

MATERIALS SCIENCE

Functional membrane separators for next-generation high-energy rechargeable batteries

Yuede Pan^{1,2}, Shulei Chou¹, Hua Kun Liu¹ and Shi Xue Dou^{1,*}

ABSTRACT

The membrane separator is a key component in a liquid-electrolyte battery for electrically separating the cathode and the anode, meanwhile ensuring ionic transport between them. Besides these basic requirements, endowing the separator with specific beneficial functions is now being paid great attention because it provides an important alternative approach for the development of batteries, particularly next-generation high-energy rechargeable batteries. Herein, functional separators are overviewed based on four key criteria of next-generation high-energy rechargeable batteries: stable, safe, smart and sustainable (4S). That is, the applied membrane materials and the corresponding functioning mechanisms of the 4S separators are reviewed. Functional separators with selective permeability have been applied to retard unwanted migration of the specific species (e.g. polysulfide anions in Li-S batteries) from one electrode to the other in order to achieve stable cycling operation. The covered battery types are Li-S, room-temperature Na-S, Li-organic, organic redox-flow (RF) and Li-air batteries. Safe, smart and sustainable separators are then described in sequence following the first criterion of stable cycling. In the final section, key challenges and potential opportunities in the development of 4S separators are discussed.

Keywords: functional, 4S separators, stable, safe, smart, sustainable

INTRODUCTION

The separator in an electrochemical battery system is typically a porous polymer membrane that is wetted by the liquid electrolyte and located between the cathode and the anode [1–5]. ‘Functional’, according to the Oxford Dictionary, means ‘*of or having a special activity, purpose, or task*’. In light of this definition, functional membrane separators refer to separators that are endowed with some specific characteristics, which are capable of ameliorating the assembled batteries in terms of electrochemical performance, safety property or battery management, etc. In this review article, the scope is limited to liquid-electrolyte batteries but excludes solid-electrolyte batteries, in which the separator is not needed because the solid electrolyte bears dual functions of both the electrolyte and the separator.

In general, regarding conventional batteries, membrane separators are made of different kinds of polymer materials depending on the different chemistries in varied battery types (e.g. lead-acid, nickel-metal hydride, lithium-ion batteries). Con-

ventional separators normally are porous structure with the pore size of hundreds of nanometers. Particularly, to satisfy the characteristic requirements of lithium-ion batteries, porous polyolefin separators have been developed and widely employed, because they possess excellent mechanical properties, high chemical stability and acceptable cost [6,7]. New functional membrane materials, whether constructed as independent separators or as integrated components, are highly required for application in next-generation high-energy rechargeable battery systems owing to their characteristic challenges different from the conventional battery types.

Herein, based on the work relating to functional membrane separators that has been reported in recent several years, the membrane materials and strategies that enable 4S (stable, safe, smart, sustainable) high-energy batteries are presented (Fig. 1). Stable cycling is indispensable for obtaining long-life energy-storage systems. For instance, the Li-S battery is attractive for its high theoretical capacity of 1675 mA h g^{-1} ; however, the cycle life needs

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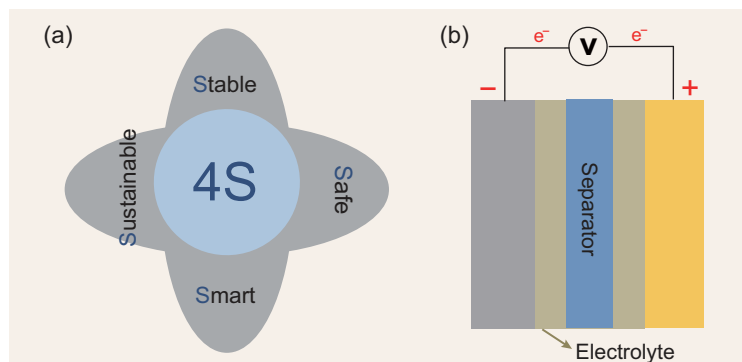


Figure 1. Schematic illustrations of (a) four important criteria, i.e. 4S (Stable, Safe, Smart, Sustainable), for next-generation high-energy rechargeable batteries based on the study of functional membrane separators and (b) structure of a rechargeable battery with a separator.

further improvement [8–10]. One important reason for this quick capacity decay can be referred to the dissolution of the intermediate product of polysulfide and the shuttling issue [11]. This similar problem also exists in several other important types of next-generation batteries such as Li-organic [12,13] and Li-air [14] batteries—that is, there is unwanted diffusion of species across the separator, which causes unstable cycling due to the loss of the electroactive material or the contamination of the other electrode. To suppress the unwanted species diffusion and allow the transport of the component ion, ion-selective separators are highly demanded for application in these battery types to achieve higher active material utilization and stable anode surface. In this review article, we try to break the boundaries among five battery types (Li-S, room-temperature Na-S, Li-organic, organic redox flow (RF) and Li-air) and focus on the applied functional separators, the component materials and the corresponding functioning mechanisms.

Following the paragraphs that focus on the aspect of ‘Stable’ for the 4S batteries, functional separators enabling ‘Safe’ operation are overviewed. The battery safety performance is an important topic of all time, particularly considering that, in the year 2016, a series of burnings or explosions of consumer electronics and electric vehicles powered by lithium-ion batteries have happened. The safety of batteries is closely related to the life and property security of customers. In this regard, ‘Safe’ separators are highly needed to enhance the battery safety performance. On the one hand, high thermal/dimensional stability of separators decreases the risk of catching fire or exploding in case of heat accumulation and temperature rise. On the other hand, separators with improved wetting capability or thermal conductivity suppress the lithium dendrite growth when the lithium metal anode is applied, lowering the safety hazards.

‘Smart’, the third criterion of the 4S separators, represents a future direction for developing advanced battery-management systems. Smart separators refer to those capable of responding to stimuli such as voltage or temperature. For instance, separators with voltage-gating nanopores control the on/off of the battery by changing the applied extra voltages. To improve the eco-friendliness of the separator, renewable polymers such as biomass-based cellulose have been employed as fascinating alternatives for fossil-based polyolefin separators, enabling ‘Sustainable’ separators. Finally, the advanced separators for 4S batteries are briefly summarized and our perspective regarding the future directions is given.

SEPARATORS FOR STABLE CYCLING

For next-generation batteries of Li-S, room-temperature Na-S, Li-organic, organic RF and Li-air, it is challenging to achieve stable cycling because, in all these battery types, the unwanted diffusion of some specific species (e.g. polysulfide in Li-S batteries) across the separator causes active material loss or unstable solid–electrolyte interface. The shuttling of polysulfide, which is solvable intermediate product in the charge/discharge process, leads to quick capacity decay in Li-S [15,16] (Fig. 2a) and room-temperature Na-S batteries [17,18] (Fig. 2b). In organic-based batteries [19–21] (Fig. 2c and d), the electrode material of organic molecules normally can be dissolved in the aprotic electrolyte, resulting in the similar shuttling problem as in Li-S batteries. In Li-air batteries [22] (Fig. 2e), the migration of moisture and oxygen from the air cathode to the lithium anode leads to unstable cycling. Therefore, ion-selective separators are highly desired to overcome this mutual issue and obtain stable cycling for these battery systems. In this section, a wide range of the applied materials for the ion-selective separator are described, as well as their structures, properties and functioning mechanisms. These functional membrane materials include Nafion (protonated, lithiated or sodiated), polymer of intrinsic microporosity (PIM), Polyurethane (PU), metal organic framework (MOF), graphene oxide (GO) and lithium superionic conductor (LISICON). With respect to Li-S batteries, in addition to the ion-selecting strategy, other approaches such as separator-cathode integration, separator coating with polysulfide reactivating materials are also described.

Nafion-based materials

Nafion, a commercial product developed and produced by DuPont company, is an important

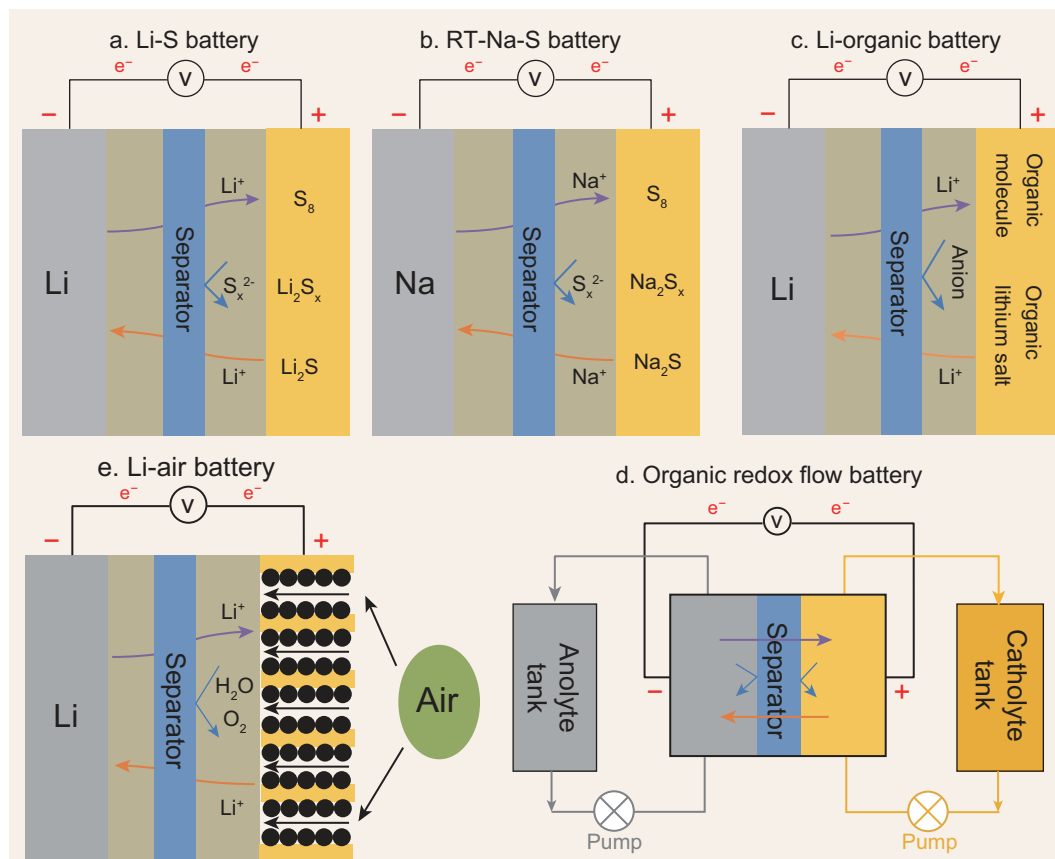


Figure 2. Schematic illustrations of stable batteries enabled by ion-selective membrane separators. The next-generation batteries include (a) Li-S, (b) room-temperature Na-S, (c) Li-organic, (d) organic RF and (e) Li-air batteries. Polysulfide or organic anions are suppressed from flowing to the lithium anode in (a, b, c). Certain component ions are selectively allowed to migrate across the separator in (d). In (e), oxygen and moisture that might contaminate the lithium anode are confined at the cathode side.

ion-selective polymer material [23,24]. Nafion is synthesized by copolymerization of tetrafluoroethylene and a perfluorinated vinyl ether comonomer [25,26]. Normally, Nafion is referred to its protonated form, but the proton can be ion exchanged with other cations such as lithium and sodium ions [27]. The chemical structure of Nafion is given in Fig. 3a.

In the early stage of research and development, Nafion perfluorosulfonate ionomer was applied as a perm-selective membrane separator in electrochemical cells for large-scale industrial production of NaOH, KCl and Cl₂. Nafion not only keeps gases of Cl₂ and H₂ separated, but also prevents the undesired migration of OH⁻ ions; meanwhile, it allows the transport of hydrated Na⁺ ions. The important applications of Nafion involve proton exchange membrane in fuel cells and the selective membrane in vanadium redox-flow batteries (RFBs) [28]. Regarding the nanostructure of Nafion, although until now there is still no universally accepted model, the following several important mor-

phological models are widely recognized for understanding of the ion selectivity of Nafion.

In the 1980s, Gierke *et al.* developed the cluster-network model (Fig. 3b) based on small-angle X-ray scattering (SAXS) studies. Gierke's model has endured for many years to be a conceptual basis for rationalizing the ion and water transport, as well as the ion permselectivity [29]. It is presumed that clusters ($d = 4$ nm) of sulfonate-ended perfluoroalkyl ether groups are organized as inverted micelles, which are connected by channels with a dimension of 1 nm. These channels with surface sulfonate groups account for intercluster ion hopping of positively charged ions and rejection of anions. Another important model is the three-phase model proposed by Yeager and Steck, based on their studies of the diffusion of varied ions [30]. Differently from Gierke's model, their model involves clusters with no strict geometrical definition. More importantly, their model includes transitional interphases between hydrophilic and hydrophobic regions—a viewpoint that has become generally

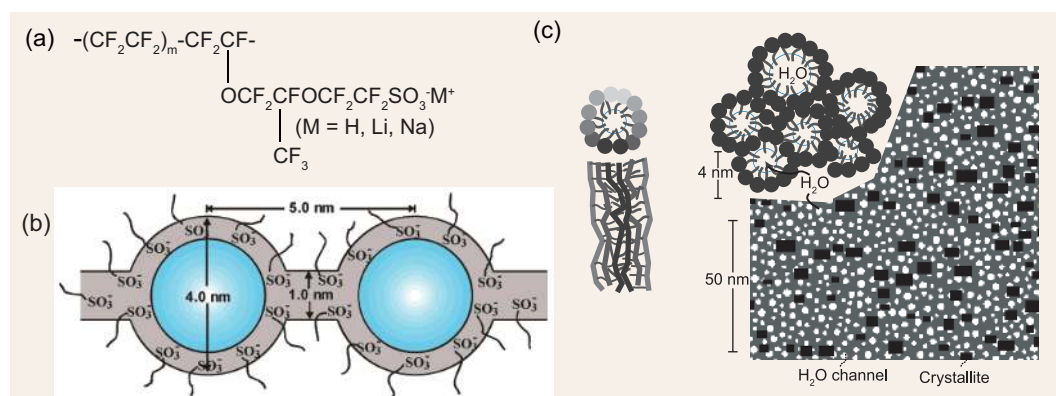


Figure 3. Structure and morphological models of Nafion. (a) Molecular structure of Nafion (protonated, lithiated and sodiated). Two typical morphological models of solvent-swelled Nafion based on (b) inverted micelles clusters and (c) nanochannels, respectively. (b) Adapted with permission from [29], Copyright 2004, American Chemical Society; (c) adapted with permission from [31], Copyright 2008, Nature Publishing Group.

accepted. Recently, Schmidt-rohr *et al.* reported a water channel model for hydrated Nafion, which is characteristic by the long parallel but randomly packed water channels (diameter ranging between ca. 2 nm and ca. 4 nm) surrounded by partially hydrophilic side branches, forming inverted-micelle cylinders (Fig. 3c) [31]. Nafion crystallites, which determine the mechanical properties of Nafion films, are elongated and parallel to the water channels.

Based on the morphological models of hydrated Nafion, Nafion swelled by other non-aqueous liquids such as organic solvents and ionic liquids have also been investigated [32,33]. Nafion can be used in its H^+ -form, or can be lithiated/sodiated to be compatible with lithium/sodium salt solutions. The applied battery systems include Li-S, room-temperature Na-S, Li-organic and organic RFBs.

Sulfur has been considered a promising candidate as the next-generation cathode materials for its high capacity (1675 mA h g^{-1}), abundance and low cost. Typically, the sulfur cathode is the composite between sulfur and a conductive material such as carbon, conductive polymer or metal oxide [34]. The sulfur cathode can be coupled with anodes of lithium metal or sodium metal to construct Li-S or room-temperature Na-S batteries, respectively. The term ‘room-temperature’ is used for distinguishing from high-temperature Na-S batteries operated at approximately 350°C with beta-alumina as the sodium-ion conducting solid electrolyte [35]. The elemental sulfur in the sulfur cathode is reduced to solid $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ or $\text{Na}_2\text{S}/\text{Na}_2\text{S}_2$ via intermediate polysulfide products of Li_2S_x or Na_2S_x ($4 \leq x \leq 8$). The lithium or sodium polysulfide is solvable in the electrolyte, resulting in not only the loss of active material from the cathode, but also diffusion of the species to the lithium metal anode to form

unstable solid–electrolyte interface on the lithium surface. Besides, the undesired shuttling problem is also produced, i.e. the dissolved sulfur species with higher oxidation state migrate to the anode for reduction at charge and then return to the cathode for re-oxidation, and so on [36].

In 2012, Li-Nafion film was first reported as the functional separator for Li-S cells (Fig. 1a) [37]. A Nafion-212 film (thickness: $51 \mu\text{m}$) purchased from DuPont company was lithiated in LiOH solution (solvent: $\text{H}_2\text{O}/\text{ethanol}$). The structure of the as-prepared Li-Nafion was characterized by Fourier Transform Infrared spectroscopy (FTIR) and the high permeability for Li^+ and against anions was proved by the as-measured superior transference number of Li^+ (0.986). As a result, compared with the cells with conventional polyolefin separators, those with the Li-Nafion separators demonstrated that both the cycling stability and the Coulombic efficiency were significantly improved. However, the 51-mm-thick Li-Nafion causes a voltage drop of approximately 0.2 V. This issue was resolved in 2014 by Bauer *et al.* [38], who reported a thin Li-Nafion coating (0.25 mg cm^{-2}) on the commercial polyolefin separator. A visual experiment revealed the suppressed diffusion of polysulfide anions by the separator coated by Li-Nafion, compared with the uncoated separator (Fig. 4a). Moreover, the significantly reduced amount of Nafion applied in the separator brings down the cost, considering the high price of Nafion. In the same year, Huang *et al.* [39] reported Nafion-coated (0.7 mg cm^{-2}) separators used in Li-S batteries, which exhibit a long life of 500 cycles and greatly improved Coulombic efficiency (Fig. 4b). In 2015, Yu *et al.* [40] reported a freestanding Li-Nafion membrane as the separator in the Li-S battery, coupled with a lithium

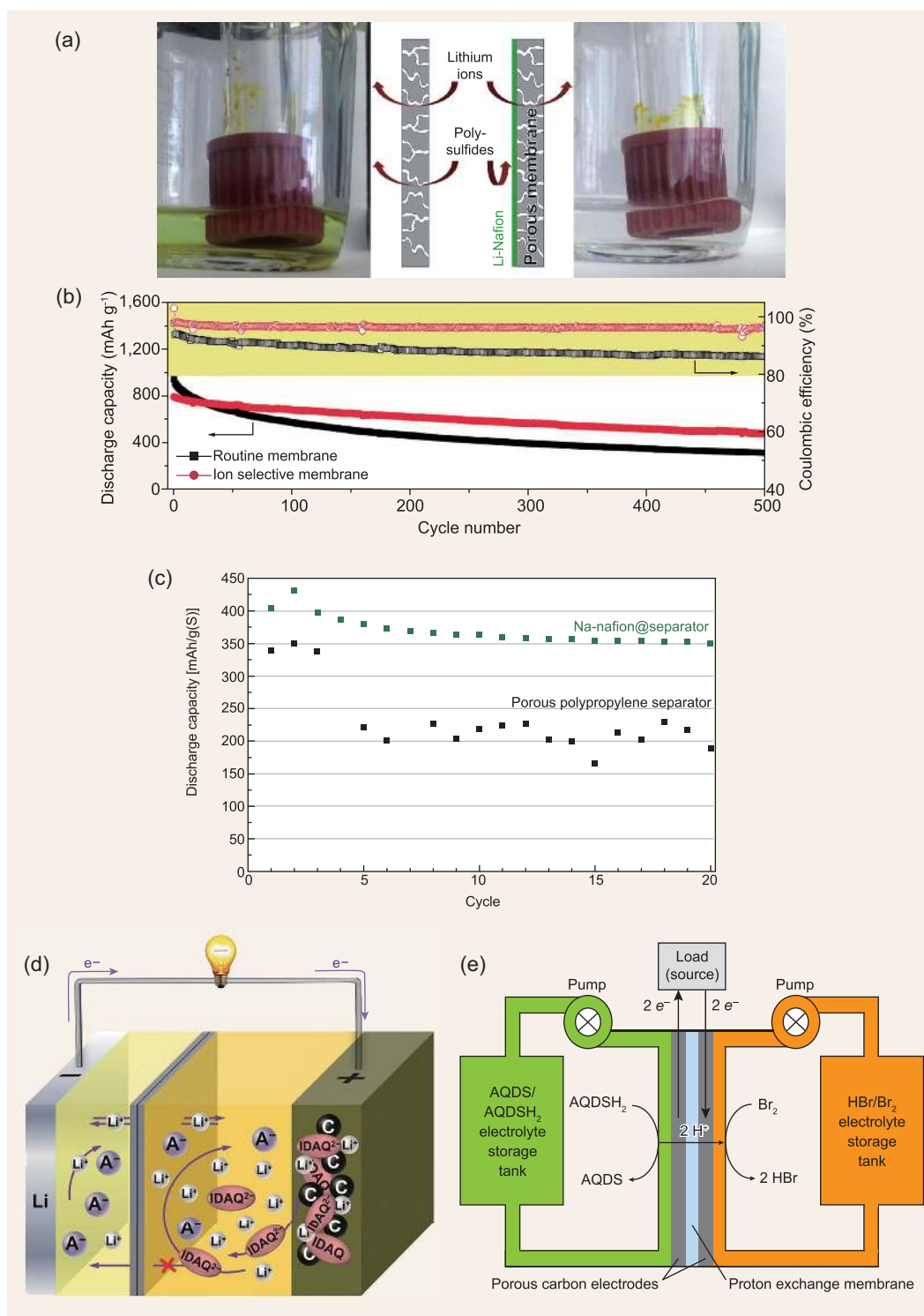


Figure 4. Applications of Nafion as ion-selective separators in varied types of batteries. (a) Li-Nafion coating blocks the migration of polysulfide anions. (b) H-Nafion coating improves the cycling property of Li-S batteries. (c) Na-Nafion-coated separator enhances the capacity of Na-S batteries. (d) Schematic illustration Li-Nafion-based sandwiched separator used in Li-organic batteries. (e) An Organic RFB with H-Nafion as the ion-selective separator. (a) Adapted with permission from [38], Copyright 2013, Elsevier B. V.; (b) adapted with permission from [39], Copyright 2013, Royal Society of Chemistry; (c) adapted with permission from [44], Copyright 2014, Royal Society of Chemistry; (d) adapted with permission from [45], Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; (e) adapted with permission from [46], Copyright 2014, Nature Publishing Group.

polysulfide catholyte, which was accommodated into a carbon nanofiber paper to form a cell configuration of Li//Li-Nafion//carbon nanofiber/activated carbon-lithium polysulfide. The cycling stability of this Li-S cell with the Li-Nafion membrane was greatly enhanced, compared to the cell with the porous polyolefin separator.

The polysulfide-blocking property of the Nafion-based separator was also proved in an in-operando imaging experiment in Li-S cells [41]. Based on the characteristic color of the intermediate polysulfides, an in-operando imaging setup was applied to directly visualize the temporal and spatial distribution of polysulfides. Compared with the pristine polyolefin separator, the Nafion-coated polyolefin separator showed significant blocking effect for the polysulfides, as was observed from reduced grey level of the electrolyte at the anode side in varied degrees of charge/discharge.

The sodiated form of Nafion (Na-Nafion) has been applied as the separator for solving the polysulfide shuttling in room-temperature Na-S batteries. Yu *et al.* developed a Na-Nafion membrane, which was prepared by the sodiation of Nafion 212 membrane, as the separator in a room-temperature Na-S battery [42]. The cell configuration was Na//Na-Nafion//carbon nanofiber/activated carbon- Na_2S_6 with the Catholyte of Na_2S_6 . The ionic conductivity of the Na-Nafion membrane was determined to be approximately $2.7 \times 10^{-5} \text{ S cm}^{-1}$. The blocked diffusion of sodium polysulfide across the Na-Nafion membrane was proved by a visual experiment. The capacity was increased by 50% for this new cell with Na-Nafion (750 mA h g^{-1}) compared with that with the conventional separator (500 mA h g^{-1}). A later paper of theirs also demonstrated the successful application of the Na-Nafion membrane as the functional separator in room-temperature Na-S batteries [43].

Bauer *et al.* described a Na-Nafion coating on the polyolefin separator for room-temperature Na-S batteries [44]. Nafion was first coated on the porous polyolefin membrane and then sodiated in aqueous NaOH solution. The as-obtained Na-Nafion-coated membrane was applied as the separator, in combination with a S/C cathode, a sodium metal anode and an electrolyte of $\text{NaClO}_4/\text{TEGDME}$ (tetraethylene glycol dimethyl ether). After 20 cycles, the capacity showed a 75% increase from $200 \text{ mA h g}_{\text{sulfur}}^{-1}$ for the cell with the pristine separator to $350 \text{ mA h g}_{\text{sulfur}}^{-1}$ for the cell with the Na-Nafion-coated separator (Fig. 4c).

Similarly to the phenomenon of polysulfide shuttling in Li-S and room-temperature Na-S batteries, the dissolution of the electroactive organic species is a challenging issue for Li-organic batteries. In

2016, Song *et al.* described a sandwich-structured polypropylene/Li-Nafion/polypropylene separator for Li-organic batteries (Fig. 4d) [45]. An optimal loading of Li-Nafion (0.5 mg cm^{-1}) was chosen. With 1,1'-iminodianthraquinone (IDAQ) as the electroactive organic molecule, a long life of 400 cycles with capacity retention of 76% was obtained, along with high Coulombic efficiencies above 99.6%. In terms of the blocking effect for the electroactive organic molecules/anions, a visual experiment gives direct evidence that the polypropylene/Li-Nafion/polypropylene separator completely prohibits the diffusion of IDAQ^{n-} .

Recently, organic RFBs have evolved into a very promising next-generation battery system for potential applications in cost-effective, large-scale stationary energy-storage systems. The Nafion membrane has been reported as a cation-selective separator for preventing the shuttle of organic molecules/ions in the organic RFBs with aqueous or non-aqueous electrolytes. Huskinson *et al.* described an aqueous flow battery with the anolyte of quinone/hydroquinone, the catholyte of Br_2/Br^- and the separator of Nafion membrane (Fig. 4e) [46]. The electrolyte was sulfuric acid, in which the quinone molecule undergoes reversible two-proton two-electron electrochemical reaction. In this environment, the Nafion membrane permits the migration of protons and retards the crossover of other species, including the quinone molecules and anions. This organic RFB system has already reached the power densities of conventional vanadium flow batteries, but lowered the cost by approximately two-thirds. Brushett *et al.* reported an all-organic non-aqueous RF battery utilizing Li-Nafion membrane as the separator [19]. Compared to aqueous batteries, the application of non-aqueous electrolytes improves the cell potential. 2,5-di-tert-butyl-1,4-bis(2-methoxyethoxy) benzene (DBBB) was employed as the cathode material, a range of quinoxaline-based species were applied as the anode species and $\text{LiBF}_4/\text{propylene carbonate}$ was the electrolyte. The Li-Nafion membrane permits the transfer of lithium ions and blocks the electroactive organic species, enabling this type of non-aqueous lithium-ion RF battery to approach the maximum theoretical energy densities.

Other ion-selective materials

Apart from Nafion, other ion-selective membrane materials, including polymers and inorganic ceramics, have been applied as the functional separator. The cation-selective mechanism of a material can be classified into two categories. One is that the nanochannels in the material (e.g. Nafion) bare negative charge and block the diffusion of negative ions

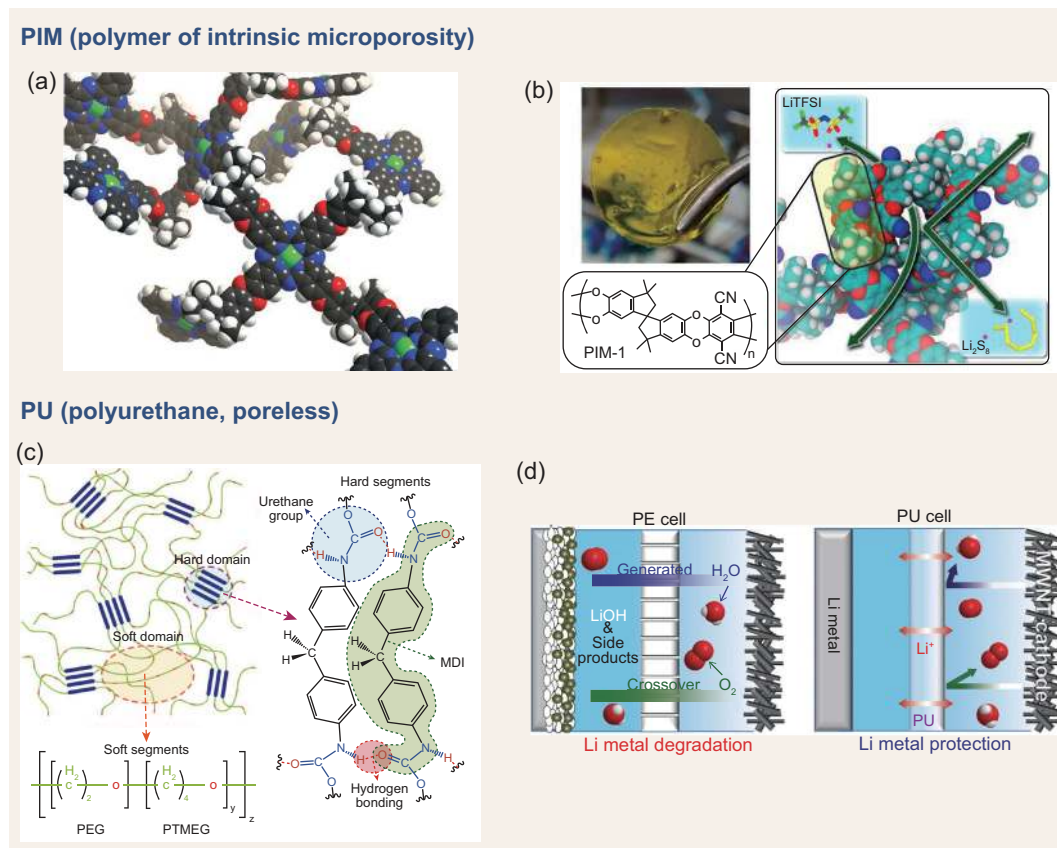


Figure 5. PIM-1 used as the ion-selective separator in a Li-S flow battery and PU as a functional separator in a Li-air battery. (a) A molecular model of the rigid fragment of PIM-1. (b) Ion-selective PIM-1 membrane separator for blocking polysulfide anions in a Li-S flow battery. (c) Molecular structure of PU. (d) PU as the separator in Li-air batteries for suppressing moisture and oxygen from crossing over to the anode side. (a) Adapted with permission from [48], Copyright 2006, Royal Society of Chemistry; (b) adapted with permission from [49], Copyright 2015, American Chemical Society; (c) adapted with permission from [50], Copyright 2013, American Chemical Society; (d) adapted with permission from [51], Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

via electrostatic repulsion. The other kind possesses small enough nanochannels allowing the transport of the relatively smaller ions such as H⁺, Li⁺ and Na⁺ but repelling larger ions such as polysulfide anions.

In 2016, Ma *et al.* reported a cation-selective membrane separator based on a cross-linked poly (ethylene glycol) (PEG) network for application in Li-S batteries [47]. To enable the function of ion selectivity, sulfonate groups were grafted onto the PEG network by copolymerizing poly (ethylene glycol) dimethacrylate (PEGDMA) and the vinylsulfonic acid salt under ultraviolet radiation. The as-prepared membrane facilitates the electrolyte wetting and lithium-ion transport but prevents the migration of polysulfide anions for both the small tortuous pores between the PEG molecules and the electrostatic repulsion of the polysulfide anions by the pendant negatively charged sulfonate groups. The transference number for lithium ions was determined to be approximately 0.99 and the blocking

effect for polysulfides was visually observed, demonstrating an impressive ion-selective transport behavior of the new membrane material. Without LiNO₃ additive in the electrolyte, the Li-S battery employing this novel membrane proved more than double the capacity after 100 cycles compared with that with the pristine PEGDMA membrane separator (1000 vs 400 mA h g⁻¹).

The PIM is a non-networked ladder polymer that is mechanically and thermally robust [48]. Its microporosity is formed by the highly rigid and contorted molecular structure. Because there is no rotational freedom for the polymer backbone, the nanopores can be maintained very well. One important representative is PIM-1, whose rigid fragment is shown in Fig. 5a. The nominal pore size of PIM-1 is 0.77 nm, and the large number of nanopores is convinced by the large specific area of around 800 m² g⁻¹. Li *et al.* determined that the pore size of PIM-1 is too small to allow the transport of the solvated lithium polysulfides in tetraglyme (> 1.4 nm) [49]. A proof-of-

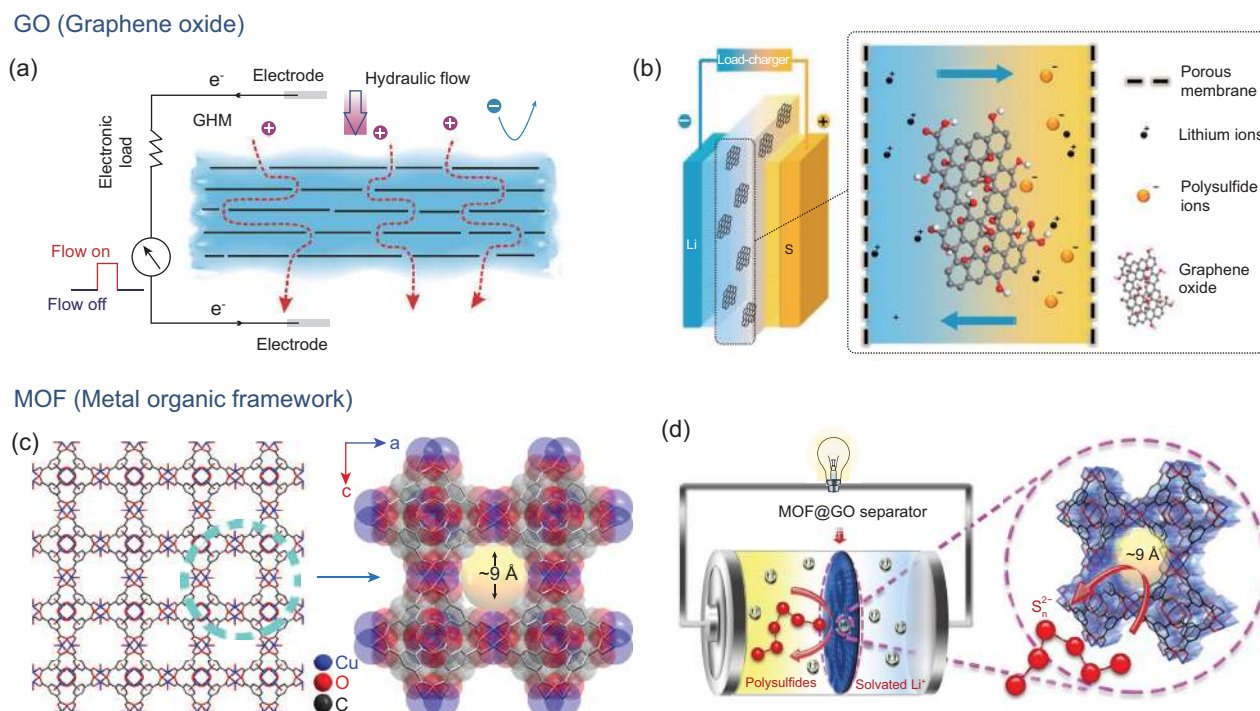


Figure 6. GO and MOF for application as ion-selective separators in Li-S batteries. (a) The ion selectivity of reconstructed GO film and (b) its utilization as the separator in Li-S batteries. (c) The microporous crystalline structure of the MOF material of HKUST-1 and (d) its use as the separator in a high-stable Li-S battery. (a) Adapted with permission from [54], Copyright 2013, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; (b) adapted with permission from [56], Copyright 2015, American Chemical Society; (c, d) adapted with permission from [58], Copyright 2016, Nature Publishing Group.

-concept membrane crossover experiment showed a 500-times polysulfide-blocking ability of the PIM membrane compared to the polyolefin membrane. A Li-S flow battery with the PIM-1 membrane separator showed energy density of 100 Wh L^{-1} after 50 cycles, while that with the conventional polyolefin separator showed 0 Wh L^{-1} .

PU, a poreless material composed of phase-separated hard and soft domains, has been proved to be an intriguing separator material with mechanical stability, low cost, thermal stability and electrolyte wettability [50]. The poreless character of the PU separator makes it impermeable for moisture and oxygen to protect the lithium metal anode [51–53]. This important property is highly desirable for Li-air batteries, in which water can be produced from the electrolyte decomposition, the reaction between the binder of poly (vinylidene fluoride) (PVDF) and an intermediate product of LiO_2 of the cathode, or ingress from the ambient. The side reaction between water and the lithium metal forms LiOH . Other side products such as LiCO_3 and ROCO_2Li on the anode surface can originate from the crossover oxygen and the reduced electrolyte. Owing to the noticeable reactivity of the lithium metal, even a low portion of water or

oxygen can cause fatal degradation of the lithium metal anode. However, these two gaseous components are inevitable for they can be dissolved into the electrolyte from the open end of the air cathode. Kim *et al.* exploited the impermeability of PU for moisture and water, and applied it as the functional separator [51]. As a result, the Li-air battery with the PU separator showed high performance of 200 cycles with capacity above 600 mA h g^{-1} .

Reconstructed GO membranes prepared by vacuum filtration possess numerous nanochannels between the GO sheets, which bear negative charge originating from the functional groups such as carboxylic acid and phenolic hydroxyl [54,55]. The typical dimension of the nanochannels ($1\sim 0 \text{ nm}$) is comparable to the Debye length, facilitating the transport of cations and blocking the migration of anion. This important property of the GO membrane has enabled its function as nanofluidic generators (Fig. 6a). The perm-selective GO membrane was employed by Huang *et al.* for application as a thin coating layer on a porous polyolefin separator to improve the cycling stability and inhibit the self-discharge of Li-S batteries (Fig. 6b) [56]. Compared to the pristine separator, the GO membrane improved the Coulombic efficiency from 67–75%

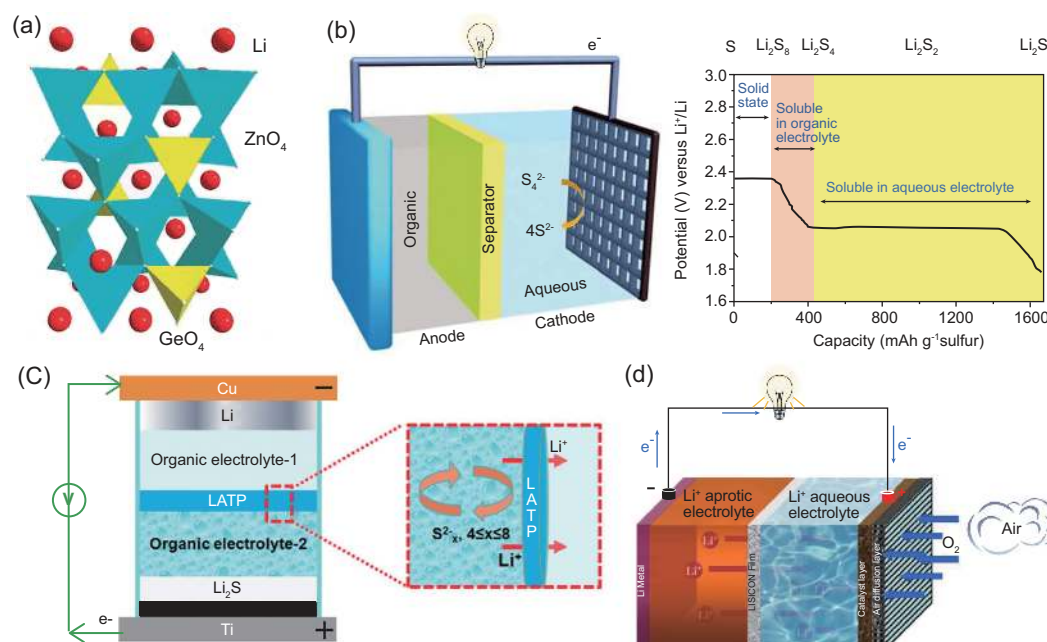


Figure 7. LISICON applications in Li-S and Li-air batteries. (a) Crystal structure of $\text{Li}_3\text{Zn}_{0.5}\text{GeO}_4$, a typical LISICON. (b) LISICON applied in a hybrid Li-S battery and the typical discharge voltage curve. (c) LATP, a kind of LISICON, used as the separator in a Li-S battery with dual-electrolytes. (d) LISICON employed as the separator for conducting lithium ion and blocking other species in a hybrid Li-air battery. (a) Adapted with permission from [60], Copyright 2014, Royal Society of Chemistry; (b) adapted with permission from [62], Copyright 2014, Royal Society of Chemistry; (c) adapted with permission from [63], Copyright 2015, Royal Society of Chemistry; (d) adapted with permission from [65], Copyright 2016, American Chemical Society.

to 95–98% at 0.1°C , reduced the capacity decay rate from 0.49 to 0.23% per cycle and enhanced the stability of the open circuit voltage from 5 h to 30 h. Later, a proof-of-concept GO/Nafion composite membrane, which combined the merits of both GO and Nafion, was successfully applied as the functional separator for Li-S batteries [57].

MOF is a kind of microporous material with pore size ranging from sub-nm to several nm. In 2016, Bai *et al.* employed HKUST-1 with a pore size of 0.9 nm in the separator for effectively suppressing the migration of polysulfide ions (Fig. 6c and d) [58]. The suppression of polysulfide ions was visually verified by a permeation experiment. In terms of the battery performance, a long life of 1500 cycles was achieved, demonstrating the excellent polysulfide-blocking ability of the functional separator.

In 2014, Li *et al.* employed a V_2O_5 -based separator for Li-S batteries, exploiting V_2O_5 as solid-state lithium-ion conductor and polysulfide anion barrier [59]. In order to supply sufficient lithium-ion transport through the separator, a thin V_2O_5 layer (1 μm thick) was coated on the polyolefin separator substrate, for the lithium-ion diffusion coefficient of V_2O_5 is inferior to that of the liquid electrolyte ($\sim 3 \times 10^{-12}$ vs 4×10^{-9} $\text{cm}^2 \text{s}^{-1}$). Moreover, to achieve a complete, well-adhered, dense, nonporous, crack-

free V_2O_5 coating for effectively preventing the crossover of polysulfide anions, V_2O_5 sol-gel was carefully coated onto a surfactant-modified polyolefin separator. The V_2O_5 -coated separator was demonstrated with a S/C composite cathode in a pouch cell. Under low rates between C/15 and C/1.5, a high capacity of $\sim 800 \text{ mA h g}^{-1}$ was obtained after 300 cycles during around 1 year.

As has been mentioned, V_2O_5 has much lower lithium-ion diffusion coefficient than that of liquid electrolyte and another inorganic ceramic material (i.e. LISICON) is featured by its high lithium-ion conductivity comparable to the liquid electrolyte (Fig. 7a) [60]. LISICON, although typically used as the electrolyte separator for solid-state lithium-ion batteries, can also be applied in liquid-electrolyte Li-S batteries as the separator for the pronounced lithium-ion conductivity and the polysulfide-blocking ability.

Among the varied types of LISICONs, the LATP produced by Ohara Inc. has received the most attention because of its integrated robustness and high ionic conductivity at the level of several $10^{-4} \text{ S cm}^{-1}$ at 298 K. The LATP glass ceramic has a formula of $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($x = 0\sim 0.25$ and $y = 0\sim 0.3$) composed of a main phase of rhombohedral $\text{LiTi}_2(\text{PO}_4)_3$ and a minor phase of AlPO_4 [61]. The

crystalline $\text{LiTi}_2(\text{PO}_4)_3$ provides a 3D lithium-ion transfer network constructed by the corner-shared TiO_6 octahedral and PO_4 tetrahedral units. LISICON separators have been applied in Li-S and Li-air batteries. Li *et al.* described an aqueous Li-S battery with aqueous solution of Li_2S_4 as the catholyte, lithium metal as the anode and LTAP as the separator (Fig. 7b) [62]. The aqueous Li_2S_4 catholyte can achieve high concentration (maximum of ~ 2.3 M), and therefore enables fast $\text{Li}_2\text{S}_4/\text{Li}_2\text{S}$ redox reactions compared to solid electrolytes and a high specific energy density of ~ 654 Wh kg^{-1} . Further, solid sulfur was dissolved in the aqueous Li_2S_4 solution as the catholyte, increasing the reversible capacity from 1030 to 1202 mA h g^{-1} . Wang *et al.* prepared a Li_2S suspension in 1 M LiClO_4 /tetrahydrofuran as the catholyte for the Li-S battery with the separator of LTAP (Fig. 7c) [63,64]. Because the fully lithiated Li_2S was applied as the cathode material, the anode of lithium metal could be replaced by varied lithium-free anode materials; two examples of aluminum and graphite were given in their work.

The LISICON film also enables Li-air batteries with hybrid electrolytes [65]. In this new-type Li-air configuration, the anode of metal lithium is oxidized to lithium ions and the cathode of O_2 is reduced to LiOH within the aqueous catholyte at discharge; meanwhile, lithium ions in the organic electrolyte solution migrate across the LISICON film to the aqueous catholyte. The charge process reverses the discharge process. The LISICON allows the electrochemical reactions at both the lithium metal anode and the air cathode to take place owing to its high lithium-ion conductivity. Further, it protects the anode from corrosion for the moisture and oxygen are unable to penetrate through the LISICON from the catholyte side. The utilization of the aqueous catholyte takes advantage of the high solubility of LiOH in water, thereby overcoming the clogging issue caused by the solid products in the conventional porous catalyst electrode.

Compared to LISICON, Prof. Zhou's group [66] developed an advanced super-hydrophobic quasi-solid separator/electrolyte with high flexibility, excellent ionic conductivity (0.91×10^{-3} S cm^{-1}), high electrochemical stability above 5.5 V and super hydrophobicity with a water contact angle of above 150° . The quasi-solid separator/electrolyte was prepared by integrating polyisobutylene and commercial super-hydrophobic silicon dioxide to form a membrane, which was then infiltrated with liquid electrolyte. Attributed to these excellent properties including the moisture-blocking capability, the super-hydrophobic quasi-solid separator/electrolyte enabled safe and long life cycling even in humid environments.

The single-crystal silicon wafer is also a promising oxygen-blocking separator for application in Li-air batteries [67]. A silicon wafer with thickness of $5 \mu\text{m}$ shows lithium-ion conductivity as high as 10^{-6} S cm^{-1} and withstands a high current density of 1 mA cm^{-1} . The diffusion coefficient of O_2 in silicon is 34 orders of magnitude lower than that of lithium ions. This high impermeability of O_2 of the single-crystal silicon wafer protects the lithium metal anode from corrosion, and therefore greatly improves the cycle life.

Separator strategies for stable Li-S batteries

Particularly, in recent years, separator strategies have been widely applied in Li-S batteries. In addition to the ion-selecting approach, herein several other kinds of separator technologies are stated. Yao *et al.* [68] prepared Super P-coated separators for application in Li-S batteries. The conductive coating addressed the problem of the sulfur species accumulation, which causes the low active material utilization and quick capacity decay. As a result, a stable cycling of 500 cycles was obtained. In other work, Super P was coated on glass fiber separator to achieve high-performance Li-S batteries [69]. Moreover, graphene [70,71], SWCNT [72], microporous carbon [73], mesoporous carbon [74] and black phosphorous [75] were also utilized as the coating material for improving the active material utilization, therefore enhancing the cycling stability of the Li-S battery. Besides, the integration of the sulfur cathode and the separator proves a promising strategy. Two configurations have been reported for integrated electrode/separator: sulfur/graphene/polyolefin [76] and sulfur-infiltrated porous carbon/polyolefin [77].

SAFE SEPARATORS

High safety performance is a basic requirement for batteries. Among all the components, the separator plays a key role in determining the safety property of the battery. Extreme failures such as burnings or explosions of the battery cause damage to customers' lives or properties, and one main reason is internal short circuit. To reduce the risk of internal short circuit, high thermal/dimensional behavior of the separator is highly needed. Besides, with regard to lithium-based batteries, functional separators that suppress the growth of lithium dendrites greatly enhance the safety performance.

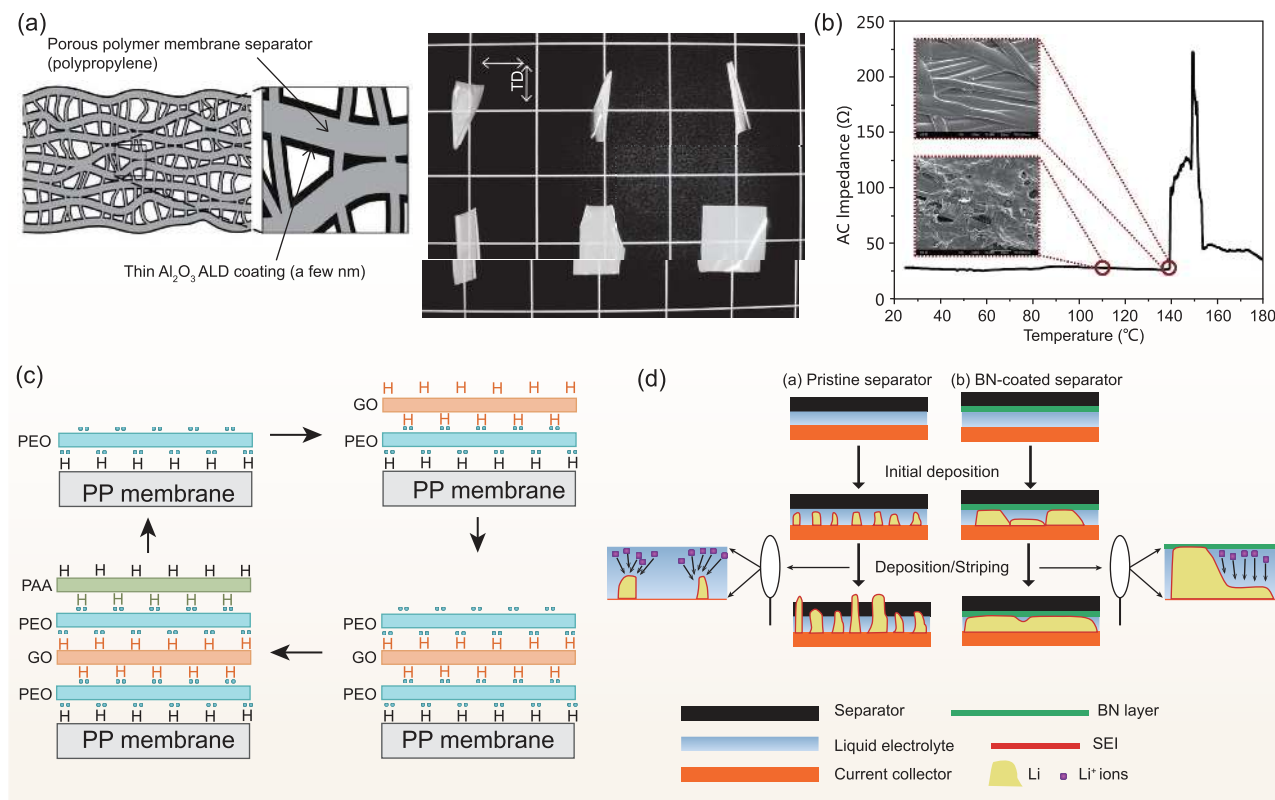


Figure 8. Separators with high thermal stability or Li-protection ability. (a) Alumina-coated separator with high thermal stability by the atomic layer deposition method. (b) Shutdown property of nonwoven separator coated with low-density polyethylene. (c) A Li-protective separator fabricated by the LBL-coating approach. (d) BN-coated separator suppressing Li dendrite growth. (a) Adapted with permission from [81], Copyright 2012, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; (b) adapted with permission from [84], Copyright 2015, Elsevier B. V.; (c) adapted with permission from [89], Copyright 2014, American Chemical Society; (d) adapted with permission from [91], Copyright 2015, American Chemical Society.

High-thermostability separators

Zhu *et al.* prepared a flame-retarding membrane separator composed of a nonwoven fabric (NWF) coated with PVDF [78]. PVDF was coated on both sides of a NWF membrane composed of polyethylene and polypropylene. The as-prepared NWF-PVDF shows improved ionic conductivity and lithium-ion transference compared to those of the commercial polyolefin separator. Moreover, the PVDF coating greatly suppresses the evaporation behavior of the electrolyte, even at elevated temperature. When put in the flame, the commercial polyolefin separator easily caught fire in a short time, while the composite membrane did not catch fire, showing an excellent flame-retarding property. However, under the flame, the composite membrane shrinks evidently, indicating that further improvement is needed.

Not only the flame-retarding, but also the non-shrinkage property at elevated temperature is a key factor for high safety separators. A thermostable and nonflammable composite membrane of glass microfiber and polyimide was prepared through

suction filtration followed by dip-coating [79]. Besides the excellent wettability to the aprotic electrolyte and the stable electrochemical performance, the composite membrane undertook an elevated temperature of 200°C without shrinkage and did not catch fire in the flame. With demonstration of LiFePO₄/Li batteries, the composite membrane enabled a stable cycling at an elevated temperature of 120°C. Another non-shrinkage membrane separator, which was made of bacterial cellulose, was reported to exhibit perfect dimensional stability up to 180°C [80].

A thin alumina layer (6 nm) was reported to be coated on the porous polymer separator through atomic layer deposition [81]. This thin coating does not increase the thickness of the pristine separator, unlike conventional coating methods. Besides, the thin coating layer effectively suppressed the thermal shrinkage of the separator and improved the wettability to the electrolyte, leading to a significantly enhanced safety property (Fig. 8a). Ceramic/polymer composite membrane separators involving tough polymers normally possess high

thermal stability. Zhai *et al.* described a thermostable and nonflammable silica/polyetherimide/polyurethane nanofibrous membrane using the electrospinning method [82]. The composite separator exhibits flame-retardant properties and excellent dimensional stability.

One important drawback of the polyolefin separator is its low thermal conductivity, which is a bottleneck barrier for heat transfer in Li-ion batteries. An $\text{Al}_2\text{O}_3/\text{PVdF-HFP}$ composite separator was demonstrated to have a high thermal conductivity five times that of the commercial polyolefin separator [83]. This design combining Al_2O_3 nano/microparticles and the polymer of PVdF-HFP facilitates heat dissipation in the battery and reduces the temperature rise in operation, greatly reducing the risk of catching fire or explosion. In case of heat runaway and temperature increase, shutdown functionalized separators are needed for protection of batteries. Kim *et al.* prepared a nonwoven polyethylene-coated separator that exhibits thermal stability at 200°C and self-shutdowns at 140°C (Fig. 8b) [84]. In addition to the enhanced safety performance, the electrochemical property of the battery was also enhanced.

Lithium dendrite-suppressing separators

High-energy batteries, such as Li-S and Li- O_2 batteries, are based on the high capacities of both the cathode and the anode. As it is known that the cathode materials of S and O_2 possess a high capacity of 1675 mA h g^{-1} , the lithium metal also features an impressive high theoretical capacity of 3860 mA h g^{-1} , around 10 times that of the state-of-the-art graphite anode, as well as the lowest reduction potential (-3.04 V vs NHE, normal hydrogen electrode). Owing to this attractive characteristics, the lithium metal anode is called the 'Holy Grail' of energy-storage systems [85,86]. However, the main problem of the lithium metal anode is the growth of lithium dendrites in the charge/discharge process, causing performance decay and serious safety issues. Lithium dendrites, together with the dendrites of other metals (e.g. Zn, Cu), are a common phenomenon in electrodeposition. In most electrodeposition experiments, the formation of metal dendrites is a one-way process. In rechargeable lithium batteries, repeated deposition and stripping of lithium metal take place and cause the accumulation of lithium dendrites, leading to many problems. For a lithium battery not working, there is no ionic concentration gradient in the electrolyte; when the battery is being charged, lithium ions transfer to the lithium metal anode side. Lithium ions are reduced

and plated onto the lithium metal anode surface. The speed of lithium deposition depends on the applied current density. Although it seems that the consumed lithium ions near the anode surface can be adequately compensated by those in the electrolyte bulk, the microscopic environment spreading the whole anode surface is inconstant and leads to inhomogeneous lithium metal deposition. The repeated deposition/stripping results in the lithium dendrites growth, which might penetrate the porous separator and lead to internal short circuit. In this regard, favorable wettability of the separator results in uniform ion flux and plays an important role in obtaining dendrite-free lithium anodes.

Ryou *et al.* treated the polyethylene separator with polydopamine (PD) without modifying the porosities using a simple dip-coating method [87,88]. Because of the hydroxyl and amino groups in the PD molecules, the surface energy of the separator was increased, hence the wettability of the electrolyte was improved. Besides, because of the excellent mechanical and thermal properties of PD, the modified separator showed improved thermal stability against dimensional shrinkage at elevated temperature. These two aspects of the PD-modified separator, the lithium dendrite suppression and the thermal shrinkage resistance together provide an effective solution for the safety issue of lithium-based batteries.

Lee *et al.* applied a layer-by-layer (LBL) approach to coat several polymers and GO on the porous separator for a homogeneous environment for lithium deposition [89]. In a LBL tetralayer, poly(ethylene oxide), GO, poly(ethylene oxide) and then poly(acrylic acid) (PAA) were successively self-assembled on the porous polymer substrate through hydrogen bonding between the adjacent materials. This LBL tetralayer were repeated for the desired times to get a certain thickness of the coating layer. In this coating layer, poly(ethylene oxide) functions as the ion-conductive polymer and GO acts as a selective barrier layer. As a result, in addition to the high ionic conductivity and lithium-ion transfer number, the as-prepared separator suppressed lithium dendrite growth for the improved wettability.

Hao *et al.* reported a dendrite-suppressing membrane separator composed of high modulus polymeric nanofibers of poly(*p*-phenylene benzobisoxazole) (PBO) [90]. The PBO nanofiber (PBO-NF) membrane was prepared by a blade-casting method. This novel separator possesses excellent wettability towards carbonate-based liquid electrolyte, which makes it suitable as the separator. Evidenced by SEM (scanning electron microscope) images, the lithium anode with the PBO-NF separator after

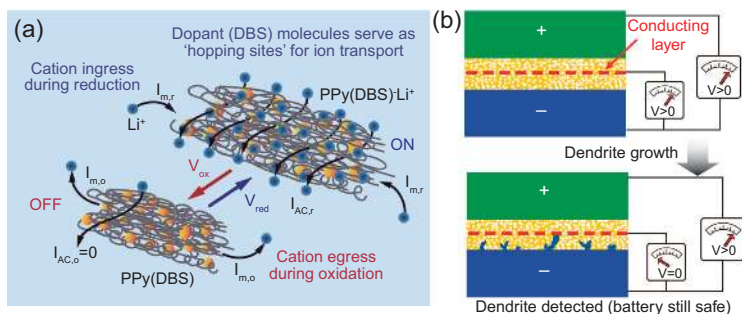


Figure 9. Smart separators with (a) voltage-gating and (b) lithium dendrite-detecting properties. (a) Adapted with permission from [94], Copyright 2016, Royal Society of Chemistry; (b) adapted with permission from [96], Copyright 2014, Nature Publishing Group.

cycling for 700 h showed a flat and smooth surface, while lithium dendrites were clearly observed for the lithium anode with the polyolefin separator. In terms of the thermal stability, this novel separator had a high stability up to 600°C and enabled the lithium-based batteries to operate at 150°C.

Luo *et al.* created a homogeneous separator surface by coating BN nanosheets on the polyolefin separator [91]. They dispersed BN nanosheets and PVDF in the solvent of NMP (N-methyl-2-pyrrolidone) and then obtained the BN-coated separator by the spray-coating method. The enhanced thermal conductivity of the novel separator was demonstrated by using an infrared camera to map the temperature distribution at the separator surface. The result showed that, at the hotspot, the temperature spike dropped to 34°C from 50°C for the original separator. This homogeneous thermal distribution suppressed the production of lithium wires and resulted in uniform deposition/strip of lithium, significantly improving the safety performance.

Glass fiber, which possesses high-density polar functional groups, has been described as an alternative separator for lithium dendrite suppression [92,93]. The polar functional groups could adsorb large amounts of lithium ions, which compensates the ionic diffusion and electrostatic interactions between the lithium ions in the electrolyte and the protuberances of the copper current collector. Therefore, lithium dendrite growth on the copper protuberances is avoided. Compared with the conventional polyolefin separator, the glass fiber membrane enabled greatly improved cycling performance of lithium deposition on the copper current collector for Li-S batteries.

SMART MEMBRANE SEPARATORS

A voltage-responsive smart membrane system based on polypyrrole doped with dodecylbenzenesul-

fonate (PPy(DBS)) was reported by Hery *et al.* [94] (Fig. 9a). In this work, PPy(DBS) was formed on Au-sputtered track-etched polycarbonate (PCTE) substrate as a smart membrane separator. The PPy(DBS) spans upon the pore of the substrate and acts as a barrier for ion transport. With an immersed electrode and the Au layer between PPy(DBS) and the substrate, an external electric field (V_m) was applied. When $V_m = 0$ V, the polymer in its oxidized state was densely packed, which caused the ion transport across the membrane to be negligibly small for an applied transmembrane potential (V_{AC}). When a reducing field ($V_m = -1$ V to -0.45 V) was applied, transport of cations (e.g. Li^+ , Na^+ , Mg^{2+}) across the membrane are facilitated for (i) the polymer becoming negatively charged and providing hopping pathways across the membrane; (ii) the pore size being expanded; and (iii) the wettability of PPy(DBS) reversibly turning from hydrophobic to hydrophilic, as revealed by the switch of the water contact angle from 122° to 64°. In this way, the ionic current across the membrane was turned ON when a certain reducing field was applied and turned OFF when no electric field was applied. This smart membrane holds great potential for application in energy-storage devices such as RFBs, which are promising candidates as next-generation energy density systems for large-scale industrial applications.

Temperature-responsive separators were reported to enable self-extinguishing lithium-ion batteries [95]. An extinguishing agent (1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-(trifluoromethyl)-pentane) (DMTP) with excellent endothermic properties encapsulated in a temperature-responsive polymeric shell of poly(methyl methacrylate) (PMMA) was used to suppress the rapid temperature rise in a Li-ion battery. A fire retardancy test showed that the DMTP@PMMA quenched the fire caused by the burning of the electrolyte. Enhanced safety was also observed in a nail-penetration test, for the DMTP@PMMA microcapsules greatly decreased the maximum temperature from 72.3°C to 37.2°C for the heat-absorption reaction of DMTP. It was assumed that, when the temperature rose, DMTP rapidly volatilized and built up the internal pressure inside the PMMA shell, which resulted in the leakage of DMTP for absorbing the heat or extinguishing the fire.

Smart batteries that are capable of monitoring the internal short circuit through a lithium dendrite sensing separator were reported by Wu *et al.* [96] (Fig. 9b). For lithium-based batteries, internal short circuit can be formed by the lithium dendrites growing from the anode surface and then penetrating

through the porous polymer separator. In this work, they used a triple-layer separator with a porous copper layer between two insulating porous polymer layers. In this way, by monitoring the potential between the copper layer and the anode, the penetration of lithium dendrites could be monitored because the connection between the copper layer and the anode by the lithium dendrites resulted in an immediate and sharp voltage drop. On detection of this signal indicating the imminent internal short circuit, the battery could be safely stopped manually or automatically, avoiding the possible further serious consequences such as fire or explosion. Similarly, another smart separator polyimide/Cu/polyimide was reported [97] for detecting lithium dendrites.

SUSTAINABLE SEPARATORS

Sustainable separators based on cellulose are interesting alternatives for the widely used fossil-based polyolefin separators. Chun *et al.* reported a cellulose nanofiber paper with high thermal/mechanical stability, nanoporous structure and excellent electrolyte wettability [98]. They showed high ionic conductivity and excellent electrochemical performance of the lithium-ion battery with the cellulose nanofiber paper. The thermal-stability property of the cellulose separator was studied by Jiang *et al.* [99]. A high dimensional stability up to 180°C for the bacterial cellulose fibrous membrane was demonstrated. The flexibility and the robust mechanical property of the cellulose material enabled its application as the separator of a paper flexible battery [100]. Moreover, composite materials of cellulose with polyborate [101], polysulfonamide [102], polydopamine [103], poly(vinylidene fluoride-co-hexafluoropropylene) [104] and colloidal silica nanoparticles [105] were explored to be robust sustainable separators.

SUMMARY AND OUTLOOK

In summary, a novel concept of 4S (Stable, Safe, Smart, Sustainable) batteries has been proposed in this review article based on the recent study of functional separators for next-generation high-energy rechargeable batteries. Stable cycling performance is the first important criterion for next-generation batteries. In order to achieve the stability level of thousands of cycles for state-of-the-art commercial lithium-ion batteries, ion-selective separators can be implemented in the described next-generation battery systems for their important role in retaining the active materials and stabilizing the solid–electrolyte interface. The battery types are Li-S, room-temperature Na-S, Li-organic, organic

RF and Li-air batteries. The applied ion-selective materials are Nafion (protonated, lithiated or sodiated), PIM, PU, MOF, GO and LISICON. Besides, particularly in Li-S batteries, modified separators that are capable of reactivating polysulfide species also improve the cycling stability. We expect that, in combination with advanced electrode materials and novel electrolytes, the development of materials and structures for the functional separator greatly enhances next-generation high-energy rechargeable batteries with high cycling stability comparable with conventional lithium-ion batteries. It should be noted that, when choosing the proper material/structure of the functional separator, the practicability and the cost are also key factors to consider.

Meeting superior safety standards is another important requirement for the 4S batteries. Although the separator is electrochemically inactive in the battery, unlike the electrodes, its role in determining the battery safety is central. Under circumstances such as elevated temperature, particularly for alkaline metal anode-based batteries, the anode–electrolyte interface breaks down and the electrolyte turns into flammable gases. The separator melts and causes direct contact between the electrodes. This internal short circuit causes sparks that ignite the electrolyte and flammable gases. Thus, the temperature still rises, leading to the burning of the polymer separator and the electrode materials, then, under some extreme conditions, even the explosion of the battery. In this regard, the separators that demonstrate excellent thermal/dimensional stability enhance the battery safety performance. Besides, particularly for lithium-based batteries, the lithium dendrites, which result from the uneven electrodeposition of lithium metal on the anode, may pierce through the porous separator to cause internal short circuit. Thus, functional separators that enhance homogeneous electrochemical reactions on the anode surface reduce the safety risk.

Smart separator membranes that are capable of responding to stimuli such as temperature or voltage result in advanced batteries with high-efficiency controllability. For example, by tuning the size or even the open/close of the pores through applying varied external voltages, the separator controls the ionic flux between the electrodes, hence determining the discharging rate or even the ON/OFF of the battery. The enhanced battery management also contributes to improving the battery safety. For instance, with the ability to detect signals of battery abnormality or failure and properly responding automatically or with the help of external devices, the smart separator prevents the burning or exploding of the battery, avoiding damage to the lives and property of

customers. Smart separators, although at their embryo stage, demonstrate a new direction for separator research and development. This intriguing approach would open a new route for controlling the battery and reducing the safety hazard to the lowest level, which holds the potential to be extended to other areas relating to electrochemical energy storage and conversion.

Sustainable separators refer to the separators that are composed of renewable polymers. Cellulose is one of the most abundant, sustainable materials with high thermal stability, excellent chemical stability and low cost. These important qualities make cellulose an intriguing alternative for sustainable separators. Although efforts have been made, much more work is needed for the further research and development of cellulose-related or composite materials as sustainable separators.

The bright future of next-generation batteries depends on how soon we can fulfill the four criteria of the 4S batteries: Stable, Safe, Smart and Sustainable. Separators that enhance stable cycling, improve safety performance, enable smart batteries and comprise sustainable materials are highly desirable. Moreover, we expect that, with the application of novel functional materials and deeper understanding of the important roles of the separator in the battery system, functional separators not only boost the existing battery systems, but also inspire new battery technologies.

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