Batteries

Gel Polymer Electrolytes for Electrochemical Energy Storage

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With the booming development of flexible and wearable electronics, their safety issues and operation stabilities have attracted worldwide attentions. Compared with traditional liquid electrolytes, gel polymer electrolytes (GPEs) are preferred due to their higher safety and adaptability to the design of flexible energy storage devices. This review summarizes the recent progress of GPEs with enhanced physicochemical properties and specified functionalities for the application in electrochemical energy storage. Functional GPEs that are capable to achieve unity lithium-ion transference number and offer additional pseudocapacitance to the overall capacitance are carefully discussed. The smart GPEs with self-protection, thermotolerant, and self-healing abilities are particularly highlighted. To close, the future directions and remaining challenges of the GPEs for application in electrochemical energy storages are summarized to provide clues for the following development.

1. Introduction

Liquid electrolytes have played essential roles in electrochemical energy storage for several decades due to their high ionic conductivities (10⁻³-10⁻² S cm⁻¹) and good contacts with electrodes. However, the use of liquid electrolytes has brought risks of leakage and even combustion of organic electrolytes. Another drawback of liquid electrolytes applied in lithium batteries is the inevitable lithium dendrite growth in liquid solution, which is caused by uneven currents when charged in the case of porous separators, especially for the use of lithium metal electrode. In this case, solid polymer electrolytes, without liquid solvents, provide promising opportunity to tackle the safety issue and prohibit the growth of lithium dendrite. However, the reported solid polymer electrolytes mostly deliver low ionic conductivities (10⁻⁸-10⁻⁵ S cm⁻¹) and poor interfaces with electrodes, resulting in deteriorated cycle performance.[1-4] The inferior mechanical property has also limited their developments. To this end, combined the advantages of both the liquid and solid electrolytes, gel polymer electrolytes (GPEs) have attracted increasing attentions as they can function as not only electrolytes but also separators.^[1,5,6] Besides, due to the workability of polymers, the GPEs can render the energy

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storage devices with adjustable shapes and high flexibility, which is promising for the burgeoning portable and wearable electronics.^[7-9] Furthermore, the flexibility and elasticity of GPEs are also prone to tolerate the volume change of electrode materials and the dendrites of lithium metal during charge and discharge processes.^[10-13] As a consequence, GPEs have become one of the most desirable alternatives among various electrolytes for the electrochemical energy storage devices, and significant progress has been made in lithium-ion batteries (LIBs), supercapacitors (SCs), lithium-oxygen (Li–O₂) batteries as well as the other kinds of electrochemical energy storage devices, such as sodium-ion batteries, lithium-sulfur batteries, fuel cells,

and zinc–air batteries.^[14–16] In order to meet the requirements of wearable devices for flexibility and deformability, more special GPEs with tough,^[17] stretchable,^[18] and compressible^[19] functionalities have been also developed.

Typically, a polymeric framework is adopted in GPEs as host material, providing high mechanical integrity. Several criteria for a good polymer host lie in:^[20-22] (i) fast segmental motion of polymer chain; (ii) special groups promoting the dissolution of salts; (iii) low glass transition temperature (T_g) ; (iv) high molecular weight; (v) wide electrochemical window; (vi) high degradation temperature. Within the framework, the salts in the GPEs serve as the sources of the charge carriers, which are generally required to have large anions and low dissociation energy for easier dissociating-induced free/mobile ions. According to the types of electrolytes, there are four categories of GPEs based on proton,^[23] alkaline,^[24] conducting salts, and ionic liquids (ILs).^[25] The criteria for an appropriate electrolyte include:^[26-28] (i) good dissociation without forming ion pairs or ion aggregation; (ii) high thermal, chemical, and electrochemical stability; (iii) high ionic conductivity. In order to dissolve both the polymer hosts and electrolytic salts, the organic/ aqueous solvents are introduced to provide the medium for ionic conduction. A good solvent should simultaneously have high dielectric constant ($\epsilon > 15$), donor number for more dissociation of ion and chemical and electrochemical stability. Organic solvents normally include ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC), dimethyl formamide (DMF), dimethyl sulphoxide, ethyl methyl carbonate, and tetrahydrofuran.

To prepare a high-performance GPE, it is essential to select the species of host polymer, solvent, and electrolytic salt, and then blend them by solution or melt processes, such as casting

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method,^[29,30] in situ polymerization,^[31,32] extraction-activation method,^[33] and phase inversion method.^[34–40] For practical applications, these requirements should be met at the same time: (i) high ionic conductivity; (ii) high lithium-ion transference number (LTN); (iii) good interfacial contacts with two electrodes; (iv) chemical stability as well as wide electrochemical and thermal windows; (v) mechanical stability and flexibility.

There exist some review papers that discussed the previous advances and major challenges related to GPEs for electrochemical devices and mainly focused on preparation processes, materials or mechanisms. Recently, a series of new and general approaches has been developed on improving the electrochemical performance of GPEs, which is of great significance but rarely included. In addition, the rapid advances of smart GPEs are produced by the necessity of intelligent energy storage devices, especially for the booming wearable and portable devices, and they have not been deeply analyzed either. To obtain an overall comprehension of the recent studies and highlight the representative achievements, it is necessary to make a summary to provide important clues for the future study on GPEs aiming at high electrochemical energy storage properties. This review covers the recent studies on various strategies to polish up the physicochemical properties of GPEs in terms of ionic conductivity and mechanical strength by introducing inorganic/organic fillers, large LTN by immobilizing anions to achieve single lithium-ion conduction in GPEs, and even the overall capacitances of supercapacitors by adding redox-active mediators into the supporting GPEs. As a result, the progresses of various functional GPEs with enriched smart capabilities such as self-protection, thermotolerance, and self-healing in response to external stimuli, are particularly and carefully discussed. Eventually, the remaining challenges and the future directions toward further applications in electrochemical energy storage are presented.

2. The Performance Improvement of the GPEs

Conventional GPEs, often belonging to dual-ion conductors, suffer from low ionic conductivity at low room temperature (typically 20-30 °C), poor mechanical property, and poor thermal stability.^[41] As a result, a variety of inorganic/ organic fillers or plasticizers had been added to enhance their properties. Some inorganic fillers can work as Lewis acids to compete with Li+ ions to react with the polymer, avoiding the ion coupling,^[42] promote the dissociation of the salt, and increase the number of the free carriers. On the other hand, the mechanical properties and thermal stability can also be improved by adding inorganic additives due to the well dispersed stress and the excellent thermal compatibility of nanosized fillers. Overall, the criteria of ideal inorganic fillers include: large specific surface area, high ionic conductivity, good mechanical property, and good thermal stability. The commonly used fillers include Li₃N, LiAlO₂, Al₂O₃, SiO₂, TiO₂, and BaTiO₃,^[43-47] the performance of which strongly depend on their morphology,^[48] size,^[49] crystallinity,^[50] and surface modification.^[51–54] In addition, the performance of the GPEs can also be increased by introducing functional or assistant polymers





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with higher ionic conductivities, better mechanical properties, and higher thermal stability. The combination of assistant polymer with the polymer matrix can be realized through alternating, blocking or grafting copolymerization. For example, by introducing polyethylene or polystyrene blocks into polyethylene oxide (PEO) matrix, three-dimensional (3D) connected



frameworks were formed, achieving high mechanical properties. Furthermore, these two blocks could form unique patterns with special pathways to increase ionic conductivities.^[55] With these improvements, the ionic conductivity of dual-ion GPEs had reached over 10^{-3} S cm⁻¹,^[56–58] with the tensile strength over 10 MPa^[59,60] and the thermal stability over 400 °C.^[61]

Recently, some other effective strategies have been further reported by immobilizing anions to realize single lithium-ion conducting GPEs or directly introducing redox-active mediators into GPEs. One of the unique advantages of single lithium-ion conducting GPEs is their unity LTN close to 1, comparing with the conventional dual-ion conducting GPEs. For redox-type GPEs, they can not only provide additional pseudocapacitances to the overall capacitance of the supercapacitors but also reduce the overcharge potential and improve the cycling stabilities of the Li– O_2 batteries.

2.1. Single Lithium-Ion Conducting GPEs

Traditional dual-ion conductor GPEs, are formed by dissolving electrolytic salts in gel polymers. These GPEs suffer from concentration polarization caused by the salt concentration change across the membrane and within the electrodes during the cycles of discharge, because there is no electrode reaction for the anions.^[62] The generation of salt concentration gradients leads to poor performances including high internal impedances, voltage losses, and undesirable reactions in the electrolyte state such as phase transition or salt precipitation. In addition, the LTN of dual-ion conducting GPEs is generally lower than 0.5 because the motion of Li⁺ is strongly related to the segmental motion of the polymer host. To avoid concentration polarization and increase LTN, the free movement of anions needs to be limited or totally eliminated. To achieve single lithium-ion conducting GPEs, several strategies for immobilizing the anions, including covalently bonding the anions to the polymeric/inorganic backbones or adding trapping agents for anions to the conventional GPEs have been developed.^[63]

The commonly developed single lithium-ion conducting GPEs with organic polymers as the backbones are synthesized by direct polymerization of lithium salt monomers or incorporating anionic groups of lithium salt into the existing polymer backbones. These lithium-polymer salts are typically Li-ion source instead of Li-ion conductors. The common way to increase the ionic conductivity is to blend them with a polymer matrix containing soft segments like PEO, in which the polymer matrix functionalizes as a transporter of Li⁺ ions.^[64-66] Plasticized single lithium-ion GPEs are typically prepared by swelling the resulting electrolyte membranes in PC or the mixed solvents of EC/DMC.^[67] The developments of single lithium-ion conducting GPEs have demonstrated several advantages over the dual-ion GPEs with large LTNs close to unity, the absence of the detrimental effect of anion polarization, and the low rate of lithium dendrite growth.^[63] For example, the lithium tartaric acid borate (PLTB)-based single lithium-ion conducting GPEs were demonstrated to improve the cyclic performances of LiMn₂O₄/Li cell and obviously alleviate the generation of lithium dendrites on Li anodes, compared with LiPF₆-based electrolyte at elevated temperature of 55 °C.[68]

Similarly, the ionic conductivity is also critical for the practical application of single lithium-ion conducting GPEs, which are governed by the ionic mobility in polymer hosts. To this end, a promising approach to increase the Li⁺ ion mobility in gel polymer is to enhance the segmental motion of the polymer backbone by lowering their $T_{\rm g}$ or introducing polymer backbones with low T_g than that of the room temperature. For PEO-based single lithium-ion conducting GPEs or single lithium-ions solid-state electrolytes, the high ionic conductivities and large LTNs are normally observed at elevated temperatures around 60 °C, which is close to its melting point (65 °C).[69] Near the melting temperature, PEO becomes increasingly soft, being beneficial for Li⁺ transfer. For example, a single lithium-ion conducting GPE was prepared by a copolymerization of lithium poly[(4-styrenesulfonyl) (trifluoromethanesulfonyl)imide and methoxy-polyethylene glycol acrylate. When blended with PEO (molecular weight, $M_{\rm w} = 5 \times 10^6$), there existed a high ionic conductivity of 10⁻⁴ S cm⁻¹ at 60 °C but only 7.6 \times 10⁻⁶ S cm⁻¹ at 25 °C.^[70] LIBs equipped with this single lithium-ion conducting GPEs are meaningful towards related applications operated at relatively high temperatures. However, the strong dependence of the performance on high temperature also severely limited their applications in portable and wearable electronics and electric vehicles which commonly work at near ambient temperatures. By incorporating inorganic filler (e.g., mesoporous SiO2 nanoparticles) into the PEO matrix ($M_w = 1 \times 10^5$),^[71] the resulting single lithium-ion electrolyte membranes exhibited high ionic conductivity of 10^{-3} S cm⁻¹ at 25 °C, a storage modulus of 10^4 Pa at 30 °C with a high LTN of 0.9. It exhibited two orders of magnitude higher ionic conductivity than the conventional nonporous SiO₂ nanoparticles-incorporated PEO matrix, suggesting that the facile transportation of lithium ions was achieved through the continuously intrinsic mesoporous structure. Another effective strategy is to choose polymers without crystallinity or with low $T_{\rm g}$, high thermal and electrochemical stability as backbones for designing single lithium-ion conducting GPEs. Compared with most of the commonly used polymers for GPEs, polysiloxanes are inherently amorphous at nature and possess low T_{α} below room temperature with high mechanical strength and thermal stability, which may serve as potential backbone polymers for designing single-ion conducting GPEs. The T_g of the resulting polysiloxane-based single-ion conducting GPEs was found to be 10 °C, and the composite membrane prepared by blending it with poly(vinylidene fluoride-co-hexa-fluoropropylene) (PVDF-HFP) ($M_w = 4 \times 10^5$, $T_g \approx -35$ °C) showed a low T_g of -17 °C. The low crystallinity of the composite membrane coupled with low T_g ensured its high flexibility and decent performance at room temperature. For example, the composite membrane exhibited a high ionic conductivity of 7.2×10^{-4} S cm⁻¹, a LTN of 0.89, good thermal stability up to 410 °C, and good electrochemical stability up to 4.1 V.[72]

Several another effective strategies have also been employed to improve the performances of single lithium-ion conducting GPEs near the ambient temperature.^[73,74] It was widely accepted that the presence of intrinsic porous structure in polymer backbones and/or polymer matrixes could not only facilitate Li⁺ ion transport in the polymers but also store a sufficient amount of organic solvents to provide the medium for





Figure 1. a) Scanning electron microscope (SEM) images of the single lithium-ion conducting GPEs porous membrane based on aromatic poly(arylene ether)s with pendant lithium perfluoroethyl sulfonates from corner view (left) and surface view (right), scale bars, 2 μ m. b) Photographs of the resulting microporous membrane saturated with organic carbonates of DEC + EC + PC (1:1:1 by volume, 92 wt%). Metal bar on the membrane: weight, 25 g; length, 1.6 in. c) Arrhenius plot of the ionic conductivity of the single lithium-ion porous membrane saturated by DEC + EC + PC (1:1:1 by volume, 92 wt%) and the conventional Celgard 2500 separator saturated by 1 M LiPF₆ in DEC + EC + PC (1:1:1 by volume). d) Impedance response of the single lithium-ion conducting GPEs porous membrane by sandwiching it between two blocking stainless steel electrodes. The inset shows time dependence of the ionic conductivity of the electrolyte membrane at 25 °C. Reproduced with permission.^[76] Copyright 2016, American Chemical Society.

ionic conduction. By designing a 3D porous melamine-terephthalaldehyde-lithium complex (MT-Li) as single lithium-ion conducting electrolytes and then blending with PVDF-HFP, the resulting single lithium-ion conducting GPEs displayed a high ionic conductivity of 6.3×10^{-4} S cm⁻¹ at room temperature with LTN of 0.86.^[75] The high ionic conductivity of the membrane is also attributed to the aromatic triazine ring in the MT-Li complex, which allows the anionic charge to be readily delocalized, and thus promoting the cationic mobility. Similarly, a highly porous single lithium-ion conducting GPEs membrane (47 wt% on the basis of the membrane density) was prepared (**Figure 1**a) by mixing the preformed aromatic poly(arylene ether)-based lithium single-ion electrolyte with poly(ethylene glycol) dimethyl ether (30 wt%) in DMF and then



extracting polyethylene glycol (PEG) from the membranes by water.^[76] The resulting porous membrane can absorb organic carbonates more than 120% of its own weight while keeping the high mechanical integrity (Figure 1b) (i.e., tensile strength of 11.7 MPa and Young's modulus of 310 MPa). It exhibited a nearly unity LTN of 0.98 and high ion conductivities (e.g., >10⁻³ S cm⁻¹ at room temperature) over a wide range of temperatures from 60 to -20 °C (Figure 1c). Moreover, the negligible changes of membrane impedance and ion conductivity with time indicate the great stability of the resulting single-ion conductor for practical applications (Figure 1d).

A highly effective single-ion conducting GPE should require a high degree of charge separation, which can be achieved by placing electron-withdrawing functional groups in the vicinities of the anions onto the polymer backbones to reduce the electrostatic interaction of cations/anions, and thus gives rise to high lithium ion mobility and high conductivity. For example, the incorporation of an sp³ boron-based polymeric backbone as a counter ion of Li⁺ ions was demonstrated to widen the operation temperatures of the PVDF-HFP blended single lithium-ion conducting GPE from 100 to 20 °C with an ionic conductivity of 2.4×10^{-4} S cm⁻¹, high LTN of 0.87, and good mechanical strength of 33 MPa at room temperature.^[77] In the lithium poly(1,2,3,4-butanetetracarboxylic acid borate) electrolyte, boron atoms covalently bonded with electron-withdrawing groups result in charge delocalization in the polymer chains. The boron incorporation in this single lithium-ion GPE naturally leads to weak electrostatic interaction of lithium ions with the anions covalently bonded to the polymers, making the Li⁺ more mobile in the polymeric backbones and thus producing high conductivity at low temperature. This type of sp³ boron in electrolytes as a counter ion of lithium ions includes polymeric lithium tartaric acid borate (PLTB),^[67] lithium bis(oxalato) borate,^[78] lithium oxalate polyacrylic acid borate,^[79] and lithium polyvinyl alcohol oxalate borate. [80]

In summary, single lithium-ion conducting GPEs are considered as promising candidates for LIBs and lithium metal batteries to replace the traditional dual-ion conducting GPEs. The benefits of single lithium-ion conducting GPEs over the conventional GPEs include large LTNs close to unity, extremely low growth rate of Li dendrite, and absence of detrimental effect of anion polarization. Among various types of single lithiumion conducting GPEs, the commonly developed ones are based on organic polymers as the backbones, which can be directly synthesized by polymerization of lithium salt monomers or incorporating anionic groups of lithium salt into the existing polymer backbones. Generally, the resulting single lithium-ion conducting GPEs are needed to blend with polymer hosts like PEO, PVDF, PVDF-HEP to improve the ionic conductivity and mechanical strength. The major limitation for their practical applications in large-scale batteries is the low ionic conductivity at medium temperature and the inferior interfacial properties with electrodes. Several possible strategies are exploited to ameliorate these aspects by designing single lithium-ion conducting GPEs with porous structure, introducing polymeric backbones with low T_{α} , adding inorganic/organic fillers, and making structural modification of anions to further improve the negative charge delocalization.

2.2. Redox-Active GPEs

Recently, an advanced and effective approach to dramatically increase the specific capacitance of supercapacitors has been developed by introducing a small amount of redox-active additives into the liquid electrolytes and GPEs. Additional Faradaic oxidation/reduction reactions of the redox couple contribute pseudocapacitance to the overall capacitance of supercapacitors (Figure 2a).^[81] In this case, the capacitances are not only contributed by electrode materials but also contributed from the electrolytes. To date, various redox-active mediators contain organic molecules like hydroquinone (HO),^[82,83] methylene blue (MB),^[84] indigo carmine,^[85] p-phenylenediamine (PPD),^[86] m-phenylenediamine,^[87] lignosulfonates,^[88] and ionic redox active species like KI,^[89,90] VOSO₄,^[91] Na₂MO₄,^[92] and CuCl₂^[93] have been extensively studied. The GPEs containing redoxactive mediators have been extensively explored in carbonbased supercapacitors, pseudocapacitors, and Li-O₂ battery.

2.2.1. Redox-Active GPEs for Supercapacitors

Carbonaceous electric double-layer capacitors (EDLCs) are well known for high power densities and high cycling performances but low energy densities. Typically, the energy densities of EDLCs could be enhanced by incorporating various pseudocapacitive materials, i.e., transition metal oxides/hydroxides, metal chalcogenides, and conducting polymers or surface functionalization of carbon electrodes by introducing nitrogen or oxygen groups. It was recently reported that iodide ions played dual roles of electrolytic solution with a high ionic conductivity and a source of pseudocapacitive effects. The carbon electrode in 1.0 M KI solution gave an extremely high specific capacitance of 1840 F g⁻¹ and the two-electrode cell also supplied a high specific capacitance of 125 F g⁻¹ at 50 A g^{-1.[94]} Directly adding HQ into the H₂SO₄ solution to make a redox-reactive electrolyte, the Faradaic reactions of the hydroquinone/quinone system in H₂SO₄ were found to give rise to a great enhancement in the capacitance for four different types of carbon-based supercapacitors (Figure 2b).^[82]

The redox active GPEs for supercapacitors can be simply prepared by mixing these redox-active species with supporting GPEs. The polymer hosts for the supporting GPEs were mainly focused on the PVA, PEO, and Nafion, and the working principles of the reactive mediators in GPEs are generally similar to those in the aqueous and organic electrolytes. For example, a redox-contained GPE was prepared by introducing 2-mercaptopyridine into the supporting polyvinyl alcohol (PVA)/H₂SO₄ GPE. A fiber-shaped supercapacitor had been then fabricated by twisting two aligned carbon nanotube (CNT)/mesoporous carbon hybrid fiber electrodes and incorporating the resulting redox-active GPE as electrolyte and separator. It exhibited obvious oxidation/reduction peaks with increased enclosed areas and delivered a high specific area capacitance of 0.5 F cm⁻², which was about nine times higher than that of the fiber-shaped supercapacitor without the 2-mercaptopyridine.^[95] By simultaneously introducing two redox additives with polypyrrole (PPy) onto the CNT-based fiber electrodes and HQ in the supporting PVA/H₂SO₄ GPE, the resulting fiber-shaped pseudocapacitor







Figure 2. a) Schematic showing the Faradaic oxidation/reduction reactions of the redox couple during the charge/discharge processes. The redox couple used at the positive electrode (which is oxidized on charging and reduced on discharging) is labeled as O_p/R_p (catholyte), and the couple used at the negative electrode (which is reduced on charging and oxidized on discharging) as O_n/R_n (anolyte). Reproduced with permission.^[81] Copyright 2015, Nature Publishing Group. b) Schematic illustration to the EDLC based on redox reaction of HQ/H₂SO₄. Reproduced with permission.^[82] Copyright 2011, Wiley. c) Schematic representation of EDLC with introducing KI/VOSO₄ redox additives into a PVA-H₂SO₄ GPE. Reproduced with permission.^[102] Copyright 2014, Royal Society of Chemistry. d) Schemes of reversible Faradaic reactions related to HQ and MB in the corresponding PVA-H₂SO₄ GPEs. Reproduced with permission.^[104] Copyright 2015, Elsevier.

delivered a high specific areal capacitance of 1.168 F cm⁻², which was about twice and 11 times higher than those of the CNT/PPy-based fiber-shaped supercapacitor and bare CNT-based fiber-shaped supercapacitor measured in the PVA/H₂SO₄ GPE without HQ, respectively.^[96] The additions of reactive mediators to the pseudocapacitors or asymmetric supercapacitors are promising for higher-energy-density supercapacitors because of the synergistic effects between the pseudocapacitive electrode materials and redox additives. These commonly used

redox-active additives for pseudocapacitive or asymmetric super-capacitors are K_3 Fe(CN)₆,^[97] KI,^[98] PPD,^[99] and HQ.^[100]

Single redox-active additive may produce high pseudocapacitive at either positive or negative electrodes. For example, an iodine-based system offered high pseudocapacitance on the positive electrode while VOSO₄ can greatly improve the performance of negative electrode.^[101] Therefore, by simultaneously introducing KI/VOSO₄ redox additives to PVA/ H_2SO_4 gel electrolyte (Figure 2c),^[102] the activated carbon



(AC)-based supercapacitors delivered a high specific capacitance of 1232.8 F g⁻¹ with an energy density of 25.4 W h kg⁻¹, which were nearly eight times higher than that of the one without KI/ VOSO₄. Thanks to the GPEs as electrolyte membrane, glassy paper separator, and Nafion 117 membrane could be left out for cost reduction in a comparison to Frackowiak's work.^[103] Another effective approach is to separately incorporate the anodic and cationic redox additives into the supporting GPEs on the positive and negative electrodes, respectively. For instance, a quasi-solid-state supercapacitor was assembled by using a pair of AC electrodes with two PVA/H₂SO₄ GPEs separately containing redox additives of HQ and MB (Figure 2d),^[104] which were separated by a Nafion 117 membrane with a sandwich-type configuration. It delivered a high specific capacitance of 563.7 F g^{-1} and an energy density of 18.7 W h kg⁻¹, increased by about fourfold in comparison with the SC without HQ-MB redox couple.

2.2.2. Redox-Active GPEs for $Li-O_2$ Battery

Rechargeable Li-O2 batteries have been considered as reliable alternatives to conventional LIBs because of their high theoretical specific energies and the unlimited resource of oxygen as cathode material.^[105,106] Significant research efforts have been made to ameliorate the cycling life and the Coulombic efficiency of the Li-O₂ battery and lower its over-charge-potential, which are mainly derived from the formation of solid-type and nonconductive $\mathrm{Li}_2\mathrm{O}_2$ discharge products. The developments of GPEs provide a feasible solution to safety issues of the Li–O₂ battery.^[107,108] Apart from the safety concerns, the Li–O₂ battery equipped with GPEs was demonstrated to exhibit enhanced cycling performance for at least 50 cycles while the one tested in liquid electrolytes faded at the 29th cycle, which was beneficial from the construction of effective protective layer that prevented the crossover of trace oxygen from the cathode to the anode and H₂O crossover toward the Li anode by the GPEs.^[109] However, in contrast to a lithium-ion battery (LIB) equipped with GPEs, the GPEs-based Li–O₂ battery would encounter a lot of more complicated factors retarding their future applications. These challenges are mainly focused on the chemical/electrochemical stability of GPEs, the interface chemistry between the GPE and electrode, and the ionic conductivity of the GPEs.^[110] As one of the key factors, the chemical stability of GPEs against the oxidization of the charge/discharge products of the Li-O₂ battery (e.g., Li₂O₂, LiO₂) plays a critical role in its cycling life. These commonly used polymers like PVDF, PVDF-HFP, PVP, PVC, and PAN are unstable and reactive in presence of Li₂O₂, and thus it is essential to select appropriate host polymers to design the GPEs for Li-O₂ battery.

Another major limiting factor for the developments of $\text{Li}-O_2$ battery is the large interfacial resistance occurring between the GPE and electrode due to the generation of low conductivity of discharge products (e.g., Li_2O_2 , $\text{Li}O_2$) that kinetically limited the Li⁺ transfer within the GPEs and through the two-phase interface, which would lead to high over-charge-potential, unfavorable cycling stability, and low round-trip efficiency. The incorporation of redox-active mediators into the supporting GPEs provides an effective approach to decrease the interfacial resistance between the GPE and Li_2O_2 . The charging redox

mediators are initially oxidized on the electrode to form oxidized species, which then chemically react with Li₂O₂ to produce O₂ and Li⁺ with a reverse reaction into the initial state. The charge voltage is thus tuned to be close to the redox potential of the mediator. These commonly used soluble redox mediators for Li-O2 batteries include LiI,^[111] lithium bromide (LiBr),^[112] tetrathiafulvalene,^[113] iron phthalocyanine (FePc),^[5] 10-methylphenothiazine,^[114] 2,2,6,6-tetramethylpiperidinyloxyl,^[115] and tris[4-(diethylamino)phenyl]amine.[116] By adding redox reactive P-benzoquinone into the poly(vinylidene fluoride) (PVDF)-based GPE for the Li-O2 battery, it resulted in the charge potential decreasing from around 4.2 to 3.3 V with an improved cycling capability from 2 to over 30 cycles.^[117] A long-life Li-air battery in ambient air was developed with GPE containing a redox mediator.^[118] The GPE efficiently alleviated the Li passivation induced by attacking air, and the reversible conversion of I⁻/I₂ in GPE acted as a redox mediator that facilitated the decomposition of discharge products. As a result, the Li-air battery equipped with LiI-contained GPE exhibited higher Coulombic efficiency nearly 100% and lower charge potential than those with GPEs free of LiI and in liquid electrolyte (Figure 3a). This Li-air battery can be stably operated for 400 cycles in ambient air with a relative humidity of 15% (Figure 3b), offering a great chance to develop the Li-air battery for operation in ambient air. X-ray diffraction (XRD) results demonstrated that crystalline Li₂O₂ and LiOH were formed in discharge products onto the reduced graphene oxide (rGO)based air electrode after discharge, and then they were decomposed during the full recharge process (Figure 3c).

In summary, an effective approach has been developed by introducing redox-active mediators into the supporting GPEs to provide additional pseudocapacitances to the supercapacitors. On the other hand, the redox-contained GPEs would also compromise the cycling stability and rate capability of the supercapacitors because of their intrinsic inferior electrochemical stability. The matching between the redox-contained GPEs and electrode materials is necessary to improve the overall performance of the supercapacitors by designing stable redox couples to simultaneously improve the capacitances of both electrodes. For Li-O₂ batteries, the combination of redox mediators with the GPEs provides a new strategy to lower the over-chargepotential and ameliorate the cycling life and the Coulombic efficiency. This is because their oxidized species can chemically oxidize the discharge product (Li₂O₂) to produce Li⁺ and O₂ gas with a reverse reaction into the initial state. The special discharge/charge products make the GPEs usage in Li-O₂ more complicated in contrast to the LIBs and supercapacitors, mainly focusing on the stability, interfacial chemistry, and ionic conductivity. Therefore, significant research efforts are required to address these fundamental issues with GPEs for the further development of the Li–O₂ batteries.

3. Functional GPEs for Intelligent Devices

Besides the traditional, single lithium-ion and redox-active GPEs discussed above, different kinds of functional GPEs have also been developed in recent years, including thermotolerant, temperature-sensitive and self-healing GPEs. The specific



Figure 3. a) Full discharge/charge curves of the Li–air battery measured in different electrolyte systems of liquid electrolyte, GPE, 0.05 M LiI-GPE at an applied current of 1.0 A g⁻¹ (refer to the weight of rGO). b) Comparative cycle performances of the Li–air battery measured in different electrolyte systems. c) Ex situ XRD patterns the rGO-based air cathodes in the pristine state, after discharge and recharge states, respectively. Reproduced with permission.^[118] Copyright 2017, Wiley.

properties and functionalities of these GPEs will largely extend their applied ranges in various fields. For example, the thermotolerant polymer-electrolyte can enable the battery to work at high temperatures, avoiding failure or explosion. Self-healing energy storage devices can be developed from self-healing polymer electrolytes, largely improving the adaptability and lifetime of the energy storage devices.

3.1. GPEs with Thermally Responsive Ability

Although the energy density, power density, and cycling life of LIBs and supercapacitors have been largely improved in the

past two decades,^[119–121] the safety issue still remains urgent to be solved, especially in large-scale applications of high-energydensity LIBs.^[122–124] LIBs are normally operated within a limited range of temperatures, current densities, and voltages to maintain good electrochemical performances.^[125] Nevertheless, once a short circuit forms, overcharging or other abuse conditions occurs, and a series of exothermic reactions will take place to largely increase the internal temperature and pressure of the LIBs, which will lead to fire or explosion.^[126–129] In this case, smart electronics with real-time safety monitoring and self-protection capabilities have been successfully fabricated by introducing thermally responsive GPEs, which possess phase separation or sol–gel transition properties at elevated temperatures to realize the inherently safe operations.

One way to realize the thermally responsive electrolyte is developing GPEs with the functionality of reversible phase separation. This kind of GPEs usually comprises of polymers with thermally responsive property and conductive ions. When the temperature rises, the polymer phase separates and the ions are therefore removed from solution to eliminate the conductive pathway between the electrodes. Furthermore, the electrolyte properties will be recovered when the polymer redissolves in solution below the thermal transition temperature. For instance, a thermally responsive polymer electrolyte^[130] was designed to control the electrochemical performance of polyaniline electrode according to the temperature (Figure 4a). The copolymer was prepared using N-isopropylacrylamide (NIPAM) and acrylic acid. In this case, NIPAM provided the electrolyte with the thermally responsive property while the acrylic acid offered the electrolyte ions (Figure 4b). When the temperature was elevated, the polymer underwent a thermally activated phase transition and the local environment around the acid groups was accordingly changed with decreasing ion concentrations and conductivities. As shown in Figure 4c, the overall capacity of the polyaniline electrodes decreased by $\approx 85\%$ with the increasing temperature from 20 to 50 °C, and the feasibility of this strategy was successfully demonstrated. To further realize inherently safe high-energy-density LIBs, a Li4Ti5O12/ LiFePO₄ rechargeable LIB (Figure 4d) adopting the thermally responsive poly(benzyl methacrylate) (PBMA) in an ionic liquid was developed.^[131] The responsive electrolyte was composed of PBMA in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [EMIM][TFSI], which would inhibit the operation of LIB at elevated temperatures. The mechanism of this electrolyte was based on the change in conductivity of the electrolyte due to the electronic insulator property of the PBMA. Once above the phase transition temperature, there existed a higher frequent occurrence of the phase separation for the polymer and the internal resistances at the electrode/electrolyte interface (Figure 4e). As shown in Figure 4f, the performance of the LIB was largely reduced at a high temperature of 150 °C, which could effectively prevent the entire LIB from heating beyond the unsafe temperature.

Another strategy to realize the thermally responsive electrolyte is to use the sol-gel transition of electrolytes. Different from the GPEs based on reversible phase separation, this kind of GPEs generally contains polymers with reversible sol-gel transition property and conductive ions. When the temperature was increased, these GPEs transform from solution to gel state



Figure 4. Different kinds of temperature-sensitive GPEs. a) Schematic of a temperature-sensitive polymer electrolyte. b) pH and ionic conductivity response to temperature of the polymer electrolyte. c) Charge–discharge curves of PANI electrodes in the polymer electrolyte under heating from 22 to 50 °C. Reproduced with permission.^[130] Copyright 2012, Wiley. d) Schematic of the LIB setup and the thermal-response mechanism of the electrolyte at high temperatures at the electrode surface. e) Effect of increasing temperatures on the Nyquist plot for 0.5 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in a 5 wt% PBMA-IL. f) Discharge curves of the responsive electrolytes at 60 and 150 °C. Reproduced with permission.^[131] Copyright 2015, Royal Society of Chemistry. g) Illustration of sol–gel transition of electrolyte which slows the migration of conductive ions between the electrodes. h) The specific capacitances of the supercapacitors generally decrease at increasing temperatures. i) Demonstration of thermal self-protection of supercapacitor using the temperature-sensitive electrolyte. Reproduced with permission.^[132] Copyright 2015, Wiley. j) Schematic of the thermally responsive gel system used as an electrolyte in energy storage device. k) The charge/discharge cycle of the supercapacitor tested at room temperature and 70 °C. I) The variation of the sol–gel transition temperatures of Pluronic solutions with different numbers of average molecular weights (MWs) (the concentration for all solutions is 30 wt%). Reproduced with permission.^[133] Copyright 2016, Wiley.

and inhibit the movement of ions to cut off the electrochemical devices. A sol-gel electrolyte^[132] using a thermally responsive poly(*N*-isopropylacrylamide-*co*-acrylamide) (PNIPAM/AM) was thus investigated for a self-protection supercapacitor (Figure 4g). With the increasing temperature, the thermal copolymers would form hydrogels through hydrophobic association and the migration of conductive ions between the electrodes was inhibited. With the decreasing temperature, the above transition was reversed and the electrochemical performance of the supercapacitor was restored. Owing to the inhibition of the migration of conductive ions with the increasing temperature, the sol-gel transition of PNIPAM/AM decreased the specific capacitance and power delivery of supercapacitors (Figure 4h). To practically demonstrate the self-protection functionality of the thermally responsive supercapacitor, an application example was shown in Figure 4i. With the temperature increased to 60 °C, the intensity of the LED light decreased from 1.39 to 0.41 mW, which indicated the thermal self-protection of the supercapacitor. Furthermore, a thermally responsive sol–gel smart polymer electrolyte with tunable transition temperature^[133] was proposed using a thermoplastic elastomer to realize a reversible sol–gel transition (Figure 4j). The smart electrolyte was composed of a Pluronic [poly(ethylene oxide)block-poly(propylene oxide)-block-poly(ethylene oxide)] aqueous solution dissolved with ions such as H⁺ or Li⁺. At low temperatures, the smart electrolyte was at a solution state and the

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ions could migrate freely between electrodes. When the temperature increased, the smart electrolyte transformed to a gel state and inhibited the movement of ions to finally cut off the electrochemical devices (Figure 4k). Surprisingly, the sol–gel transition temperature of the smart electrolyte could be easily adjusted toward different applications since the transition temperature of the Pluronic solution is tunable over a wide temperature range from room temperature to above 90 °C by changing the average molecular weight of the polymer (Figure 4l).

In conclusion, the safety issue of LIBs such as fire or explosion can be inherently solved by using the thermally responsive GPEs, which can transfer ions at desired temperatures while reversibly cut off the LIB at higher temperatures. The mechanisms of these GPEs are usually based on the reversible change in conductivity of the electrolyte due to the phase separation or sol–gel transition of the GPEs at high temperatures. Although great efforts have been made to develop thermally responsive GPEs, most of them were used in self-protection supercapacitors rather than LIBs. The safety concerns of high-energy power sources such as LIBs and lithium–sulfur battery under high temperatures are still urgent to be solved. Therefore, it remains challenging to develop thermally responsive GPEs which can effectively replace the traditional GPEs.

3.2. GPEs with High Thermal Stability

Due to the relatively low melting points of the traditional polymer backbones (such as 65 °C for PEO), the resulting GPEs generally demonstrate poor thermal stability. Therefore, the corresponding energy storage devices are not able to be operated at high temperatures, which has largely limited their applications. Energy storage devices with high thermal stability are highly desired in many fields including heat-resisting robots and electric automobiles that are commonly used at high temperatures. Herein, it is of great importance to develop GPEs with higher thermal stability and higher safety. The general method to improve the thermal stability of the GPEs is introducing different kinds of inorganic/organic fillers with high thermal stability and compatibility or directly developing ionic liquid-based GPEs.

The introduction of heat-resistant additives can tremendously improve the thermal stability of GPEs. Therefore, various polymers and inorganic particles of high heat resistance are introduced to the GPEs, including PEG-borate ester, polyvinylidene fluoride-graft-polyacrylonitrile (PVDF-g-PAN) and TiO₂ nanoparticles. Due to the high thermal stability of these additives, the thermostability of the GPE can be thus largely enhanced. To this end, a new type of solid polymer electrolyte with high thermal stability was produced with PEG-borate ester as plasticizer.^[134] The relationship between the ethylene oxide (EO) chain length of PEG-borate esters and the ionic conductivity, thermal stability, and electrochemical stability of the GPEs were carefully investigated. When the EO chain of the PEG-borate ester (CH₃O(CH₂CH₂O)_nH) had a repeating unit number of n = 3, the resulting polymer electrolyte showed the highest ionic conductivity with high thermal and electrochemical stability. The GPEs were thermally stable up to 300 °C and electrochemically stable up to 4.2 V versus Li⁺/Li at 60°C. Besides the PEG-borate ester, PVDF demonstrates good mechanical strength and chemical stability, which is another candidate to improve the thermal stability of polymer electrolyte. A hybrid of PVDF-graft-PAN copolymer with PEO (referred as m-PVDF) was prepared^[135] and showed high thermal stability up to 400 °C and good dimensional stability at 150 °C (**Figure 5**a), where PAN was used for improving the compatibility between PVDF and PEO polymers. The hybrid membrane was then applied as a conductive gel polymer electrolyte for LIBs, which showed good electrochemical stability up to 5 V (vs Li⁺/Li) (Figure 5b) and high capacity retention with a capacity decay of only 9.1% after 300 cycles. The introduction of PVDF-g-PAN largely improved the chemical and thermal stability, wettability as well as electrochemical performance of the polymer electrolyte.

Inorganics generally show better thermal stability compared with organics. Thus, introducing inorganic particles such as TiO₂^[136–138] and Al₂O₃^[56,139] nanoparticles is another strategy to improve the thermal stability of GPEs. PVDF-HFP and polymethylmethacrylate (PMMA) polymer matrixes have attracted much attention owing to their great mechanical, chemical stability and decent wettability. However, their drawbacks such as low thermal and electrochemical stability, poor cyclic and rate performances have limited their further applications. A new kind of PVDF-HFP/PMMA-based gel polymer electrolyte comprising 0-7 wt% TiO2 nanoparticles was developed to overcome the above problems.^[140] The thermal stability of the resulting polymer electrolyte was remarkably improved with the introduction of TiO₂ nanoparticles (Figure 5c). When the working temperature reached 90 °C, the weight loss of GPE with 7% TiO₂ was only 12.8% of that without TiO₂. The polymer composite electrolyte also exhibited much higher ionic conductivity $(2.49 \times 10^{-3} \text{ S cm}^{-1})$ and better electrochemical stability (5.0 V) (Figure 5d).

Last but not least, ionic liquids are competitive candidates in terms of improving the thermal stability and compatibility of the GPEs. Different kinds of ionic liquids have been developed and carefully investigated since the first air-stable ionic liquid was reported in 1992. Ionic liquids generally show high ionic conductivity and desirable thermal stability. Some ionic liquids were reported to be capable of enduring high temperatures above 400 °C. The polymerization of ionic liquids was therefore used to investigate the thermally stable GPEs. Nevertheless, the ionic conductivity of the ionic liquid would decrease with the polymerization of ionic liquid monomers, owing to the decrease of the number of mobile ions. Based on ionic liquids, a kind of GPEs with high thermally stability and high ionic conductivity had been prepared.^[141] A good thermal stability above 400 °C (Figure 5e) can be achieved by the homopolymerization of ionic liquid-based cross-linking monomers, which was key to obtain polymer network with high thermal stability. Furthermore, the ionic conductivities of the GPEs were improved (Figure 5f) by the copolymerization process of cross-linkers and ethylimidazolium-type ionic liquid monomers. The obtained polymer electrolyte films exhibited high ionic conductivity and high thermal stability.

To summarize, the thermotolerant GPEs have been developed in recent years to expand their application fields and improve the safety of the devices at high temperatures. The



Figure 5. Different kinds of GPEs with high thermal stability. a) T_g curves of the m-PVDF and PVDF blended with PAN and PEO (b-PVDF) electrolytes. b) Linear sweep voltammograms of m-PVDF and b-PVDF electrolytes at a scan rate of 1 mV s⁻¹. Reproduced with permission.^[135] Copyright 2016, Royal Society of Chemistry. c) T_g curves of PVDF-HFP/PMMA/TiO₂ electrolytes under the temperature ranging from 30 to 700 °C and 30 to 90 °C. d) Linear sweep voltammograms for PVDF-HFP/PMMA/TiO₂ polymer electrolyte. The inset shows TiO₂ content dependence of current onset potential. Reproduced with permission.^[140] Copyright 2015, Elsevier. e) T_g curves for polymers with a heating rate of 10 °C min⁻¹. f) The relationship between T_g and ionic conductivity of the salt-added systems. The numbers in panel (f) are the salt concentration (mol%). Reproduced with permission.^[141] Copyright 2005, Elsevier.

enhancement of thermal stability of the electrolyte may be realized by introducing different kinds of polymers or inorganic particles with high thermal stability and compatibility or developing ionic liquid-based polymer electrolytes. The developed thermotolerant GPEs show a high thermal stability up to 400 °C, which is very meaningful for future LIBs with both higher thermal stability and safety. Great efforts are still needed to further improve the chemical and thermal stability, wettability, and electrochemical performance of the thermally stable GPEs.

3.3. GPEs with Self-healing Ability

In recent years, the rapid development of flexible and wearable electronic devices strongly needs the corresponding



Figure 6. Self-healing GPEs. a) The molecular structure of self-assembled supramolecular gel. b) The reversible sol-gel phase transition of the supramolecular gel. c) Schematic of proposed mechanisms of self-healing behavior of the supramolecular gels. d) The initially cracked aerogel film being self-healed after introducing the supramolecular gel. Reproduced with permission.^[153] Copyright 2015, American Chemical Society. e) Preparation of the vinyl hybrid silica nanoparticle electrolyte. f) Schematic of the self-healing mechanism arising from interfacial hydrogen bonding. Reproduced with permission.^[154] Copyright 2015, Nature Publishing Group. g) Photographs of the self-healing process of carbanilated agarose ionogel in an open atmosphere. Reproduced with permission.^[151] Copyright 2015, Wiley.

power systems.^[107,142–144] These devices are generally fabricated with rather low thicknesses, aiming to guarantee a high flexibility. However, these compact structures may also result in complete breaking under complex deformations, which makes them fail to work, even cause some serious safety problems.^[145] Self-healing materials,^[146,147] which can repair their internal or external damages, have attracted great interests in both academy and industry due to their potential applications ranged from self-healing electronics, artificial electronic skin to soft robotics. Recently, several self-healing energy storage devices such as self-healing supercapacitors^[148–151] and aqueous LIBs^[152] have been fabricated with better adaptability and longer lifetime, which can be easily healed after the incidental

damages. To realize the self-healing functionality of the energy storage device, the GPEs used in according devices are required to possess similar function. Therefore, it is urgent to develop a new family of self-healing GPEs for such energy storage devices.

A self-healing hybrid gel (**Figure 6**a–c) was synthesized from supramolecular gel and nanostructured polypyrrole.^[153] The synergy between the metal-ligand supramolecule with dynamic assembly/disassembly nature and conductive polypyrrole hydrogel endowed the hybrid gel with high electrical conductivity (0.12 S cm⁻¹), good mechanical and electrical self-healing property (Figure 6d), and also enhanced their mechanical strength as well as flexibility. The "guest-to-host" strategy here



took advantage of chemical and physical features of each component, presenting an effective way to design and synthesize functional hybrid gel electrolytes. The self-healing property of the hybrid gel was further demonstrated by a flexible and selfhealing electrical circuit, which are promising in electronic devices, artificial skins, soft robotics, biomimetic prostheses, and energy storage devices.

To simultaneously realize the self-healability and high stretchability, a polymer electrolyte comprising of polyacrylic acid dual crosslinked by hydrogen bonding and vinyl hybrid silica nanoparticles^[154] was developed (Figure 6f). The polymer electrolyte demonstrated tunable ionic conductivity, self-healability, and high stretchability (over 3700% strain). Once cutting, it can be simply healed by combing the broken interfaces under ambient conditions (Figure 6g) and the properties could be recovered after breaking/healing processes. The supercapacitors based on this kind of polymer electrolytes showed intrinsic self-healability, and the specific capacitance was well maintained during 20 breaking/healing cycles, which exceeded those with conventional PVA-based acidic electrolytes. Furthermore, the polymer electrolyte exhibited an equivalent electrode capacitance compared with the commonly used PVA/H₃PO₄ electrolyte due to the movable protons in the polymer electrolyte. As an emerging greener alternative to conventional organic solvents, ILs are another candidate to develop self-healing polymer-electrolyte. A self-healing ionogel from a protic-aprotic mixed-IL system (1-butyl-3-methyl-imidazolium chloride and N-(2-hydroxyethyl) ammonium formate) was successfully prepared.^[151] As shown in Figure 6e, the ionogel demonstrated superior self-healing property. The carbanilated agarose ionogels proved suitable as a flexible solid electrolyte for activated-carbon-based supercapacitors. The resulting supercapacitors showed high electrochemical performances in terms of specific capacity and long-term durability, which proved a high potential of the ionogel for commercial applications.

Beside self-healing supercapacitors, self-healing aqueous LIBs have also been successfully fabricated by incorporating self-healing electrodes with a new aqueous lithium sulfate/ sodium carboxymethylcellulose (Li₂SO₄/CMC) as both GPE and separator.^[152] The Li₂SO₄/CMC GPE was composed of a physically cross-linked CMC gel and Li₂SO₄ aqueous solution, which showed a decent ionic conductivity of 0.12 S cm⁻¹ at room temperature. Different from the combustible and toxic organic electrolytes, the aqueous Li₂SO₄/CMC GPE was nontoxic and stable in air. The Li₂SO₄/CMC GPE displayed a good contact with the electrode. The synergy between self-healing electrode with high electrical and healing properties and aqueous Li2SO4/CMC GPE was vital to realize highly mechanically and electrochemically self-healing performance of the LIB. In particular, the electrochemical storage capability of this aqueous LIB can be well maintained during several cutting and self-healing cycles.

To summarize, self-healing GPEs that can be healed by simply combining the broken interfaces have also been explored, which offers a new and efficient strategy in the development of high-performance energy storage devices. The selfhealing energy storage devices may be particularly useful for portable and wearable electronic facilities that may easily break during use. Several self-healing GPEs have been developed and successfully applied in self-healing supercapacitors, which can be easily healed after the incidental damages and show better adaptability and longer lifetime. Although a lot of efforts have been made to develop this kind of electrolytes, most of them are merely used in self-healing supercapacitors. It remains challenging to develop self-healing GPEs with better mechanical and electrochemical performance and further apply them in batteries.

4. Conclusion and Outlook

To resolve the safety issue of toxic liquid leakage and growth of lithium dendrite derived from liquid electrolyte, it is necessary to develop a family of GPEs with higher safety and better flexibility and elasticity, which can function as both electrolyte and separator for energy storage devices. Moreover, due to their unique advantages, these GPEs are also promising for flexible and wearable electronic devices. Many attempts have been made to develop new GPEs and improve their performances with higher ionic conductivity, higher ion transfer number, better interfacial contacts between GPE and electrodes, wider electrochemical and thermal windows, and better stability and flexibility. Representative GPEs including single lithium-ion and redox-active GPEs with enhanced performances are carefully analyzed. Functional GPEs including thermotolerant, temperature-sensitive, and self-healing properties have been further highlighted on how to largely extend their applications.

The major limitations for the practical applications of singleion conducting GPEs are low ionic conductivity and inferior interfacial properties with electrodes at low temperatures, especially at ambient temperatures. The addition of redox-active mediators into the supporting GPEs benefits the performance enhancement of supercapacitors and Li-O2 batteries, while it would also lead to poor cycling stabilities because of their intrinsic inferior electrochemical stability. Great efforts have been made to develop functional GPEs for energy storage, while it is mainly limited to supercapacitors. The safety concerns of various batteries such as LIBs and lithium-sulfur batteries at high temperatures are still urgent to be solved. Besides, above functional GPEs are still limited to the lab level and are far away from real applications. It becomes urgent to study these promising properties for energy storage devices from a viewpoint of large-scale applications at preparation, structure control, and property enhancement. To this end, more efforts should be made to find appropriate GPEs for a variety of batteries that have been more used at industry and daily life.

It is also necessary to achieve the other smart functionalities such as color change to further expand the application range of GPEs for energy storage and beyond. With the rapid advance in implanted biomedical devices, it is highly desired to assemble energy storage devices in our body, and the use of GPEs is the key as the safety problem of implanted power system becomes much more important under this case. Similarly, flexible and stretchable electronic devices represent another emerging and promising direction in the future, and it is well recognized to replace liquid electrolytes with GPEs in energy storage devices that may easily break under deformation. To summarize, the development of GPEs represents a general and effective direction in making high-performance energy storage devices, and





it will continue as a mainstream direction in material, energy, biomedicine, and engineering.

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Conflict of Interest

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- [1] I. Osada, H. de Vries, B. Scrosati, S. Passerini, Angew. Chem., Int. Ed. 2016, 55, 500.
- [2] M. J. Park, I. Choi, J. Hong, O. Kim, J. Appl. Polym. Sci. 2013, 129, 2363.
- [3] J. Kalhoff, G. G. Eshetu, D. Bresser, S. Passerini, ChemSusChem 2015, 8, 2154.
- [4] S. Tan, Y. J. Ji, Z. R. Zhang, Y. Yang, ChemPhysChem 2014, 15, 1956.
- [5] J. Zhang, B. Sun, X. Huang, S. Chen, G. Wang, Sci. Rep. 2014, 4, 6007
- [6] A. Arya, A. L. Sharma, Ionics 2017, 23, 497.
- [7] Y. Cui, J. Chai, H. Du, Y. Duan, G. Xie, Z. Liu, G. Cui, ACS Appl. Mater. Interfaces 2017, 9, 8737.
- [8] Y. Zhang, Y. Zhao, X. Cheng, W. Weng, J. Ren, X. Fang, Y. Jiang, P. Chen, Z. Zhang, Y. Wang, H. Peng, *Angew. Chem., Int. Ed.* 2015, 54, 11177.
- [9] W. Weng, Q. Sun, Y. Zhang, S. He, Q. Wu, J. Deng, X. Fang, G. Guan, J. Ren, H. Peng, *Adv. Mater.* 2015, *27*, 1363.
- [10] Y. Takeda, O. Yamamoto, N. Imanishi, *Electrochemistry* 2016, 84, 210.
- [11] L. Porcarelli, C. Gerbaldi, F. Bella, J. R. Nair, Sci. Rep. 2016, 6, 19892.
- [12] Q. Lu, Y.-B. He, Q. Yu, B. Li, Y. V. Kaneti, Y. Yao, F. Kang, Q.-H. Yang, Adv. Mater. 2017, 29, 1604460.
- [13] J. Hu, J. Tian, C. Li, ACS Appl. Mater. Interfaces 2017, 9, 11615.
- [14] H. Gao, B. Guo, J. Song, K. Park, J. B. Goodenough, Adv. Energy Mater. 2015, 5, 1402235.
- [15] J. Jin, Z. Wen, X. Liang, Y. Cui, X. Wu, Solid State Ionics 2012, 225, 604.
- [16] S.-Y. Lee, A. Ogawa, M. Kanno, H. Nakamoto, T. Yasuda, M. Watanabe, J. Am. Chem. Soc. 2010, 132, 9764.
- [17] J. Chen, M. Asano, T. Yamaki, M. Yoshida, J. Membr. Sci. 2006, 269, 194.
- [18] C. Zhao, C. Wang, Z. Yue, K. Shu, G. G. Wallace, ACS Appl. Mater. Interfaces 2013, 5, 9008.
- [19] Y. Huang, M. Zhong, F. Shi, X. Liu, Z. Tang, Y. Wang, Y. Huang, H. Hou, X. Xie, C. Zhi, Angew. Chem., Int. Ed. 2017, 56, 9141.

- [20] W. H. Meyer, Adv. Mater. 1998, 10, 439.
- [21] M. Armand, Adv. Mater. 1990, 2, 278.
- [22] C. Berthier, W. Gorecki, M. Minier, M. B. Armand, J. M. Chabagno, P. Rigaud, *Solid State Ionics* **1983**, *11*, 91.
- [23] H. Sun, X. Fu, S. Xie, Y. Jiang, H. Peng, Adv. Mater. 2016, 28, 2070.
- [24] J. Qiao, J. Fu, R. Lin, J. Ma, J. Liu, Polymer 2010, 51, 4850.
- [25] W. Lu, K. Henry, C. Turchi, J. Pellegrino, J. Electrochem. Soc. 2008, 155, A361.
- [26] M. Grünebaum, M. M. Hiller, S. Jankowsky, S. Jeschke, B. Pohl, T. Schürmann, P. Vettikuzha, A.-C. Gentschev, R. Stolina, R. Müller, H.-D. Wiemhöfer, Prog. Solid State Chem. 2014, 42, 85.
- [27] M. Marcinek, J. Syzdek, M. Marczewski, M. Piszcz, L. Niedzicki, M. Kalita, A. Plewa-Marczewska, A. Bitner, P. Wieczorek, T. Trzeciak, M. Kasprzyk, P. Łężak, Z. Zukowska, A. Zalewska, W. Wieczorek, *Solid State Ionics* **2015**, *276*, 107.
- [28] V. Aravindan, J. Gnanaraj, S. Madhavi, H.-K. Liu, Chem. Eur. J. 2011, 17, 14326.
- [29] H. Y. Sung, Y. Y. Wang, C. C. Wan, J. Electrochem. Soc. 1998, 145, 1207.
- [30] N. S. Mohamed, A. K. Arof, J. Power Sources 2004, 132, 229.
- [31] H.-S. Kim, S.-I. Moon, J. Power Sources 2005, 146, 584.
- [32] J. J. Xu, H. Ye, Electrochem. Commun. 2005, 7, 829.
- [33] J. M. Tarascon, A. S. Gozdz, C. Schmutz, F. Shokoohi, P. C. Warren, Solid State Ionics 1996, 86, 49.
- [34] T.-H. Young, L.-W. Chen, Desalination 1995, 103, 233.
- [35] A. Du Pasquier, P. C. Warren, D. Culver, A. S. Gozdz, G. G. Amatucci, J. M. Tarascon, *Solid State Ionics* 2000, 135, 249.
- [36] A. M. Stephan, D. Teeters, *Electrochim. Acta* 2003, 48, 2143.
- [37] W. Pu, X. He, L. Wang, C. Jiang, C. Wan, J. Membr. Sci. 2006, 272, 11.
- [38] Z. H. Li, P. Zhang, H. P. Zhang, Y. P. Wu, X. D. Zhou, *Electrochem. Commun.* 2008, 10, 791.
- [39] W. Pu, X. He, L. Wang, Z. Tian, C. Jiang, C. Wan, J. Membr. Sci. 2006, 280, 6.
- [40] M. Gu, J. Zhang, Y. Xia, X. Wang, J. Macromol. Sci. B 2007, 47, 180.
- [41] S. Thayumanasundaram, V. S. Rangasamy, J. W. Seo, J.-P. Locquet, Eur. J. Inorg. Chem. 2015, 2015, 5395.
- [42] M. Moskwiak, I. Giska, R. Borkowska, A. Zalewska, M. Marczewski, H. Marczewska, W. Wieczorek, J. Power Sources 2006, 159, 443.
- [43] N. T. K. Sundaram, A. Subramania, Electrochim. Acta 2007, 52, 4987.
- [44] C. H. Park, D. W. Kim, J. Prakash, Y.-K. Sun, Solid State Ionics 2003, 159, 111.
- [45] A. Magistris, P. Mustarelli, E. Quartarone, C. Tomasi, Solid State Ionics 2000, 136–137, 1241.
- [46] Y. Liu, J. Y. Lee, L. Hong, J. Appl. Polym. Sci. 2003, 89, 2815.
- [47] T. Itoh, Y. Miyamura, Y. Ichikawa, T. Uno, M. Kubo, O. Yamamoto, J. Power Sources 2003, 119–121, 403.
- [48] C. Capiglia, J. Yang, N. Imanishi, A. Hirano, Y. Takeda, O. Yamamoto, Solid State Ionics 2002, 154, 7.
- [49] B. Kumar, L. G. Scanlon, J. Power Sources 1994, 52, 261.
- [50] Z. Wen, T. Itoh, M. Ikeda, N. Hirata, M. Kubo, O. Yamamoto, J. Power Sources 2000, 90, 20.
- [51] J.-W. Kim, K.-S. Ji, J.-P. Lee, J.-W. Park, J. Power Sources 2003, 119, 415.
- [52] J. Xi, X. Tang, Chem. Phys. Lett. 2004, 400, 68.
- [53] Y. Liu, J. Y. Lee, L. Hong, J. Power Sources 2002, 109, 507.
- [54] V. Zoulalian, S. Monge, S. Zürcher, M. Textor, J. J. Robin, S. Tosatti, J. Phys. Chem. B 2006, 110, 25603.
- [55] W.-S. Young, T. H. Epps, Macromolecules 2012, 45, 4689.
- [56] Z. Li, G. Su, X. Wang, D. Gao, Solid State Ionics 2005, 176, 1903.
- [57] L. Lee, S.-J. Park, S. Kim, Solid State Ionics 2013, 234, 19.
- [58] J. Nunes-Pereira, M. Kundu, A. Gören, M. M. Silva, C. M. Costa, L. Liu, S. Lanceros-Méndez, *Composites, Part B* 2016, 96, 94.





- [59] W. Li, Y. Xing, Y. Wu, J. Wang, L. Chen, G. Yang, B. Tang, *Electrochim. Acta* 2015, 151, 289.
- [60] C. J. Leo, A. K. Thakur, G. V. S. Rao, B. V. R. Chowdari, J. Power Sources 2003, 115, 295.
- [61] G. P. Pandey, S. A. Hashmi, J. Power Sources 2013, 243, 211.
- [62] X.-G. Sun, J. B. Kerr, Macromolecules 2006, 39, 362.
- [63] H. Zhang, C. Li, M. Piszcz, E. Coya, T. Rojo, L. M. Rodriguez-Martinez, M. Armand, Z. Zhou, *Chem. Soc. Rev.* 2017, 46, 797.
- [64] R. Meziane, J.-P. Bonnet, M. Courty, K. Djellab, M. Armand, *Electrochim. Acta* 2011, 57, 14.
- [65] A. A. Rojas, S. Inceoglu, N. G. Mackay, J. L. Thelen, D. Devaux, G. M. Stone, N. P. Balsara, *Macromolecules* 2015, 48, 6589.
- [66] Q. Ma, H. Zhang, C. Zhou, L. Zheng, P. Cheng, J. Nie, W. Feng, Y.-S. Hu, H. Li, X. Huang, L. Chen, M. Armand, Z. Zhou, Angew. Chem., Int. Ed. 2016, 55, 2521.
- [67] X. Wang, Z. Liu, C. Zhang, Q. Kong, J. Yao, P. Han, W. Jiang, H. Xu, G. Cui, *Electrochim. Acta* **2013**, *92*, 132.
- [68] B. Qin, Z. Liu, G. Ding, Y. Duan, C. Zhang, G. Cui, *Electrochim. Acta* 2014, 141, 167.
- [69] Y. Zhang, W. Cai, R. Rohan, M. Pan, Y. Liu, X. Liu, C. Li, Y. Sun, H. Cheng, J. Power Sources 2016, 306, 152.
- [70] S. Feng, D. Shi, F. Liu, L. Zheng, J. Nie, W. Feng, X. Huang, M. Armand, Z. Zhou, *Electrochim. Acta* **2013**, *93*, 254.
- [71] Y. Kim, S. J. Kwon, H.-k. Jang, B. M. Jung, S. B. Lee, U. H. Choi, *Chem. Mater.* 2017, 29, 4401.
- [72] R. Rohan, K. Pareek, Z. Chen, W. Cai, Y. Zhang, G. Xu, Z. Gao, H. Cheng, J. Mater. Chem. A 2015, 3, 20267.
- [73] Q. Pan, Y. Chen, Y. Zhang, D. Zeng, Y. Sun, H. Cheng, J. Power Sources 2016, 336, 75.
- [74] R. Rohan, Y. Sun, W. Cai, K. Pareek, Y. Zhang, G. Xu, H. Cheng, J. Mater. Chem. A 2014, 2, 2960.
- [75] R. Rohan, K. Pareek, W. Cai, Y. Zhang, G. Xu, Z. Chen, Z. Gao, Z. Dan, H. Cheng, J. Mater. Chem. A 2015, 3, 5132.
- [76] H. Oh, K. Xu, H. D. Yoo, D. S. Kim, C. Chanthad, G. Yang, J. Jin, I. A. Ayhan, S. M. Oh, Q. Wang, *Chem. Mater.* **2016**, *28*, 188.
- [77] Y. Zhang, R. Rohan, Y. Sun, W. Cai, G. Xu, A. Lin, H. Cheng, RSC Adv. 2014, 4, 21163.
- [78] V. Aravindan, P. Vickraman, Ionics 2007, 13, 277.
- [79] Y. S. Zhu, X. J. Wang, Y. Y. Hou, X. W. Gao, L. L. Liu, Y. P. Wu, M. Shimizu, *Electrochim. Acta* **2013**, *87*, 113.
- [80] Y. S. Zhu, X. W. Gao, X. J. Wang, Y. Y. Hou, L. L. Liu, Y. P. Wu, Electrochem. Commun. 2012, 22, 29.
- [81] S.-E. Chun, B. Evanko, X. Wang, D. Vonlanthen, X. Ji, G. D. Stucky, S. W. Boettcher, *Nat. Commun.* 2015, *6*, 7818.
- [82] S. Roldán, C. Blanco, M. Granda, R. Menéndez, R. Santamaría, Angew. Chem., Int. Ed. 2011, 50, 1699.
- [83] S. T. Senthilkumar, R. K. Selvan, N. Ponpandian, J. S. Melo, RSC Adv. 2012, 2, 8937.
- [84] S. Roldán, M. Granda, R. Menéndez, R. Santamaría, C. Blanco, *Electrochim. Acta* 2012, 83, 241.
- [85] S. Roldán, Z. González, C. Blanco, M. Granda, R. Menéndez, R. Santamaría, *Electrochim. Acta* 2011, 56, 3401.
- [86] G. Ma, E. Feng, K. Sun, H. Peng, J. Li, Z. Lei, *Electrochim. Acta* 2014, 135, 461.
- [87] H. Yu, L. Fan, J. Wu, Y. Lin, M. Huang, J. Lin, Z. Lan, RSC Adv. 2012, 2, 6736.
- [88] G. Lota, G. Milczarek, Electrochem. Commun. 2011, 13, 470.
- [89] H. Yu, J. Wu, L. Fan, K. Xu, X. Zhong, Y. Lin, J. Lin, Electrochim. Acta 2011, 56, 6881.
- [90] J. Han, G. Huang, Y. Ito, X. Guo, T. Fujita, P. Liu, A. Hirata, M. Chen, Adv. Energy Mater. 2017, 7, 1601933.
- [91] S. T. Senthilkumar, R. K. Selvan, N. Ponpandian, J. S. Melo, Y. S. Lee, J. Mater. Chem. A 2013, 1, 7913.

- [92] S. T. Senthilkumar, R. K. Selvan, J. S. Melo, C. Sanjeeviraja, ACS Appl. Mater. Interfaces 2013, 5, 10541.
- [93] L.-Q. Mai, A. Minhas-Khan, X. Tian, K. M. Hercule, Y.-L. Zhao, X. Lin, X. Xu, Nat. Commun. 2013, 4, 2923.
- [94] G. Lota, E. Frackowiak, Electrochem. Commun. 2009, 11, 87.
- [95] S. Pan, J. Deng, G. Guan, Y. Zhang, P. Chen, J. Ren, H. Peng, J. Mater. Chem. A 2015, 3, 6286.
- [96] R. Xu, F. Guo, X. Cui, L. Zhang, K. Wang, J. Wei, J. Mater. Chem. A 2015, 3, 22353.
- [97] S. Maiti, A. Pramanik, S. Mahanty, ACS Appl. Mater. Interfaces 2014, 6, 10754.
- [98] S. T. Senthilkumar, R. K. Selvan, M. Ulaganathan, J. S. Melo, *Electrochim. Acta* 2014, 115, 518.
- [99] L. Su, L. Gong, H. Lü, Q. Xü, J. Power Sources 2014, 248, 212.
- [100] C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang, J. Zhang, Chem. Soc. Rev. 2015, 44, 7484.
- [101] G. Lota, K. Fic, E. Frackowiak, Electrochem. Commun. 2011, 13, 38.
- [102] L.-Q. Fan, J. Zhong, J.-H. Wu, J.-M. Lin, Y.-F. Huang, J. Mater. Chem. A 2014, 2, 9011.
- [103] E. Frackowiak, K. Fic, M. Meller, G. Lota, ChemSusChem 2012, 5, 1181.
- [104] J. Zhong, L.-Q. Fan, X. Wu, J.-H. Wu, G.-J. Liu, J.-M. Lin, M.-L. Huang, Y.-L. Wei, *Electrochim. Acta* **2015**, *166*, 150.
- [105] J.-J. Xu, Q.-C. Liu, Y. Yu, J. Wang, J.-M. Yan, X.-B. Zhang, Adv. Mater. 2017, 29, 1606552.
- [106] Q.-C. Liu, T. Liu, D.-P. Liu, Z.-J. Li, X.-B. Zhang, Y. Zhang, *Adv. Mater.* 2016, 28, 8413.
- [107] T. Liu, Q.-C. Liu, J.-J. Xu, X.-B. Zhang, Small 2016, 12, 3101.
- [108] T. Liu, Z. Chang, Y. Yin, K. Chen, Y. Zhang, X. Zhang, Solid State Ionics 2017; https://doi.org/10.1016/j.ssi.2017.08.001.
- [109] J. Zhang, B. Sun, X. Xie, K. Kretschmer, G. Wang, *Electrochim. Acta* 2015, 183, 56.
- [110] J. Yi, S. Guo, P. He, H. Zhou, Energy Environ. Sci. 2017, 10, 860.
- [111] X. Zeng, L. Leng, F. Liu, G. Wang, Y. Dong, L. Du, L. Liu, S. Liao, *Electrochim. Acta* **2016**, 200, 231.
- [112] Z. Liang, Y.-C. Lu, J. Am. Chem. Soc. 2016, 138, 7574.
- [113] Y. Chen, S. A. Freunberger, Z. Peng, O. Fontaine, P. G. Bruce, *Nat. Chem.* 2013, 5, 489.
- [114] N. Feng, P. He, H. Zhou, ChemSusChem 2015, 8, 600.
- [115] B. J. Bergner, A. Schürmann, K. Peppler, A. Garsuch, J. Janek, J. Am. Chem. Soc. 2014, 136, 15054.
- [116] D. Kundu, R. Black, B. Adams, L. F. Nazar, ACS Cent. Sci. 2015, 1, 510.
- [117] J. Yi, S. Wu, S. Bai, Y. Liu, N. Li, H. Zhou, J. Mater. Chem. A 2016, 4, 2403.
- [118] Z. Guo, C. Li, J. Liu, Y. Wang, Y. Xia, Angew. Chem., Int. Ed. 2017, 129, 7613.
- [119] J. B. Goodenough, K.-S. Park, J. Am. Chem. Soc. 2013, 135, 1167.
- [120] Y. Shi, L. Peng, Y. Ding, Y. Zhao, G. Yu, Chem. Soc. Rev. 2015, 44, 6684.
- [121] Z. Yu, L. Tetard, L. Zhai, J. Thomas, *Energy Environ. Sci.* 2015, *8*, 702.
- [122] Z. Chen, P.-C. Hsu, J. Lopez, Y. Li, J. W. F. To, N. Liu, C. Wang, S. C. Andrews, J. Liu, Y. Cui, Z. Bao, *Nat. Energy* **2016**, *1*, 15009.
- [123] X. Feng, J. Sun, M. Ouyang, F. Wang, X. He, L. Lu, H. Peng, J. Power Sources 2015, 275, 261.
- [124] N.-S. Choi, Z. Chen, S. A. Freunberger, X. Ji, Y.-K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho, P. G. Bruce, *Angew. Chem., Int. Ed.* 2012, *51*, 9994.
- [125] L. Lu, X. Han, J. Li, J. Hua, M. Ouyang, J. Power Sources 2013, 226, 272.
- [126] D. P. Finegan, M. Scheel, J. B. Robinson, B. Tjaden, I. Hunt, T. J. Mason, J. Millichamp, M. Di Michiel, G. J. Offer, G. Hinds, D. J. L. Brett, P. R. Shearing, *Nat. Commun.* **2015**, *6*, 6924.



- [127] Y. Tang, Y. Zhang, J. Deng, J. Wei, H. L. Tam, B. K. Chandran, Z. Dong, Z. Chen, X. Chen, Adv. Mater. 2014, 26, 6111.
- [128] Y. Xu, Y. Zhang, Z. Guo, J. Ren, Y. Wang, H. Peng, Angew. Chem., Int. Ed. 2015, 54, 15390.
- [129] H. Zhang, Y. Zhang, Z. Yao, A. E. John, Y. Li, W. Li, B. Zhu, *Electrochim. Acta* **2016**, 204, 176.
- [130] J. C. Kelly, M. Pepin, D. L. Huber, B. C. Bunker, M. E. Roberts, *Adv. Mater.* 2012, 24, 886.
- [131] J. C. Kelly, N. L. Degrood, M. E. Roberts, Chem. Commun. 2015, 51, 5448.
- [132] H. Yang, Z. Liu, B. K. Chandran, J. Deng, J. Yu, D. Qi, W. Li, Y. Tang, C. Zhang, X. Chen, Adv. Mater. 2015, 27, 5593.
- [133] Y. Shi, H. Ha, A. Al-Sudani, C. J. Ellison, G. Yu, Adv. Mater. 2016, 28, 7921.
- [134] Y. Kato, K. Hasumi, S. Yokoyama, T. Yabe, H. Ikuta, Y. Uchimoto, M. Wakihara, Solid State Ionics 2002, 150, 355.
- [135] C.-Y. Hsu, R.-J. Liu, C.-H. Hsu, P.-L. Kuo, RSC Adv. 2016, 6, 18082.
- [136] S. Zhang, J. Cao, Y. Shang, L. Wang, X. He, J. Li, P. Zhao, Y. Wang, J. Mater. Chem. A 2015, 3, 17697.
- [137] W. Chen, Y. Liu, Y. Ma, W. Yang, J. Power Sources 2015, 273, 1127.
- [138] B. Kurc, Electrochim. Acta 2014, 125, 415.
- [139] H.-S. Jeong, D.-W. Kim, Y. U. Jeong, S.-Y. Lee, J. Power Sources 2010, 195, 6116.
- [140] D. Song, C. Xu, Y. Chen, J. He, Y. Zhao, P. Li, W. Lin, F. Fu, Solid State Ionics 2015, 282, 31.
- [141] H. Nakajima, H. Ohno, Polymer 2005, 46, 11499.
- [142] H. Nishide, K. Oyaizu, Science 2008, 319, 737.

- [143] G. Zhou, F. Li, H.-M. Cheng, Energy Environ. Sci. 2014, 7, 1307.
- [144] L. Hu, H. Wu, F. La Mantia, Y. Yang, Y. Cui, ACS Nano 2010, 4, 5843.
- [145] E.-H. Kil, K.-H. Choi, H.-J. Ha, S. Xu, J. A. Rogers, M. R. Kim, Y.-G. Lee, K. M. Kim, K. Y. Cho, S.-Y. Lee, *Adv. Mater.* **2013**, *25*, 1395.
- [146] P. Cordier, F. Tournilhac, C. Soulie-Ziakovic, L. Leibler, Nature 2008, 451, 977.
- [147] C.-H. Li, C. Wang, C. Keplinger, J.-L. Zuo, L. Jin, Y. Sun, P. Zheng, Y. Cao, F. Lissel, C. Linder, X.-Z. You, Z. Bao, *Nat. Chem.* 2016, *8*, 618.
- [148] H. Sun, X. You, Y. Jiang, G. Guan, X. Fang, J. Deng, P. Chen, Y. Luo, H. Peng, Angew. Chem., Int. Ed. 2014, 53, 9526.
- [149] H. Wang, B. Zhu, W. Jiang, Y. Yang, W. R. Leow, H. Wang, X. Chen, *Adv. Mater.* 2014, 26, 3638.
- [150] Y. Huang, Y. Huang, M. Zhu, W. Meng, Z. Pei, C. Liu, H. Hu, C. Zhi, ACS Nano 2015, 9, 6242.
- [151] T. J. Trivedi, D. Bhattacharjya, J.-S. Yu, A. Kumar, ChemSusChem 2015, 8, 3294.
- [152] Y. Zhao, Y. Zhang, H. Sun, X. Dong, J. Cao, L. Wang, Y. Xu, J. Ren, Y. Hwang, I. H. Son, X. Huang, Y. Wang, H. Peng, *Angew. Chem.*, *Int. Ed.* **2016**, *55*, 14384.
- [153] Y. Shi, M. Wang, C. Ma, Y. Wang, X. Li, G. Yu, Nano Lett. 2015, 15, 6276.
- [154] Y. Huang, M. Zhong, Y. Huang, M. Zhu, Z. Pei, Z. Wang, Q. Xue, X. Xie, C. Zhi, *Nat. Commun.* **2015**, *6*, 10310.