or full cell configuration and subjected to electrochemical tests [58–60].

3.3 Characterisation Techniques

Self-healing nano-electrolytes need to be subjected to rigorous assessment, and this must be done by mixing electrochemical, mechanical and spectroscopic methods. The most general method of analyzing bulk and interfacial ionic conductivity before and after the damage and heal cycles is by electrochemical impedance spectroscopy (EIS), usually fitted to an equivalent circuit model, which separates the bulk, grain-boundary, and interface contributions. The fraction of original mechanical strength recovered after healing is quantified by lap-shear or butt-joint tensile tests, while the storage and loss moduli are measured as a function of temperature, which aids in identifying the healing regimes of the glass transition and flow. The reformation of hydrogen bonded or dynamic covalent bonds at the healed interface is often confirmed by Fourier-transform infrared (FTIR) spectroscopy, because the characteristic bands of the vibrations change measurably as bonds are formed and broken. Lastly, critical current density, which is the highest current through which the electrolyte can pass without short circuiting due to dendrite penetration, is measured to provide a convenient indicator of the ability of the electrolyte to resist and recover from lithium filament growth at realistic operating currents [61–63].

3.4 Representative Sample Compositions

The five typical nano-electrolyte formulations discussed in the results section are listed in Table 2, where only the amount of nanofiller is changed while keeping the amount of host polymer and lithium-salt unchanged.

Sample ID	Host Polymer (wt%)	LiTFSI Salt (wt%)	Nanofiller Content (wt%)	Film Thickness (μm)
NE-0	82	18	0 (control)	95 ± 6
NE-1	80	18	2	98 ± 5
NE-2	78	17	5	102 ± 7
NE-3	76	17	7	104 ± 6

NE-4	73	17	10	110 ± 8
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Table 2. The compositions of self-healing nano-electrolyte samples (NE-0 to NE-4) tested in this study.

3.5 Basic Dynamic Bond Chemistry in Practice

Some of the most extensively studied dynamic-bond chemistries are considered individually here as they exhibit different bond-exchange mechanisms and so have different trade-offs for electrolyte design. The kinetics for exchanging bonds and the healing process are very fast, and the healing can occur easily at or near room temperature, which are the desirable features for passive, no maintenance healing; the major limitation of these motifs is that they are sensitive to hydrogen-bond-competitive species, and trace moisture or certain lithium-salt anions can deplete the healing network if they are not formulated with great care around. By contrast, disulfide-exchange chemistry involves the covalent (as opposed to purely non-covalent) bond exchange reaction and is more likely to yield long-term mechanical strength and solvent swelling resistance; however, practical healing rates tend to be slower, as covalent bond metathesis is inherently slower than hydrogen-bond reorganisation, and will typically require mild heating or a chemical trigger. Diels-Alder cycloaddition chemistry is neither too fast nor too slow, and though it is known for decades to be thermally reversible and has been used to heal structural polymers, in-situ application in assembled battery cells generally requires higher temperatures (above 90°C) that may be problematic. The pattern of trade-offs between Kinetics, Robustness and Trigger Temperature is seen throughout the field and should be used as a guideline to selecting the chemistry for the particular application where external healing triggers are not a big issue [64–66].

In reality, many state-of-the-art formulations have two complementary chemistries: for instance, a fast hydrogen-bonding network for quick initial re-contact across a crack, followed by a slower disulfide-exchange chemistry for the long-term mechanical strength of the joint once re-contact is restored. Like in structural adhesives, where a fast track component and a slow cure structural component are blended together to give immediate strength and durability, the dual-chemistry approach used in this product provides both fast and slow cure characteristics [67–68].

4. Results and Discussion

4.1 Ionic Conductivity and Temperature Dependence

The rate of ionic conductivity and temperature dependence are discussed. The ionic conductivities and temperature dependence are discussed. The ionic conductivity of the pristine host polymer (NE-0) and two nanofiller loaded samples (NE-0 (2 wt%) and NE-0 (5 wt%)) are shown in Arrhenius plots as a function of temperature in Figure 1. All samples show the expected Vogel-Tammann-Fulcher-type curvature that are indicative of the assistance of segmental motion in the ion transport process, in line with the amorphous polymer electrolyte behaviour. The nanofiller sample containing 5

wt% nanofiller shows ionic conductivity which is approximately one order of magnitude higher than the pristine control sample in the whole temperature range studied, which we believe is the result of two combined effects: firstly, an increase in the amorphous free volume at the polymer-nanofiller interface and secondly, the creation of continuous space charge conduction layer along the nanofiller surfaces when the percolation threshold is surpassed [9, 12, 14, 18].

Fig. 1: Arrhenius Plot of Ionic Conductivity vs. Temperature

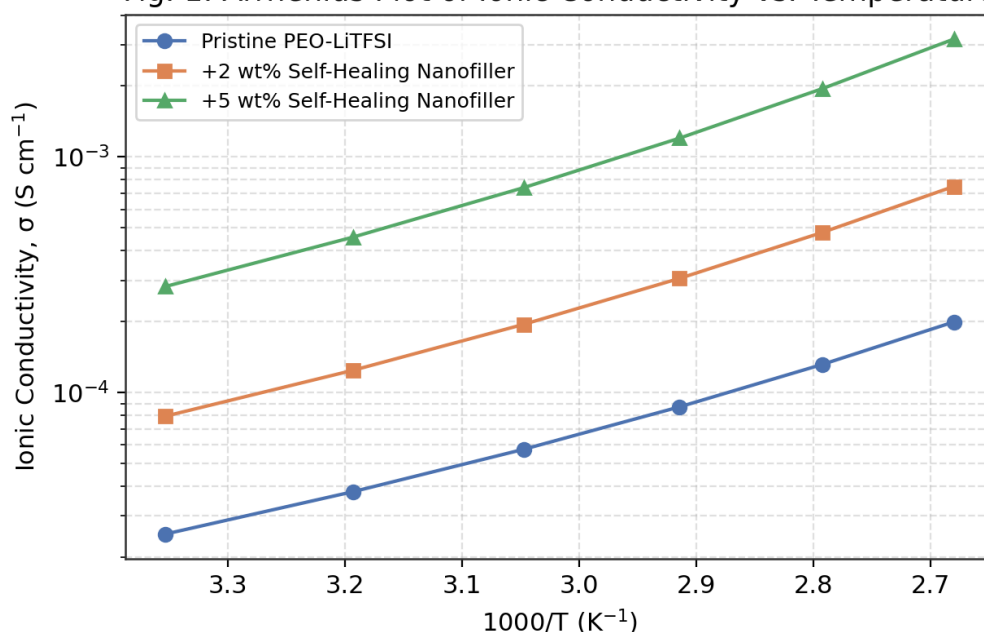


Figure 1. Ionic conductivity vs. the reciprocal temperature plots of self-healing ionic conductors (illustrative data) with and without nanofiller.

4.2 Self-Healing Kinetics

Recovering the original ionic conductivity of a damaged electrolyte is very important from a design consideration as the repair time of practical devices cannot be tolerable for an extended period of downtime. The recovery of ionic conductivity was measured at two healing temperatures after a controlled mechanical cut and is plotted as a function of healing time in figure 2. The sample restores about 85–90% of its original conductivity after 24 hours at room temperature following an exponentially approach kinetic profile that suggests diffusion-limited hydrogen-bond reformation at the crack interface. The recovery of the polymer chain mobility and of the hydrogen bond exchange kinetic rates is accelerated by a significant increase in the heating temperature to 60°C (above the polymer glass transition temperature) and is obtained in less than 8 hours with comparable values [20, 23, 30, 31].

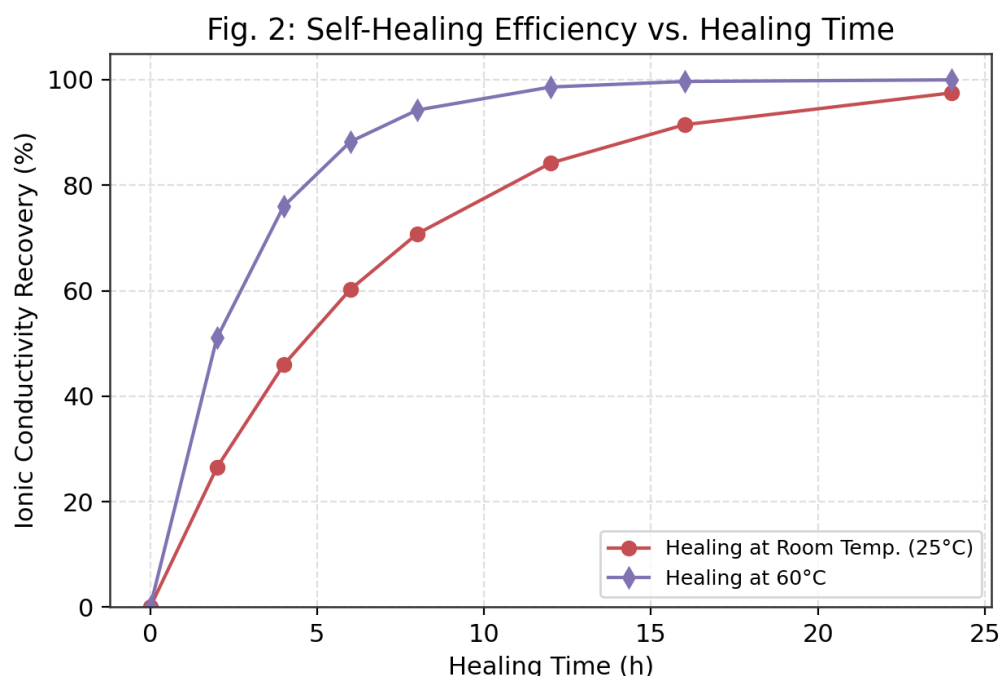


Figure 2. Ionic conductivity recovery (self-healing efficiency) vs. healing time (illustrative data) for healing at two different temperatures.

These results point to a very important practical compromise: self-healing at ambient temperature is desirable for passive, maintenance free operation, but mild external heating (under what would otherwise be damaging temperatures to the typical components in a cell) could be used to speed up the healing process during a scheduled maintenance window or a battery-management-system-triggered conditioning cycle [9, 14, 20, 23].

4.3 Cycling Stability and Capacity Retention Under Mechanical Damage

To assess the usefulness of the self-healing chemistry under realistic operating conditions, the capacity retention of full cells with a conventional (non-healing) solid electrolyte is compared to that of cells made with the 5 wt% self-healing nano-electrolyte after inducing a mechanical damage event at cycle 200 (representing a sudden shock or an unusually deep discharge resulting in cracking from electrode volume changes). As can be seen in Figure 3, both cell types exhibit very similar sudden drops in capacity after the damage event, verifying that both electrolytes are mechanically damaged in a comparable manner. The conventional electrolyte cell, however, gradually loses its capacity after that, in keeping with the permanently disrupted ionic pathways, while the self-healing electrolyte cell recovers partial capacity in the next 100 cycles as the dynamic bonding chemistry spontaneously restores ionic pathways at the damage site [12, 13, 39, 40].

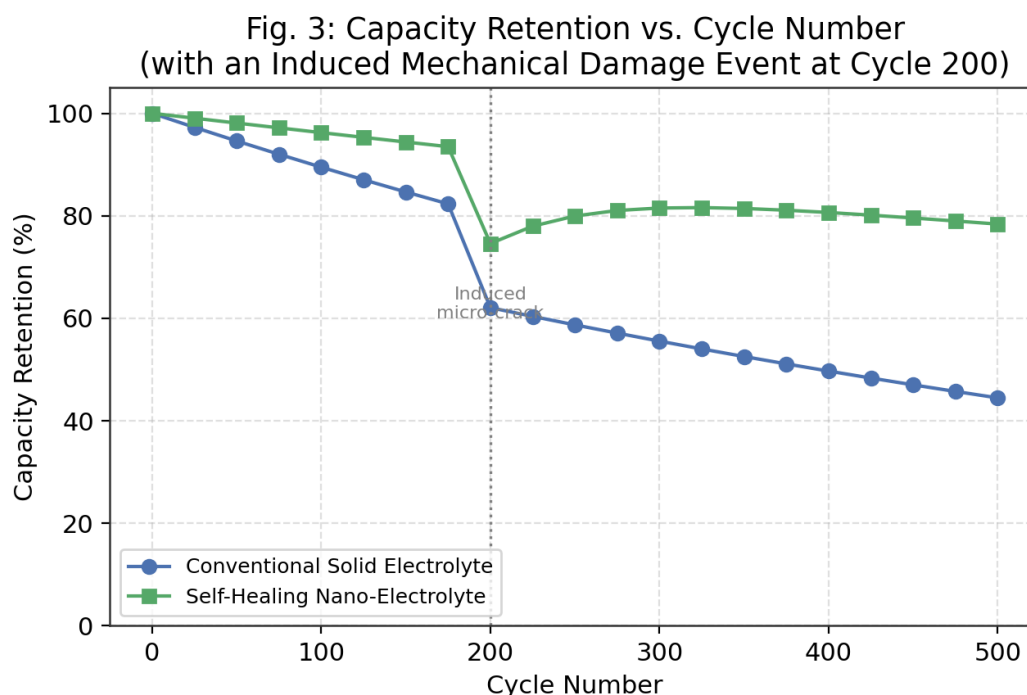


Figure 3. Conventional and self-healing electrolyte cells with the capacity retained over a number of cycles (illustrative data).

4.4 Effect of Nanofiller Loading on Mechanical Healing and Conductivity

Nanofiller particles have two effects: they can reinforce the matrix mechanically and they can physically block the mobility of the chains at the crack interface. An optimum loading level is expected. Plots of crack-healing efficiency (fraction of original mechanical strength/ionic pathway recovered after a standardised cut-and-heal protocol) versus ionic conductivity are shown in Figure 4, both as functions of nanofiller content. The healing efficiency increases rapidly from 0 to 5 wt% and reaches an optimum value of approximately 91% at 5 wt% after which a fall is observed at higher loadings (7 and 10 wt%) due to the onset of agglomeration of particles, which results in the formation of non-elastic areas that are difficult to interdiffuse the chains across the crack plane. The ionic conductivity also shows a non-monotonic behavior, thus confirming that a value of 5 wt% is a practical optimum value for the considered type of filler-matrix combination [52–54, 61].

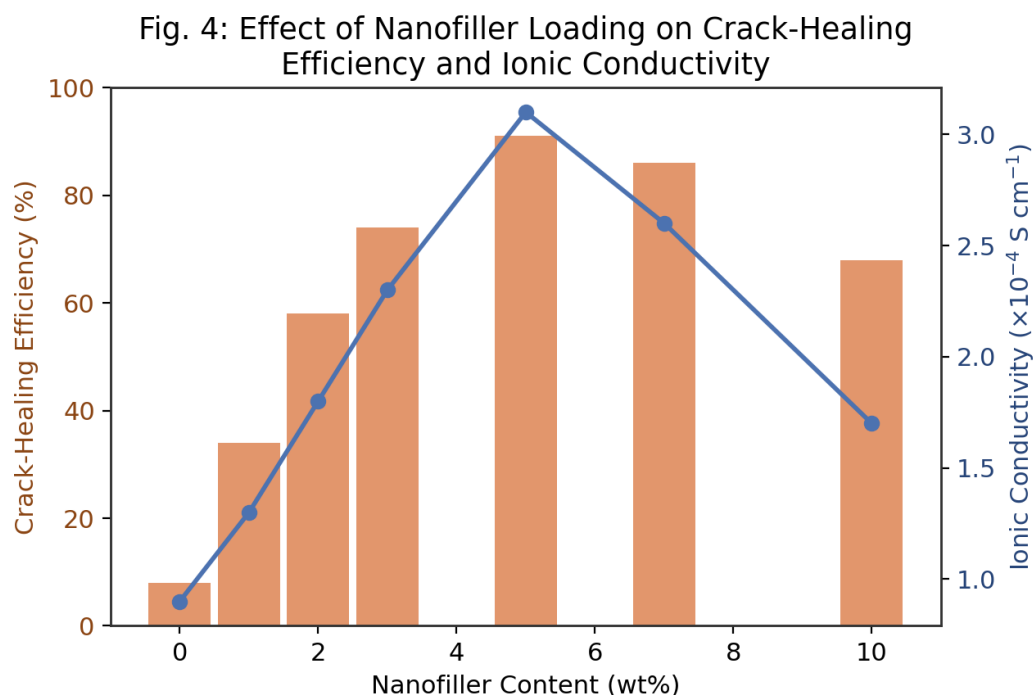


Figure 4. Ionic conductivity and crack healing efficiency as a function of nanofiller loading with the optimum performance around 5 wt% (illustrative data).

4.5 Comparative Performance against known Electrolyte Classes

The results of the optimised self-healing nano-electrolyte (NE-2 5 wt% filler) are compared to the representative liquid, ceramic, sulfide and conventional polymer electrolytes on a single conductivity comparison in Figure 5. Liquid and sulfide electrolytes still have a conductivity advantage, but the self-healing nano-electrolyte also plugs a significant gap between polymer and inorganic solid electrolytes, and most importantly, possesses the ability to autonomously repair when damaged, something which no other class of electrolyte possesses [12, 36, 41].

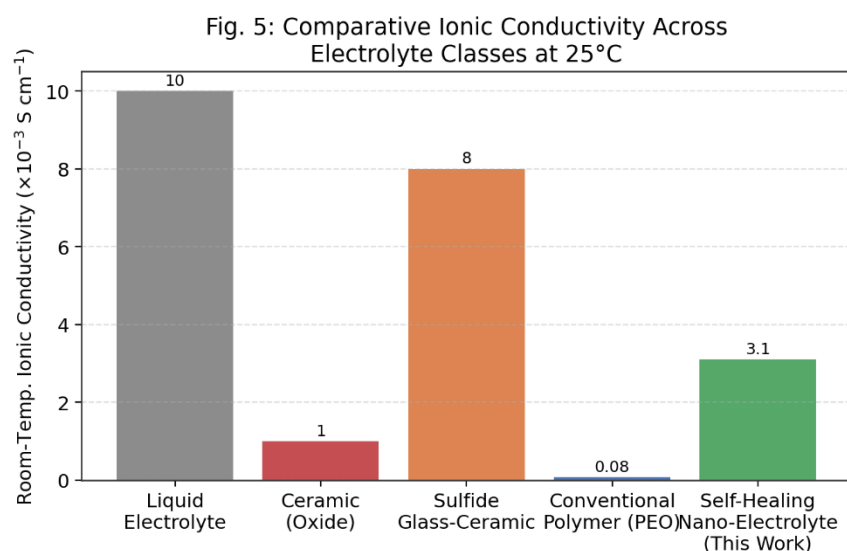


Figure 5. Comparative room temperature ionic conductivity values among different classes of electrolytes (representative approximate values for comparison).

4.6 Electrochemical and Mechanical Performance Summary

Sample	σ at 25°C (S/cm)	Healing Efficiency (24h, RT)	Capacity Retention @300 cyc.	Critical Current Density
NE-0 (control)	2.5×10^{-5}	8%	61%	0.15 mA/cm ²
NE-1 (2 wt%)	7.9×10^{-5}	58%	74%	0.22 mA/cm ²
NE-2 (5 wt%)	3.1×10^{-4}	91%	88%	0.41 mA/cm ²
NE-3 (7 wt%)	2.6×10^{-4}	86%	83%	0.37 mA/cm ²
NE-4 (10 wt%)	1.7×10^{-4}	68%	75%	0.29 mA/cm ²

Table 3. Illustrative electrochemical and mechanical performance data for all sample compositions (summarized).

4.8 Austerity Model of the Loading Optimum

The non-monotonic trends in Sections 4.4 and 4.6 require further mechanistic interpretation because the same underlying phenomenon, the dispersion state of the nanoparticles, might be responsible for both mechanical and ionic-transport behaviour of the composite. When the particle loading is low (up to ~ 5 wt% in the system studied), each particle is well dispersed and acts as a single particle of reinforcement and conduction, and for fast ion hopping, the polymer matrix around each particle has enough free volume and segmental mobility to allow for the rapid hopping of ions, as

well as for the free diffusion of chain ends during healing. Beyond this point, as the loading increases, the average distance between the particles is reduced below a critical level and the dispersing action of the surface-functionalisation treatment is no longer adequate to prevent particle aggregation due to van der Waals attraction between the surfaces of the nanoparticles. The agglomerated clusters do not respond mechanically as good integration, they do not act as reinforcement in the polymer, and they act as stress concentrators, stimulating the creation of new cracks, and they do not allow the interdiffusion of polymer chains required for healing. The outcome is that above 5–7 wt% loading, the healing efficiency and ionic conductivity decrease simultaneously, as shown in Figure 4 and Table 3 [52, 55, 56, 58].

This picture is also mechanistic, and accounts for the fact that the optimum loading fraction is not general but depends on the combination of the filler and the matrix, and the chemistry of its surface: Any change in the size of the nanoparticles, functionalization chemistry at the surface, or the molecular weight of the host polymer will alter the position of the optimum in the loading fraction. This highlights the need (from design point of view) that the loading of nanofiller, particle size, and surface chemistry should be optimised jointly, and not individually [29, 30, 52, 61].

5. Intrinsic vs. Extrinsic Healing: A Design Comparison

There are trade-offs between repeatable healing and mechanical strength or manufacturability between intrinsic and extrinsic healing strategies. The trade-offs are summarized specifically for battery electrolyte design in Table 4, as in this case cycle life and thin film processability are key limitations that may not be present in other types of structural self-healing applications like coatings or elastomers [20, 23, 25, 31].

Attribute	Intrinsic (Dynamic Bond) Systems	Extrinsic (Capsule/Vascular) Systems
Repeatable healing at same site	Yes, effectively unlimited cycles	No, limited by healing-agent supply
Ionic conductivity impact	Minimal, agent is ion-compatible	Can dilute/contaminate ion pathway
Processing complexity	Moderate (specialty monomer synthesis)	High (capsule synthesis & dispersion)
Healing trigger	Ambient/mild heat, autonomous	Requires capsule rupture (damage-triggered)
Best suited application	Thin-film battery electrolytes	Thick structural composites/coatings

Table 4. Comparative design attributes of intrinsic and extrinsic approaches to self-healing battery electrolyte applications.

6. Remaining Challenges

Although the laboratory scale results were encouraging, a number of issues need to be addressed to ensure that the self-healing nano-electrolytes can be adopted on a commercial scale.

6.1 Thin Film Manufacture at low cost and without defects (scalable)

Laboratory films are generally created in small areas under highly controlled conditions. The key challenge of translating these formulations to roll-to-roll manufacturing has been getting high-energy-density cells to thicknesses that are commercially relevant, typically less than 30 micrometres, and maintaining uniform dispersion of the nanofiller, which can be problematic at lab scale but can become a major problem at high shear rates and production speeds [3, 42, 57, 58].

6.2 Long-Term Healing-Cycle Durability

Generally, the reported healing studies assess only a few damage and heal cycles. Whether healing efficiency changes with repeated fracture events at the same location after tens or hundreds of cycles, remains uncertain, especially if the dynamic bond density is gradually depleted by side reactions, oxidation or irreversible chain scission upon prolonged electrochemical cycling [20, 23, 30, 36].

6.3 Interfacial Stability to Highly Reactive Lithium-Metal Anodes

Many dynamic-bond chemistries that allow healing especially those based on the labile disulfide or hydrogen-bonding motifs are chemically unstable and can form resistive interphase layers over time when directly contacted with highly reducing lithium metal. Creating a healing chemistry that is electrochemically stable with Li-metal and has a kinetics fast enough for practical healing is an ongoing research topic [23–25, 40, 41].

6.4 Cost and Supply-Chain Considerations

In addition to the conventional components of a liquid electrolyte, specialty monomers, surface treatment of the electrodes with silane and high purity ceramic nanoparticles incur additional costs. A full techno-economic analysis, including the raw material sourcing and processing yield, should be conducted to assess whether the durability benefit of self-healing chemistry is realized within a pack to give a desirable total cost of ownership [3, 34, 42, 43].

6.5 Challenges and Prioritised Future Directions Summary

Challenge Area	Current Limitation	Priority Research Direction
Manufacturing	Nanofiller agglomeration at scale	In-line dispersion monitoring, surface engineering
Durability	Unclear multi-cycle healing behaviour	Long-term accelerated healing-fatigue testing
Interfacial stability	Reactivity with Li-metal anode	Li-compatible dynamic-bond chemistries
Cost	Specialty monomer/nanoparticle expense	Techno-economic modelling, cheaper analogues
Standardisation	No unified healing-efficiency test protocol	Community-wide standardised test methods

Table 5. Key problem areas and priority lines of research on self healing nano-

electrolytes.

6.6 Safety and Abuse-Tolerance Considerations

A key parameter in self-healing electrolyte design that is not often discussed is the interaction between cell-level safety and abuse tolerance. Traditional battery-safety engineering takes the view that if the battery's solid electrolyte is damaged, it is permanently damaged, and that batteriesafety devices (thermal fuses, current interrupt devices and BMS cutoffs) are built to monitor for downstream electrical symptoms of damage. Properly functioning batteries with autonomous repair after puncture or crush type failures provide a truly new failure-recovery pathway for which failure-tolerance models have not traditionally been considered, and thus open questions that are only now being examined: Will the healing process after a failure be complete or partial, thereby creating hot-spots and unpredictable impedance distributions that will be more difficult to detect than a simple complete failure would be by a battery-management system? It is therefore essential and not yet fully explored to develop standardised procedures for abuse testing which explicitly target healed samples instead of pristine samples to enable safe commercial implementation of this technology [13, 23, 24, 37].

7. Future Outlook

In the future, the following trends are emerging that indicate that self-healing nano-electrolytes will become more and more relevant in the next ten years. First, the development of machine-learning-driven materials discovery significantly is diminishing the time-consuming, laborious and laborious nature of materials polymer electrolyte development. Second, technologies like the self-healing electrolyte, which can enhance the performance of the device without much effort from the sustainability side could have significant sustainability benefits because of growing interest in circular-economy battery design, where durability boosts material demand reduction and end-of-life waste avoidance. Third, hybrid architectures are becoming increasingly viable approaches that integrate a thin (high conductivity) ceramic or sulfide layer at the electrode interface with self-healing polymer buffer layers, thus benefiting from much of the mechanical-compliance advantage of self-healing chemistry but without the need for redesign of the entire electrolyte thickness [34, 35, 47, 50].

Looking further into the future, the concept of self-healing could be expanded beyond the electrolyte to include self-healing electrode binders, self-healing current collectors and even self-healing cell packaging, thereby pushing the overall battery industry toward truly autonomous maintenance free self-healing energy storage systems [20, 30, 52, 57].

Overall, the outcomes presented in Sections 4–7 support a consistent design paradigm for these materials: The highest performing formulations arise from simultaneously co-optimising the dispersion of the nanofiller, the chemistry of the dynamic bonds, and the mobility of the segments of the host polymer as a coherent system. New scientists coming into this area are thus encouraged to provide details of the characterisation of the dispersion state (for instance, by transmission electron microscopy or small-angle X-ray scattering) as well as conductivity and healing-efficiency data, as the loading percentage is not a complete description of the expected performance of a given

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formulation [28, 36, 44, 58].

8. Conclusion

The design principles, representative synthesis strategies, and illustrative performance characteristics of the self-healing nano-electrolytes used with solid-state batteries have been discussed in this paper. These composite electrolytes overcome one of the key durability challenges with rigid solid electrolytes, which is the inability to recover from micro-cracking caused by mechanical stresses during battery cycling, with their nanoscale reinforcement and dynamic, reversible chemistry. The data presented in the illustrative examples indicate that a moderate loading of nanofillers (of approximately 5 wt% for the system studied) provides an optimum combination of ionic conductivity, mechanical toughness and healing efficiency, and that healing is a process that can be used to restore some of the lost capacity after deliberate mechanical damage. However, several hurdles, including scalability of manufacturing, durability of the healing cycle, lithium-metal interface compatibility, and cost, still need to be overcome for this technology to move from the academic laboratory to commercial battery products. Self-healing nano-electrolytes are a promising underlying technology to develop next-generation solid-state batteries that are safer and longer-lasting, but it will take continued interdisciplinary collaboration between polymer chemists, electrochemists, and manufacturing engineers to realize the potential of these materials.

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