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Porous membranes in secondary battery technologies

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Secondary batteries have received huge attention due to their attractive features in applications of large-scale energy storage and portable electronic devices, as well as electrical vehicles. In a secondary battery, a membrane plays the role of separating the anode and cathode to prevent the occurrence of a short circuit, while allowing the transport of charge carriers to achieve a complete circuit. The properties of a membrane will largely determine the performance of a battery. In this article, we review the research and development progress of porous membranes in secondary battery technologies, such as lithium-based batteries together with flow batteries. The preparation methods as well as the required properties of porous membranes in different secondary battery technologies will be elucidated thoroughly and deeply. Most importantly, this review will mainly focus on the optimization and modification of porous membranes in different secondary battery systems. And various modifications on commercial porous membranes along with novel membrane materials are widely discussed and summarized. This review will help to optimize the membrane material for different secondary batteries, and favor the understanding of the preparation–structure–performance relationship of porous membranes in different secondary batteries. Therefore, this review will provide an extensive, comprehensive and professional reference to design and construct high-performance porous membranes.

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1. Introduction

The exhaustion of energy sources and severe problems of environmental pollution make it more and more significant

to accelerate the utilization of renewable energy sources. Their wide utilization can be realized by developing and exploring electrochemical energy storage (EES) technologies or battery technologies. In a battery, the energy is directly stored or released by the conversion of chemical energy to/from electric energy. Therefore, battery technologies can convert and store the electricity generated from renewable energy sources, thereby surmounting the mismatch between the generation and end-use. The intermittence and instability of renewable energy sources are thus well and effectively solved.¹ As a consequence,

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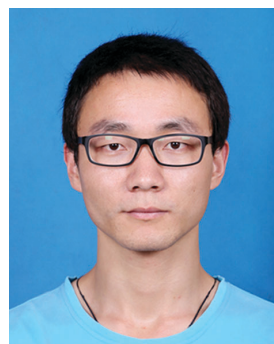
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increasing attention has been paid to battery technologies to expedite the development and utilization of sustainable energy sources.

Secondary batteries, such as lithium-ion batteries (LIBs), lithium-sulfur (Li-S) batteries and flow batteries (FBs), undergo reversible charge/discharge processes repeatedly, which is more cost-effective and owns more environmental benignity.^{2–6} The investigations of secondary battery technologies are indispensable for the extensive use of portable mobile electronic devices as well as electric vehicles, and important for the process of large-scale energy storage. For example, LIBs with high energy density and high output voltage have become the main technology to power portable electronic devices (such as cell phones and laptops in the current market), and electric vehicles.⁷ And FBs are one of the most attractive and promising technologies for large-scale energy storage. This is due to their intriguing characteristics of high safety, high efficiency, long cycle life, flexible modular design, low cost and so on.^{1,8} There are various FBs nowadays, like iron-chromium flow batteries, zinc-bromine flow batteries, vanadium

flow batteries (VFBs), *etc.* It is worth noting that nearly 30 VFB demonstration projects have been implemented by Rongke Power Co. Ltd so far, including the world largest 5 MW/10 MW h system (in 2012), which is combined with a 50 MW wind farm.⁹ However, some critical issues still exist for different secondary battery technologies, like safety problems of lithium-based batteries and the low energy density of FBs. Thus, investigations into various secondary battery technologies to improve their performance together with reliability, and to reduce their cost for further commercial processes are becoming more and more important.

The most common method to improve secondary battery performance is optimizing their key materials. A normal secondary battery is composed of electrodes (the anode and cathode), electrolytes (the positive and negative electrolyte) and a membrane, which are assembled together and connected to an external source or load (Fig. 1a).^{10–14} Among them, the membrane is a key component, serving as a separator to isolate the anode and cathode to prevent the occurrence of a short circuit. At the same time, the membrane must also allow the transport of charge



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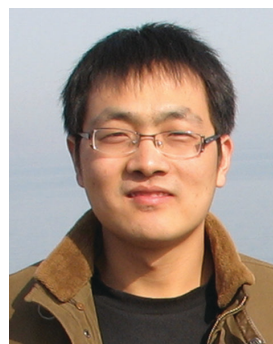
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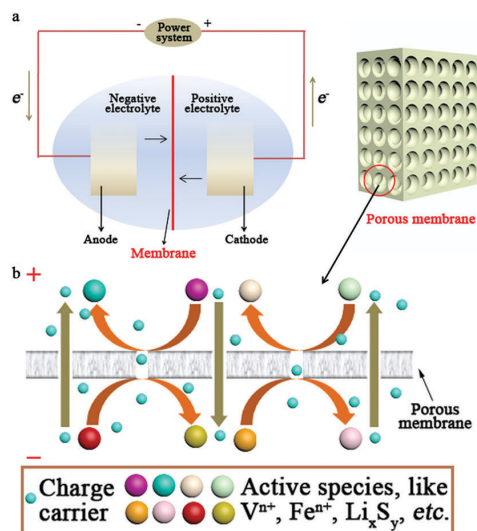


Fig. 1 (a) A schematic diagram of a normal secondary battery and a porous membrane; (b) a schematic diagram of the porous membrane in a secondary battery.

carriers, such as protons and lithium ions, to achieve a complete circuit.^{15,16} For example, in a VFB, the membrane plays the role of separating vanadium ions from protons to realize high ion selectivity. As for a Li-S battery, it must help the inhibition of the distribution and migration of polysulfide species to suppress the capacity decay.

The properties of the membrane usually determine the final performance of a secondary battery.^{17,18} Hence, membranes used in secondary batteries should co-possess excellent electric insulativity and good ion conductivity,^{3,15} in order to realize high efficiencies, high rate capacity and great safety. Another very important characteristic for a membrane is high selectivity for the active species. Of course, high stability and low cost are also extremely important for the large-scale commercial application of secondary battery technologies.

In secondary battery technologies, the membranes can be classified as ion exchange membranes (IEMs) and porous membranes. The former depends on the ion exchange groups attached to the membranes to realize the transport of charge carriers. Differently, the latter relies on the principle of ion sieving based on pore size exclusion (Fig. 1b). It is believed that the poor chemical stability of IEMs is caused by ion exchange groups, which easily induce membrane degradation.^{19,20} The poor chemical stability of IEMs has always been a pivotal barrier for their large-scale application in secondary battery technologies, especially in FBs. Moreover, the fact that ion exchange groups cannot dissociate in most of the organic electrolytes makes IEMs lose their ability to transport charge carriers in non-aqueous secondary batteries. And some kinds of IEMs are very expensive, like perfluorinated membranes (*e.g.* DuPont Nafion, 600–800 \$ m^{-2}). Inversely, porous membranes without ion exchange groups usually have better stability and lower cost. So they have been widely applied in gas separation,

water treatment, battery technologies and so on.^{21–25} Porous membranes applied in secondary battery technologies include microporous membranes (MMs), nanofiltration membranes (NFs) and ultrafiltration membranes. These porous membranes are mostly made from organic polymers, such as polypropylene (PP) and poly(vinylidene fluoride) (PVDF).^{26–28} Except for the excellent chemical stability and low cost, porous membranes also own many other advantages like successful commercialization, versatile and robust fabrication methods and flexible membrane shapes.²⁹ Diverse methods can be utilized to fabricate polymer porous membranes, such as sintering, stretching, track-etching, electrospinning and phase separation methods.^{22,30–32}

However, it is generally hard for secondary batteries assembled with pure pristine porous membranes to obtain high performance. As a consequence, various methods focusing on modifying the porous membranes have been investigated extensively. Selecting appropriate membrane materials and optimizing the membrane structures are the frequently-used methods. The former largely relies on the intrinsic properties of the membrane materials. And the latter is based on structure design and optimization. It is worth noting that the operating principles of different secondary batteries are quite different. For instance, a LIB is based on lithium ion intercalation and deintercalation processes, while the basis of FBs is the oxidation and reduction reaction of redox couples in liquid electrolytes.^{1,33,34} Therefore, the requirements for porous membranes in different secondary batteries are variable, bringing about different modification methods on them. As an illustration, surface modification is nowadays the most commonly used method in LIBs, while blending or compositing with conductive materials is frequently used in Li-S batteries.^{28,35}

The preparation methods, pore structures and performance of porous membranes in different secondary batteries are closely correlative. The principle of various preparation methods is different, creating porous membranes with variable structures. Porous membranes with variable structures perform differently in various secondary batteries, because of the diverse demands of batteries. The necessary modification methods are then conducted to offset the drawbacks to improve the membrane performance. Therefore, illuminating the preparation–structure–performance relationship of porous membranes in different secondary batteries is significant for further membrane design and optimization.

The purpose of this review is to describe the utilization of porous membranes in various secondary battery technologies. Preparation methods of porous membranes in different secondary batteries are elucidated in detail. The operating principle of different secondary batteries and corresponding desirable requirements for porous membranes are explained as well. Importantly, the reasons why modifications are needed, the basic principles of different modification methods, the further improvement of these methods and the properties of diverse modification materials, *etc.* are illustrated and discussed thoroughly and deeply. The utilization of variable novel membrane materials in secondary batteries is also summarized. The preparation–structure–performance relationship of porous membranes in secondary batteries is discussed as well.

Therefore, it will help to understand the status, limitations and optimizations of currently developed porous membranes in different secondary battery technologies. An extensive, comprehensive and professional reference will be provided to direct future research to enhance the performance of current porous membranes in different secondary batteries.

2. Overview of preparation methods of porous membranes

2.1 Phase separation method

The phase separation method is able to obtain membranes with various porous structures, so as to meet the various requirements of different secondary battery technologies. As a result, the phase separation method has already been widely applied for the fabrication of porous membranes in secondary battery technologies, especially in FBs and LIBs.^{22,26,28,31,36–38} In this method, a molecularly homogeneous polymer solution with a certain composition is firstly formed. The thermodynamic equilibrium of the solution is then broken up in some physical ways, accompanying the transformation of the solution from the single phase into two phases. A polymer-lean phase and a polymer-rich phase are thus formed. The polymer-rich phase will form the membrane matrix in the end, while the dispersive polymer-lean phase produces the pores. Therefore, membranes with a porous structure are formed after removing the polymer-lean phase.²³

The thermodynamic states of the solution can be typically demonstrated by a phase diagram (Fig. 2). In a phase diagram, the binodal curve is calculated based on the Flory–Huggins theory or by measuring the cloud point, while the spinodal curve is obtained by the derivatives of the binodal curve.^{30,39–41} The phase separation is usually based on the nucleation and growth (NG) mechanism and/or the spinodal decomposition (SD) mechanism. When the composition of the solution locates in the meta-stable region, the solution phase will be separated by the NG mechanism, leading to closed and cellular pores (Fig. 2). In contrast, when the composition of the solution locates in the unstable region, the solution phase is separated spontaneously by the SD mechanism. The membrane derived

from the SD mechanism has a bi-continuous or a droplet morphology (Fig. 2).^{22,30,42–50} The key during the process of phase separation lies in the variation in the thermodynamic states of the polymer solution. Hence, on the basis of different physical ways of changing the thermodynamic states of the solution, phase separation methods can be categorized to thermally induced phase separation (TIPS), nonsolvent induced phase separation (NIPS), vapor induced phase separation (VIPS) and solvent evaporation-induced phase separation (SIPS).

2.1.1. Thermally induced phase separation (TIPS). The TIPS method is suitable for a binary mixture consisting of a polymer and a solvent, where the latter is usually referred to as the diluent. The process of TIPS involves liquid–liquid or solid–liquid demixing (Fig. 3a).^{22,51–54} A polymer/diluent system is heated to above the upper critical solution temperature (UCST) to attain a homogeneous solution firstly. Secondly, the temperature is decreased below the UCST to cool the solution and induce phase separation, forming the polymer-rich phase and polymer-lean phase, respectively. Finally membranes with porous structures are prepared by a subsequent extracting process to remove the diluent (e.g. polymer-lean phase) in the polymer matrix, like immersing in a nonsolvent bath (traditionally containing water). When the binary mixture undergoes liquid–liquid demixing, a typical cellular structure is formed (Fig. 3a). However, when the binary mixture undergoes solid–liquid demixing, the subsequent extraction process is unnecessary and a typical structure full of spherulites is produced (Fig. 3a).^{24,52,53,55–59}

The easy controllability together with less influencing parameters for membrane fabrication makes the TIPS method

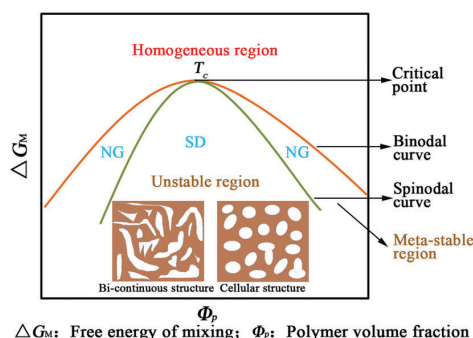


Fig. 2 The schematic representation of a phase diagram.

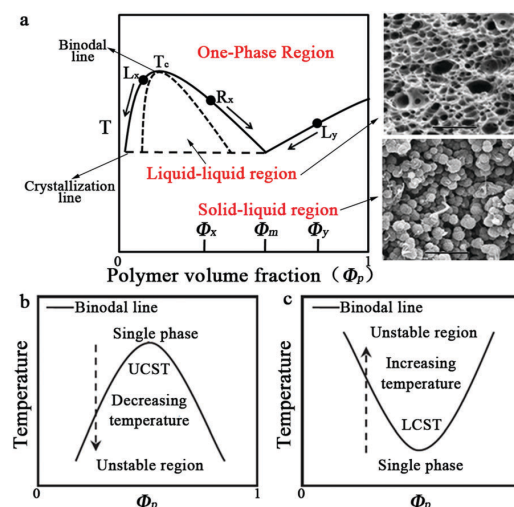


Fig. 3 (a) Temperature–composition phase diagram for a system showing liquid–liquid and solid–liquid phase separation (note monotectic point, Φ_m), and the typical cross-section morphology of (top) cellular pores and (bottom) spherulites. The bar: 5 μm ; and schematic representation of the phase diagram for a polymer solution with a (b) UCST or (c) LCST.^{55,59,60} Reproduced from ref. 55 with permission, copyright Elsevier, 2013; ref. 59 with permission, copyright Elsevier, 2008; and ref. 60 with permission, copyright Elsevier, 1991.

possess high versatility and reproducibility.^{38,54,61–64} A membrane prepared by this method normally owns a morphology with more uniform structure, high porosity, narrow pore size distribution and good mechanical stability.^{24,55,56,65,66} In general, TIPS is suitable for fabricating porous membranes from semi-crystalline thermoplastics,^{51,67–71} because of their poor solubility in various solvents (diluent) at room temperature.⁷² In fact, an ideal diluent used for TIPS should possess features like low molecular weight, high boiling point, low volatility, high miscibility with polymers at high temperature, good thermal stability, low toxicity and environmental friendliness.^{65,73,74} Lower molecular weight can create smaller and more interconnected pores, increasing the porosity of membranes. And the high boiling point and low volatility of diluents help hinder their evaporation above the UCST.

Hence, the main challenges that the TIPS method is confronted with are the selection of appropriate diluents and the large energy consumption derived from the high UCST.²⁴ To solve these problems, Zhao *et al.* proposed a novel concept of lower critical solution temperature-TIPS (LCST-TIPS), in other words reverse thermally induced phase separation (RTIPS) (Fig. 3b vs. Fig. 3c).⁵⁵ They succeeded in preparing microporous poly(ether sulfone) (PES) flat-sheet membranes using this method at a low membrane-forming temperature.

2.1.2. Nonsolvent induced phase separation (NIPS). The NIPS method, or immersion precipitation is suitable for a ternary system, composed of a polymer, a good solvent and a nonsolvent (the poor solvent), sometimes containing additives.⁷⁵ The basis of NIPS is the difference in the solubility of polymers in the solvent and nonsolvent, respectively. The mass transfer of NIPS can be illustrated by the phase diagram of a polymer–solvent–nonsolvent system (Fig. 4a). A homogeneous casting solution including a polymer and a solvent is produced in the one-phase region (the blue region, the purple one is the two-phase region). Subsequently, the solution is cast on a support to form a film. When the film is immersed into a coagulation bath containing a nonsolvent, the solvent and nonsolvent will exchange under the driving force caused by the gradient in the chemical potential.⁷⁶ The composition of the polymer–solvent–nonsolvent system thus transfers from the one-phase region to the two-phase one. This transference also accompanies the variation in thermodynamics of polymers from dissolving in the solvent to being solidified in the nonsolvent. The porous structure is hence formed after the solvent is exchanged completely by the nonsolvent.^{23,30,41,76–83} It is worth noting that the solvent and nonsolvent must be miscible.

The membrane formation mechanism of NIPS can be further divided into instantaneous demixing and delayed demixing, depending on the rate of solvent–nonsolvent exchange (Fig. 4a). Fast solvent–nonsolvent exchange will make the composition path of the solution pass through the binodal curve rapidly and directly. The system thus transfers from the one-phase region to the two-phase one immediately after immersion. This process is called instantaneous demixing, finally leading to a finger-like morphology. A typical finger-like structure is composed of a dense skin layer, macrovoids and a dense bottom layer (Fig. 4a and b). In contrast, if the composition path does not pass through the

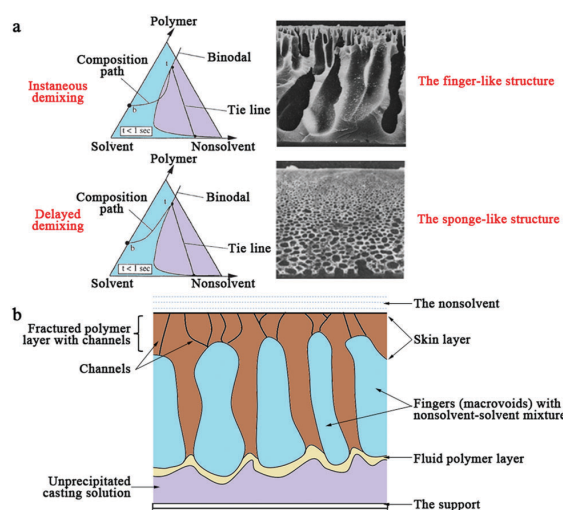


Fig. 4 (a) The principle of (top) instantaneous demixing and (bottom) delayed demixing as well as their corresponding typical structures; (b) a schematic diagram of a membrane with a finger-like structure during membrane formation.^{41,78} Reproduced from ref. 41 with permission, copyright American Chemical Society, 2011; and ref. 78 with permission, copyright Elsevier, 1975.

binodal curve, a sponge-like morphology is produced. A representative structure of the sponge-like morphology consists of a dense skin layer and large pores penetrating the entire membrane cross-section (Fig. 4a).^{22,30,38,41,55,75,84,85}

During the process of NIPS, the rate of solvent–nonsolvent exchange is the most dominant factor in determining the final membrane pore structure. The reason lies in whether the rupture of the initial solidified skin layer occurs. Fast solvent–nonsolvent exchange causes a fractured skin layer by the creep relaxation of the polymer, allowing quicker solvent–nonsolvent exchange under the fractured skin layer. More polymer-lean phase droplets will form and coalesce, and macrovoids are thus produced. On the other hand, the casting solution between macrovoids is protected by the unbroken skin layer, undergoing comparably slow solvent–nonsolvent exchange. Hence, there is longer time for the formation of polymer-rich phase droplets and polymer-lean phase droplets, and a relatively uniform spongy like pore structure is thus produced (Fig. 4b).^{76,78}

The NIPS method is one of the most commonly used methods to fabricate porous membranes in secondary batteries, due to its permission for the fabrication of various membrane structures, especially for FBs.^{27,41,86–89} During the procedure of NIPS, many factors will affect the final morphology of porous membranes, such as the constituent of the casting solution, the composition of the solvent or the coagulation bath, additives in the casting solution, the miscibility of the solvent and nonsolvent, *etc.*^{26,41,89–105} In general, lower polymer concentration, higher miscibility of the solvent and nonsolvent, higher hydrophilicity or lower viscosity of the casting solution will lead to quicker solvent–nonsolvent exchange. A more open porous structure with a larger pore size and wider pore size distribution is produced and *vice versa*.

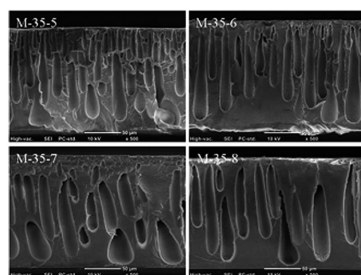


Fig. 5 Cross-section morphology of porous PES/SPEEK blend membranes prepared with different SPEEK contents (increasing SPEEK content). The bar: 50 μm .⁸⁹ Reproduced from ref. 89 with permission, copyright the Royal Society of Chemistry, 2014.

For example, the addition of hydrophilic sulfonated poly(ether ether ketone) (SPEEK) into PES casting solution will favor the realization of different pore morphologies. Because, when the SPEEK concentration is low, its addition will increase the hydrophilicity of the casting solution, contributing to faster solvent–nonsolvent exchange. However, the increase in SPEEK concentration will improve the viscosity of the casting solution at the same time, preventing the exchange of the solvent and nonsolvent. Delayed demixing thus occurs and sponge-like pores are more inclined to form (Fig. 5).^{89,94,106} Furthermore, some preparation parameters will influence the properties of porous blend membranes sometimes. For example, the improved SPEEK content in PES casting solution will increase the hydrophilicity of porous PES/SPEEK blend membranes as well.

Nonetheless, the conventional NIPS method is more complicated than the TIPS method, mostly thanks to there being too many preparation parameters. In addition, the asymmetric morphology containing finger-like macrovoids generally has poorer mechanical strength. The difficulty in recovery of solvents is another disadvantage of this method.^{61,63,107} But, it is notable that the lower processing temperature and facile operation adds to the flexibility of the NIPS method.

2.1.3. Vapor induced phase separation (VIPS). The VIPS method is similar to the NIPS method to some degree and has been widely used in FBs to date.^{108–110} Differently, the solution containing a polymer and a solvent is exposed to a vapor atmosphere consisting of a nonsolvent (typically water). And the nonsolvent will then permeate into the solution to induce phase separation (Fig. 6). Commonly, an immersing process is needed after being exposed to the nonsolvent vapor. The membranes

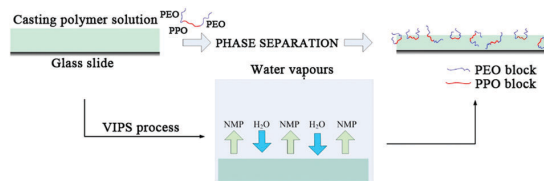


Fig. 6 Schematic illustration of the preparation process of porous poly-sulfone (PSF) membranes via VIPS.¹¹⁶ Reproduced from ref. 117 with permission, copyright Elsevier, 2012.

prepared using this method often have a highly porous surface, because the solvent employed for VIPS has lower volatility than the nonsolvent.^{22,36,48,50,66,86,111–123}

Besides, various membrane structures from symmetric to asymmetric can be realized using VIPS by controlling the preparation parameters, such as the polymer concentration, the relative humidity (RH) of the vapor atmosphere, the exposure time to vapor atmosphere, *etc.*^{36,42,48,50,117,124,125}

Such factors will determine whether the mechanism of phase separation during VIPS is the NG or SD mechanism. For instance, the membrane morphology can be transferred from macrovoids to the bi-continuous structure and finally to cellular pores by the combination of adjusting the polymer concentration and exposure time, because different polymer concentrations result in different areas of the meta-stable region, and different exposure times lead to different duration times in this region (Fig. 2 and 7). Therefore, the amount of the polymer solution that undergoes the NG or SD mechanism is variable. Various porous structures are thus formed.^{36,48}

The RH of the vapor atmosphere can also tune the pore size of membranes. Lower RH generally brings about slower exchange of the solvent and nonsolvent vapor, and larger pore size is thereby preferable. This is because the slower phase separation can provide more time to coarsen the phase separated structure in the polymer solution, consequently causing larger pores.^{36,42,118,126} Furthermore, low vapor temperature expedites the crystallization process, contributing to the formation of a porous skin layer and particle morphology.¹²¹ In short, the structure of porous membranes fabricated using the VIPS method is not affected by a monotonous factor. It is facile to tune the membrane morphology from macrovoids to a bi-continuous structure to cellular pores by adjusting the preparation parameters. On the other hand, comparably various influencing factors during the preparation process may exert large effects on the final membrane morphology, similarly to NIPS. As a consequence, it is significant to use the combination of many process parameters to

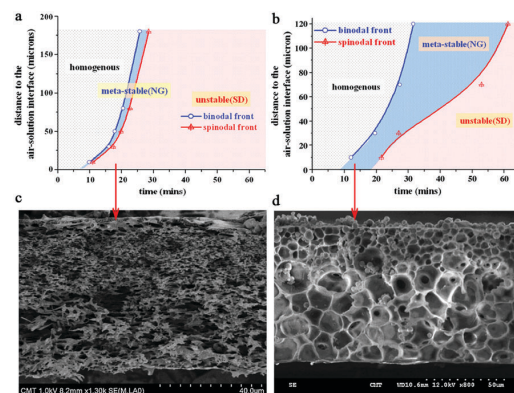


Fig. 7 (a) Binodal and spinodal fronts for the 10 wt% case (25.5 $^{\circ}\text{C}$, 64.4% RH); (b) binodal and spinodal fronts for the 20 wt% case (26.0 $^{\circ}\text{C}$, 62.3% RH); (c) the bi-continuous structure, the bar: 40 μm ; (d) the cellular structure, the bar: 5 μm .⁴⁸ Reproduced from ref. 48 with permission, copyright Elsevier, 2009.

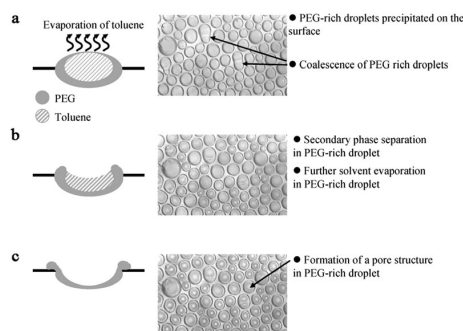


Fig. 8 Schematic diagrams and pictures taken using a microscope in visual observation mode to explain the formation of the pore structure during SIPS (PEG: polyethylene glycol).¹³⁰ Reproduced from ref. 130 with permission, copyright American Chemical Society, 2007.

achieve the desirable membrane structure by VIPS for different secondary batteries.

2.1.4. Solvent evaporation-induced phase separation (SIPS).

A polymer dissolves in the mixture of a solvent and a nonsolvent, where the volatility of the solvent is higher than that of the nonsolvent. By controlled evaporation of the solvent, phase separation is induced due to the growth and coalescence of droplets rich in the nonsolvent. The porous morphology is thus formed by the thermal removal of nonsolvent enriched droplets. This method is called SIPS, dry-casting, or air-casting (Fig. 8).^{79,127–131} Compared with other phase separation methods, the SIPS method is relatively simple, due to the dispensation of a following coagulation bath and it also has good reproducibility.^{38,127,129} However, it is not usual to use the SIPS method to prepare porous membranes for secondary batteries. Therefore, we won't pay much attention to this method.

In summary, the most common methods used to prepare porous membranes for secondary battery technologies are TIPS and NIPS, because of their outstanding features as listed in Fig. 9. It is notable that the coalescence of various phase inversion methods can be used to combine their benefits and avoid their drawbacks.^{61,64,107,132–134} As an illustration, by combining the advantages of both TIPS and NIPS as illustrated in Fig. 9, membranes with high permeability and strong mechanical properties are realized.^{132–135}

2.2 The electrospinning technique

Electrospinning is a straightforward method to produce polymer fibers from polymer solutions, with diameters ranging from 40 to 2000 nm.^{138,139} In an electrospinning process, a polymer solution is stored in a reservoir, which is typically a capillary tube or a pipette. And its surface tension can hold itself at the end of the pipette (Fig. 10).¹⁴⁰ When the polymer solution is faced with an electric field, free charges are created on the solution surface. The increased intensity of the electric field will make the surface of the solution at the tip of the pipette deform to be in a conical shape known as a Taylor cone. When the electric field reaches a critical value, at which the

applied electric voltage overcomes the surface tension force, one or more charged jets of the polymer solution are ejected from the tip of the Taylor cone towards the collector. The trajectory of these charged jets can be controlled by the electric field. The solvent then rapidly evaporates and the jets are elongated. The charged polymer fibers are thus laid randomly on the collector and the continual layout of fibers forms a fibrous membrane at the end.^{140–145}

This method can be used to create fibrous membranes with complex architectures, like core-shell fibers or hollow fibers.¹⁴² In general, electrospun membranes own high porosity, large surface area, and fully interconnected open pore structures.^{141,147} These features are in favor of ion conduction. Therefore, the electrospinning technique is commonly utilized in LIBs. To date, polymers such as PVDF, polyethylene terephthalate (PET), poly(phthalazinone ether sulfone ketone) (PPESK), polyacrylonitrile/polyurethane (PAN/PU) composite and other composites have been used as the materials to prepare porous membranes by the electrospinning technique as separators for LIBs.^{141,146,148–154}

The successful electrospinning of fibers is affected by many factors, including the properties of the polymer solution and the variables. The former includes the solution viscosity, conductivity, surface tension and so on. The latter is made up of electric voltage, hydrostatic pressure in the reservoir, the distance between the tip and the collector, the shape of the collector and so on.^{144–146} Notably, these variables are often controlled.

It is worth noting that the electrospun membranes often possess poor mechanical properties, which is the main drawback of the electrospinning technique. The inferior tensile strength, insufficient thermal stability and shut down behavior of electrospun membranes seriously restrict their further application in secondary batteries.^{146,153} To overcome this issue, the appropriate choice of polymer materials and the suitable adjustment of electrospinning parameters are very significant. Yang *et al.* succeeded in preparing porous PVDF fibrous membranes with better mechanical properties as the separators for LIBs.¹⁴⁶ Moreover, they also adopted a novel electrospinning system utilizing a spherical hat collector instead of the plane collection target (Fig. 10 vs. Fig. 11a). The as-prepared fibers fabricated by this method had uniform thickness and fiber diameter, which led to flatter membranes with higher porosity (Fig. 11b vs. Fig. 11c). By tuning the corresponding parameters, they found that a higher solution concentration, a smaller fiber diameter, and a more uniform thickness and fiber diameter led to higher mechanical strength of the PVDF membranes.

2.3 The stretching technique

The stretching technique is commonly used in lithium-based batteries, particularly for the production of microporous polyolefin separators.^{28,155,156} This technique is usually divided into the dry process and the wet process.¹⁵⁷

The dry process is also called the melt-spinning and cold-stretching (MSCS) method. A typical dry process involves four steps: heating, extruding, annealing and stretching (Fig. 12). Firstly, the polymer resin is heated to form a homogeneous fused polymer solution. The fused solution is then extruded to

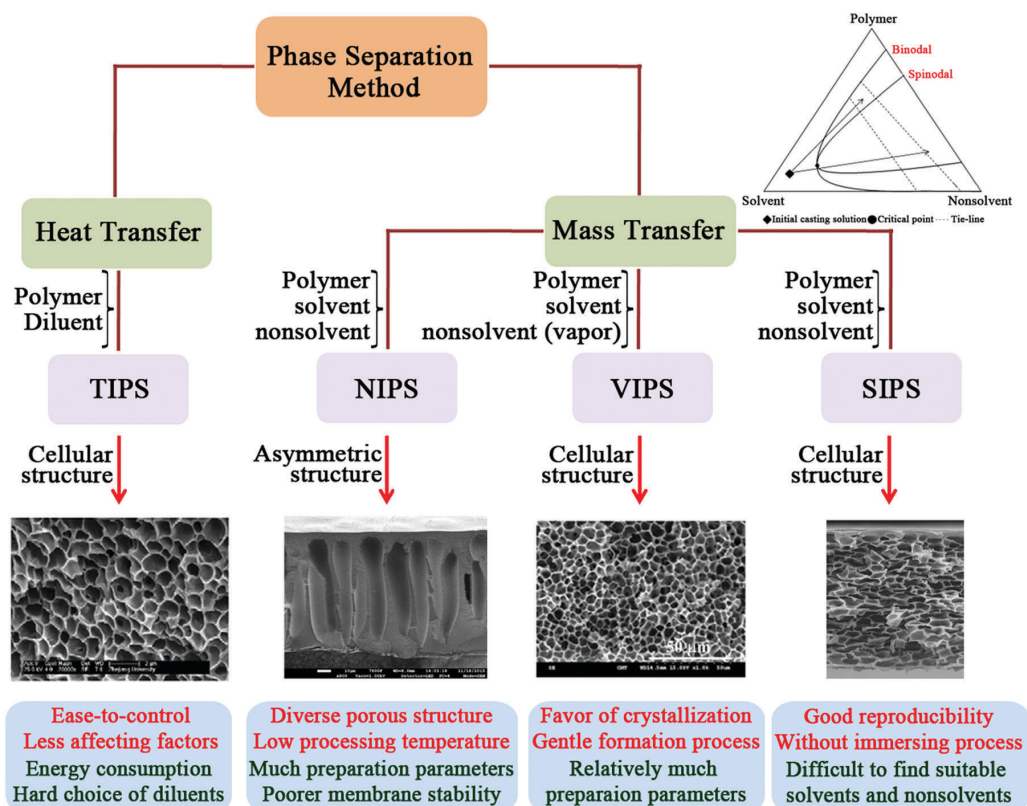


Fig. 9 The summary and comparison of different phase separation methods.^{56,101,116,136,137} Reproduced from ref. 56 with permission, copyright Elsevier, 2012; ref. 101 with permission, copyright the Royal Society of Chemistry, 2016; ref. 116 with permission, copyright Elsevier, 2012; ref. 136 with permission, copyright Elsevier, 2005; and ref. 137 with permission, copyright John Wiley and Sons, 2015.

create a prefab film. A thermal annealing step helps to eliminate deficiencies and accelerate the crystallization. Finally, the prefab film is stretched to induce a microporous membrane. The wet process is also called the TIPS method. The wet process involves five steps: mixing and heating, cooling and phase separating, extruding, solvent extraction and stretching. Similarly, a mixture of a polymer resin, a hydrocarbon liquid or some other substance with low molecular weight (playing the role of the diluent), and some appropriate additives are heated and melted to form a homogeneous polymer solution. Then the solution is cooled to induce its phase separation. Differently from the TIPS method as described above, the phase separated film is not immersed into a nonsolvent bath to generate a porous phase separated membrane but extruded to generate a prefab film (Fig. 12). Subsequently, this film is stretched to form micropores with the required pore structure (mainly including pore size and porosity). Finally, the hydrocarbon liquid and additives are extracted with a volatile solvent to create a microporous membrane with interconnected pores. It is notable that the stretching step can also be carried out after the solvent extraction step (Fig. 12). In general, the dry process is simpler than the wet process, thanks to the addition and removal of diluents. Besides, the utilization of diluents will bring about high cost and environmental problems in the most time.^{28,60,73,157–169}

The stretching method is appropriate for semi-crystalline polymers, like PP and polyethylene (PE). In this method, the structure of microporous membranes is affected by many factors, such as the melt-draw ratio, spinning temperature, and annealing temperature in the dry process and the properties of diluents as well as polymers, and the cooling velocity in the wet process as mentioned above.^{170–172} At present, the stretching technique has been extensively used to fabricate commercial microporous polyolefin separators. For example, Asahi Kasai uses the wet technique to fabricate PE separators and Celgard LLC uses the dry technique to produce PP as well as PE separators.¹⁵⁶

Different preparation methods produce porous membranes with different pore structures. The membrane structures formed by phase separation methods are various, like cellular pores, and finger-like and sponge-like pores, because of the different mechanisms of the various phase separation methods. And the pore structure, including pore size, porosity, pore size distribution, pore interconnectivity and so on, can be effectively optimized by tuning the corresponding preparation parameters. Thus, these structures can meet the diverse performance requirements of different secondary batteries. The features of porous membranes prepared by the electrospinning technique and stretching technique are that they often have fibrous morphology with

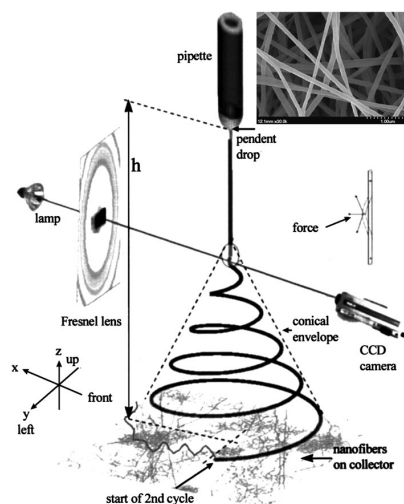


Fig. 10 Schematic drawing of the electrospinning process, showing the jet path, reference axes, relative arrangement of parts of the apparatus at different scales, and the region where the bending instability grew rapidly. (Inset) The morphology of an electrospun membrane.^{140,146} Reproduced from ref. 140 with permission, copyright AIP Publishing LLC, 2000; and ref. 146 with permission, copyright Elsevier, 2009.

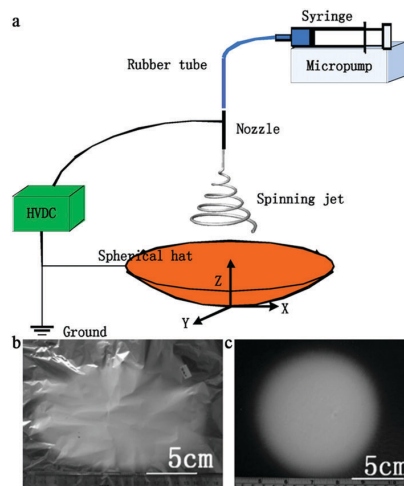


Fig. 11 (a) The novel electrospinning system with a spherical hat collection target; deposition patterns with (b) a plane collection target and (c) a spherical hat collection target after 70 min.¹⁴⁶ Reproduced from ref. 146 with permission, copyright Elsevier, 2009.

large surface area, high porosity and high pore interconnectivity. Such kinds of porous structures favor ion conduction, consequently satisfying the demands for secondary batteries. Investigating the principles and influencing factors of various preparation methods clarifies the relationship between them and the membrane structures. Therefore, we can use such a relationship to choose the best fabrication method to create desirable porous structures, and their performance is thus optimized. Nevertheless, the

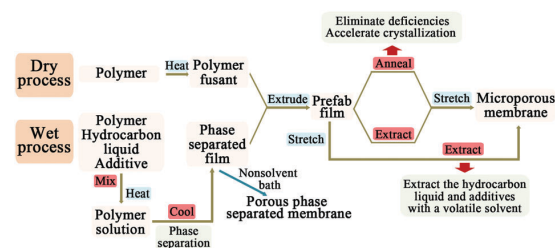


Fig. 12 The comparison of the dry process and wet process.

relationship between the membrane structure and its performance in different secondary batteries must be illuminated above all.

3. Porous membranes for secondary battery applications

3.1 Vanadium flow batteries (VFBs)

3.1.1. Desirable properties of porous membranes in a VFB.

The VFBs are one of the most attractive FB technologies, due to their intriguing characteristics of independently tuned power and capacity, long cycle life, high safety, high efficiency and environmental friendliness.^{1,173–178} A VFB uses the reversible redox reactions of V^{2+}/V^{3+} in the positive electrolyte and VO^{2+}/VO_2^+ in the negative electrolyte to realize the storage and release of energy. The crossover of vanadium ions in the positive and negative electrolytes will cause self-discharge of the batteries. Therefore, the membrane is extremely critical in a VFB, which plays the role of preventing cross-mixing of vanadium ions to hinder the capacity loss of the batteries. And it can still allow the transport of ions to complete an electrical circuit. A perfect membrane in a VFB should have the following features:⁹

- (1) Capable of conducting ions freely and rapidly to achieve high ion conductivity.
- (2) Able to prevent the crossover of vanadium ions effectively to realize high ion selectivity.
- (3) High chemical stability under the strong acid and oxidized operating conditions of VFBs.
- (4) Low cost for commercialization.

The key to improve the ion selectivity of membranes in VFBs lies in the effective separation of vanadium ions from protons. And the key for accelerating the ion conductivity is the free and rapid transport of protons. Nonetheless, it is generally known that high ion selectivity will sacrifice the ion conductivity, because high vanadium ion/proton (V/H) selectivity means blocked transport of protons as well. Thus, the final target of investigations of membranes in VFBs is to obtain a high-performance membrane with high ion selectivity and proton conductivity (namely ion conductivity in VFBs) simultaneously, while possessing high chemical stability and low cost.

However, the most commonly used commercial membranes in VFBs, like the series of Nafion membranes, have low ion selectivity, because such membranes have larger ion transport channels or more obvious microphase separated structures, which originate from the rearrangement of hydrophobic and

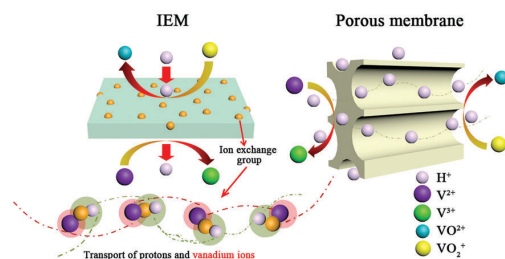


Fig. 13 Schematic diagram of the transport mechanism of protons and vanadium ions through an IEM and a porous membrane, respectively.

hydrophilic segments. Moreover the negatively charged ion exchange groups also help the transference of vanadium ions (Fig. 13). And their high cost further restricts the development of VFBs.^{9,179–182} On the other hand, another widely researched type of membrane in VFBs is non-perfluorinated ion exchange membranes, on account of their high thermal and mechanical stability, high ion selectivity and low cost. However, the presence of ion exchange groups attached to non-perfluorinated membranes leads to poor chemical stability. This shortcoming makes it hard for them to meet the required properties of VFBs.^{183–187} Thus, designing and developing high performance novel membranes is highly significant for the commercial process of VFB application.

3.1.2. The introduction of porous membranes. In 2011, we proposed a completely novel concept to introduce a porous NF membrane without ion exchange groups into VFBs (Fig. 14).²⁶ This concept was on the basis of pore size exclusion, which can overcome the limitation caused by ion exchange groups.^{20,26} The feasibility and availability of this concept lie in that the Stokes radius and charge density of vanadium ions are much larger than those of hydrated protons (Fig. 13 and 14).^{188–190} The efficient separation of vanadium ions from protons can thereby be realized by tuning the pore structure (like pore size, porosity and pore size distribution) of porous membranes.

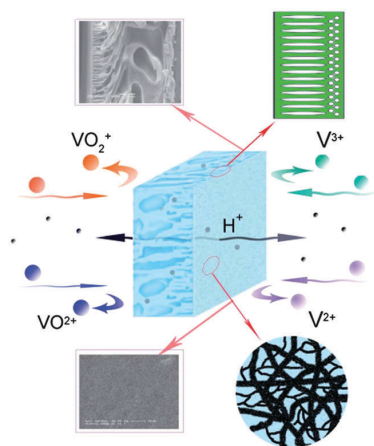


Fig. 14 Schematic principle of NF membranes in VFBs.²⁶ Reproduced from ref. 26 with permission, copyright the Royal Society of Chemistry, 2011.

The frequently-used evolution indicators of the performance for porous membranes in VFBs are efficiencies, rate performance, cycling performance and chemical stability. Efficiencies of porous membranes include coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE). CE is defined as the ratio of a battery's discharge capacity to its charge capacity. Higher CE represents higher ion selectivity and lower capacity loss. VE is defined as the ratio of a battery's discharge voltage to its charge voltage. Higher VE results from lower resistance or higher proton conductivity. And EE is the product of multiplying CE by VE, serving as an indicator of energy conversion. In addition, the cycling performance indicates the chemical stability of porous membranes under VFB operating conditions. For the first reported NF membranes, the CE of the VFB with the as-prepared porous polyacrylonitrile (PAN) membrane was around 95% at a current density of 80 mA cm⁻², which was higher than that of commercial Nafion 115 (CE = 93.4%, VE = 88.3%, EE = 82.4%). This result confirmed the versatility and practicability of NF membranes in VFBs. Besides, they also successfully utilized porous PSF/SPEEK blend membranes in VFBs and realized an EE of 71%, further verifying the availability of NF membranes in VFBs. On the other hand, their EEs were still lower than those of Nafion 115 at the same current density. Hence, even though porous membranes have been successfully used in VFBs, their relatively low ion selectivity and proton conductivity are the primary challenges that need to be solved. Consequently, various modification methods have been carried out to optimize the structure and performance of porous membranes in VFBs.

3.1.3. The optimization of porous membranes. The optimization of porous membranes in VFBs concentrates on adjusting their pore structure. The pore structure parameters, including pore size, porosity, pore size distribution, pore interconnectivity and so on, can be effectively tuned to realize a relatively ideal structure, thus achieving an impressive performance in VFBs. In general, the following methods can be adopted to improve the ion selectivity of VFBs assembled with porous membranes:

(1) Pore size exclusion: decreasing the pore size and porosity, narrowing the pore size distribution, and breaking up the pore interconnectivity to form more circuitous passages for the transference of vanadium ions.

(2) Donnan exclusion: introducing positively charged groups into the membrane matrix.

Alternatively, to increase the proton conductivity of porous membranes we can use the following methods:

(1) Pore size exclusion: increasing the pore size and porosity, widening the pore size distribution, and improving the pore interconnectivity to form more smooth passages for the transport of protons.

(2) Electrostatic interaction: introducing negatively charged functional groups into the membrane matrix.

Obviously, there is a conflict between ion selectivity and proton conductivity of porous membranes in VFBs. As an illustration, higher resistance of proton transport across the membranes will be induced by smaller pore size, which is preferred for higher selectivity on the other hand. Therefore,

seeking an appropriate tradeoff between ion selectivity and proton conductivity is the key to realizing the performance optimization of porous membranes in VFBs.

3.1.3.1. The optimization of preparation parameters. The primary aim of this modifying method is to adjust the pore size and porosity of membranes. Porous membranes are commonly prepared by phase separation methods and the most widely used method is NIPS. Thus as described above, optimization of preparation parameters during the process of phase separation is very effective to improve the membrane performance. As for NIPS, changing the polymer concentration of the casting solution, introducing additives in the casting solution, changing the properties and constituent of solvents and non-solvents, controlling the casting thickness and so on can be used to adjust the pore structure of membranes.^{80,87,191–195} The principle of optimizing preparation parameters lies in adjusting the process of membrane formation, mainly changing the rate of solvent–nonsolvent exchange. As an illustration, Cao *et al.* tuned the morphology of porous PVDF membranes *via* the NIPS method using dual-coagulation with different water/ethanol compositions (Fig. 15).⁸⁰ The adjustable pore structures originated from the changes in the thermodynamic properties and the kinetic nature under the membrane forming process. These changes were closely related to the solubility parameter difference, the mutual affinity and compatibility between constituents (water and ethanol) in the coagulation bath, and the solvent in the casting solution. And the diffusion coefficient between the nonsolvent and solvent, the composition of the coagulation bath and so on also played an important role. The final result was that the addition of ethanol in the coagulation bath caused a delayed demixing process, and a spongy like structure was easier to produce. Therefore, the appropriate porous membrane structure and performance in VFBs could be obtained after optimizing the relevant parameters including the ethanol content and immersion time in the coagulation bath. An EE of 80.1% was realized with the 7 : 3 volume ratio of water/ethanol at 80 mA cm^{−2}, while the CE and EE were still relatively lower.

Li *et al.* also prepared porous PES membranes with tuned pore structures by changing the hydrophilic poly(vinyl pyrrolidone) (PVP) content and molecular weight in casting solutions.⁸⁷

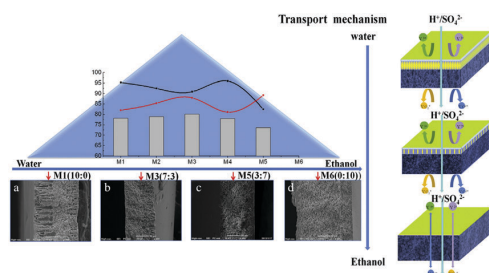


Fig. 15 Cross-section morphology of PVDF membranes with respect to their performance in VFBs and membrane transport mechanism (M1–M6: increasing ethanol content in the coagulation bath).⁸⁰ Reproduced from ref. 80 with permission, copyright Elsevier, 2014.

PVP actually worked as the pore-forming material. Wei *et al.* prepared hydrophobic asymmetric porous PVDF membranes as alternatives by changing the composition of casting solutions and the casting thickness during NIPS as well.²⁷ However, the EEs of both the resultant membranes after being optimized were lower than 80% at 80 mA cm^{−2}, while their CEs and VEs are lower as well.

In addition to phase separation methods, a novel solvent-template method can also be used to manufacture membranes with tunable pore structures for VFBs.¹⁹⁶ This method is analogous to the SIPS one, where a relatively volatile solvent and a nonvolatile template solvent are applied. Differently, the template solvent is not a nonsolvent and it is removed by an immersion process, not an evaporation procedure (Fig. 16a vs. Fig. 8). During the process of solvent evaporation, the strong “solvation effect” between the solvent template and polymer chains helped to form a thoroughly interpenetrated solvent–polymer network, which led to ion conducting membranes (ICMs) with the maximum porosity. Compared with the traditional immersion precipitation method, porous membranes prepared by this method had more regular and interconnected structures (Fig. 16b). Moreover, by tuning the proportion of the volatile solvent and nonvolatile solvent template, a dramatically changed microstructure of ICMs could be obtained. Ion transport channels with different sizes were thus formed. The physiochemical properties and battery performance of these ICMs were effectively adjusted in accordance as well. Although the CE of the resultant membrane at 80 mA cm^{−2} was very high, its VE was still relatively low.

Hence, only optimizing the preparation parameters is not thorough and efficient enough to produce porous membranes with good performance for their large-scale application in VFBs. That is to say the effectiveness of only pore size exclusion is restrained to achieve high ion selectivity and proton conductivity at the same time. Some novel modification methods should be exploited and designed to be combined with the pore size exclusion effect.

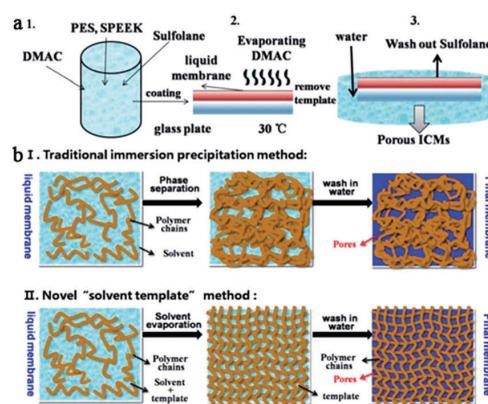


Fig. 16 (a) An illustration of the solvent template method; (b) an illustration of the solvent-template method vs. the traditional immersion precipitation method.¹⁹⁶ Reproduced from ref. 196 with permission, copyright the Royal Society of Chemistry, 2014.

3.1.3.2. The introduction of hydrophilic inorganic based materials. As for the asymmetric membrane, the pores in the skin layer determine the selectivity of porous membranes. Smaller pores in the skin layer are preferred to realize higher ion selectivity but cause higher resistance to the transport of protons. Oppositely, larger pores are in favor of the transport of protons but lead to more cross-mixing of vanadium ions. The introduction of hydrophilic inorganic based materials can effectively solve this conflict, by tuning the process of phase separation or optimizing the properties of the resultant composite membranes. Their introduction is beneficial to forming spongy like porous structures, leading to smaller pore size or narrower pore size distribution. Improved ion selectivity can be achieved, while their high hydrophilicity helps to obtain good proton conductivity simultaneously.^{88,197–201} Thus the filling of inorganic based materials won't damage the proton conductivity of porous membranes too much. To date, ceramic materials are the most commonly used hydrophilic modifying materials. For example, silica is widely used to solve the conflict between high ion selectivity and proton conductivity.^{197,198,200} Zhang *et al.* successfully prepared porous membranes with *in situ* assembled silica on the surface and in the pores of porous PAN membranes (Fig. 17).¹⁹⁷ This method induced decreased pore size and a much denser skin layer, and improved V/H selectivity was thus realized. Besides, sulfonic acid could be absorbed by assembled silica nanoparticles under the VFB operating environment, which promoted the transport of protons. High proton conductivity was therefore also well maintained. As a consequence, VFBs assembled with silica modified membranes demonstrated much higher CE and similar VE compared with those of original porous membranes at 80 mA cm⁻².

Furthermore, Wang *et al.* successfully prepared nanoporous polytetrafluoroethylene/silica (PTFE/SiO₂) composite membranes and used them in the mixed-acid VFB system.²⁰² In this design, submicron sized silica particles helped to produce nanoporous structures and their high hydrophilicity was in favor of proton conduction. Differently from PAN/SiO₂ composite membranes, the PTFE fibril network provided a membrane with both high flexibility and good mechanical strength for flow battery operation. The similarity was that ion selectivity was also assured through pore size exclusion. By means of combining the advantages of PTFE and SiO₂, the membrane demonstrated excellent electrochemical cycling performance and chemical stability compared to those of Nafion 115. Although its final

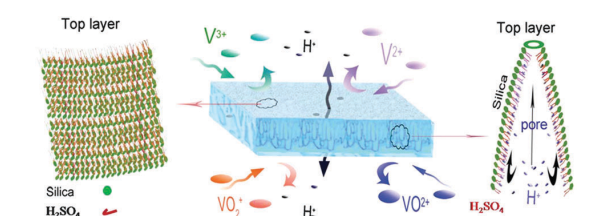


Fig. 17 Schematic principle of silica modified porous membranes in VFBs.¹⁹⁷ Reproduced from ref. 197 with permission, copyright the Royal Society of Chemistry, 2012.

EE was lower than that of Nafion 115 under the same VFB operating conditions, the extremely low cost of the PTFE/SiO₂ membrane made it a promising alternative for commercial Nafion 115.

Apart from silica, a zeolite with negatively charged sites could also be used in porous membranes.¹⁰⁹ On the one hand, its filling can reduce the pore size and narrow the pore size distribution, accordingly acquiring a comparably compact porous structure. On the other hand, negatively charged groups attached to the zeolite can ensure the transport of protons by electrostatic interaction. That could offset the decreased conductivity caused by a denser pore structure. It is noteworthy that the favorable transference of vanadium ions resulted from the electrostatic interaction between negatively charged sites and can be efficiently reduced by the pore size exclusion effect. For instance, Yuan *et al.* introduced an ultra-thin ZSM-35 zeolite flake onto a porous PES based membrane, because such crystalline microporous zeolites had regular arrangements of cages, well-defined channels and anionic sites (AlO₄⁻) (Fig. 18a and b).^{109,203–207} Nevertheless, the most significant reason was that its pore size (*ca.* 0.5 nm) was just right, intermediary between that of hydrated vanadium ions (>0.6 nm) and protons (<0.24 nm). An excellent V/H selectivity could hence be achieved.^{189,207–209} Besides, AlO₄⁻ sites provided good proton conductivity (Fig. 18a and c). Consequently, a VFB

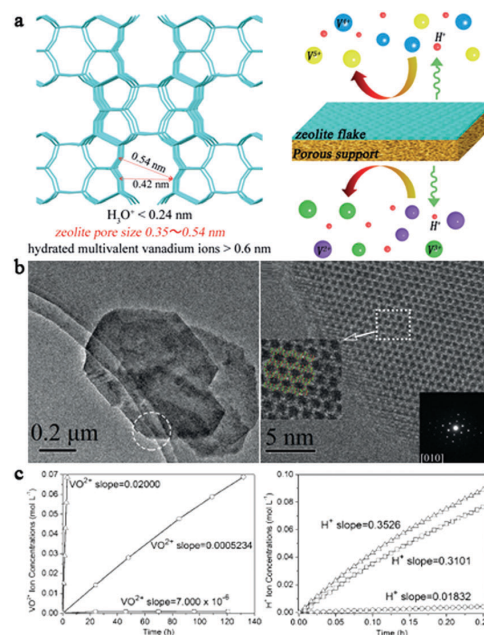


Fig. 18 (a) Design principles of a VFB with a porous membrane bearing a zeolite flake layer; (b) (left) TEM image of ZSM-35 zeolite; (right) HRTEM image of ZSM-35 zeolite viewed in the [010] direction; (c) (left) VO₂⁺ concentration and (right) H⁺ concentration *versus* time at the diffusion side of a diffusion cell using substrate, Nafion 115 and zeolite-coated membranes. Key: substrate (–Δ–), zeolite-coated membrane (–□–), and Nafion 115 membrane (–○–).¹⁰⁹ Reproduced from ref. 109 with permission, copyright John Wiley and Sons, 2016.

assembled with the resultant zeolite-coated membrane showed an excellent performance with a CE of 98.6%, a VE of 92.7% and an EE of 91.4% at 80 mA cm^{-2} . But then, the most notable result was that an EE of over 81% was obtained at 200 mA cm^{-2} , which was among the highest values ever reported at such a high current density. Therefore, a great balance between high ion selectivity and proton conductivity could be realized by introducing hydrophilic inorganic based materials.

3.1.3.3. The introduction of charged groups. This modifying method can efficiently adjust charges on the pore walls and in the membrane matrices to achieve a better balance between ion selectivity and proton conductivity. Introducing negatively charged groups into the porous membrane matrix is a common way to improve proton conductivity, because the transport of protons is based on the Grotthuss mechanism (Fig. 13).²¹⁰ At the same time, pore size should be reduced to ensure high ion selectivity, based on pore size exclusion. To date, the traditional negatively charged groups used in VFBS are sulfonic acid groups.^{88,201} For instance, by introducing an ultrathin ion selective (Nafion) layer on the porous membrane support, high proton conductivity was well maintained by the negatively charged sulfonic acid groups and relatively large pores on the skin layer. Although, negatively charged sulfonic acid groups could also favor the transference of vanadium ions, high ion selectivity was realized by the formation of an ultrathin top layer and adjustable pore size of the porous membrane support.⁸⁸

When positively charged groups are introduced into porous membranes, the combination of pore size exclusion and the Donnan exclusion mechanism is very much available to improve their ion selectivity in VFBS.^{110,195} Pyridine (Py), PVP, imidazolium and polypyrrole (PPY) containing N groups have been applied, because the positively charged N groups can be easily protonated under acidic conditions, promoting the transport of protons in the meantime.^{110,195,199,211} Zhang *et al.* specially designed and prepared a kind of positively charged porous membranes with highly symmetric spongy structures for VFBS.¹¹⁰ By grafting alkaline groups, a unique stack of closed cells consisting of positively charged ultrathin walls were formed (Fig. 19a). The positively charged groups and sufficiently disconnected pores helped the improvement in ion selectivity. And the weak alkaline groups could also bind sulfuric acid, facilitating the transport of protons. Therefore, a better balance between ion selectivity and proton conductivity was achieved. Finally, an EE of about 85% for the resultant membrane was realized at 80 mA cm^{-2} , which was much higher than that of Nafion 115. However, its VE was still lower, due to the disconnected pores. And the chemical stability of the resultant membranes was relatively poor, because of the introduction of minor charged groups (Fig. 19b).

To further improve the chemical stability of membranes with positively charged groups, an advanced porous membrane with positively charged internal cross-linked networks on pore walls was designed and fabricated.¹⁹⁵ These internal cross-linked networks were formed *via* the reaction between the positively charged imidazole groups and chloromethylated PSF (CMPSF) (Fig. 19c). The purpose of designing such an

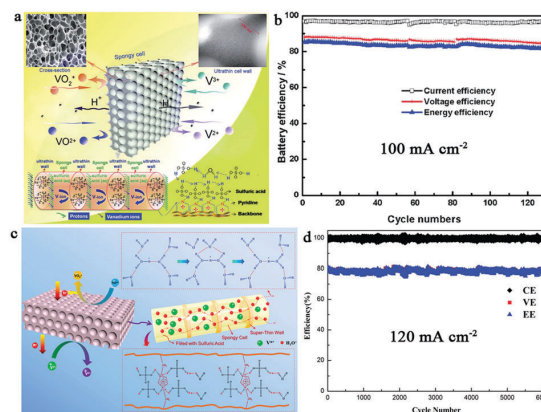


Fig. 19 (a) Principle of designed membranes with symmetric spongy structures in a VFB; (b) the cycling performance of a VFB single cell assembled with CMPSF-Py at 100 mA cm^{-2} ; (c) principle of the advanced charged spongy-like membrane with an internal cross-linked network applied in a VFB; (d) the cycling performance of a VFB single cell assembled with CMPSF-72 at 120 mA cm^{-2} .^{110,195} Reproduced from ref. 110 with permission, copyright the Royal Society of Chemistry, 2013; and ref. 195 with permission, copyright John Wiley and Sons, 2016.

internal cross-linked network was to realize ultrahigh stability and selectivity *via* combining superiorities of anion exchange membranes and porous membranes. The Donnan exclusion effect of positively charged imidazole groups together with the pore size sieving effect of porous membranes ensured high ion selectivity. Therefore, an ultrahigh CE of 99% was realized for the resultant membrane at 80 mA cm^{-2} (CMPSF-72). Besides, internal cross-linked networks built on pore walls led to excellent chemical stability of membranes. The VFB single cell assembled with CMPSF-72 exhibited a highly stable battery performance over more than 6000 cycles at a high current density of 120 mA cm^{-2} , showing excellent stability (Fig. 19d). And the VFB single cell using CMPSF-72 showed an EE of 86% at 80 mA cm^{-2} , which was much higher than that of Nafion 115. In this design, the proton conductivity of the as-prepared membranes could be assured through the adjustable pore size and typical “Grotthuss mechanism” from ion exchange groups. But then, the relatively lower VE (87%) still needed to be further improved.

As mentioned above, the combination of the sponge-like porous structure and charged groups is in favor of the realization of better performance for porous membranes in VFBS. The sponge-like structure accelerates the improvement in the ion selectivity, and charged groups can help to ensure high proton conductivity. To further solve the conflict between high ion selectivity and proton conductivity, Li *et al.* continued perfecting this kind of structure (Fig. 20). However, the difference was that they adopted a novel polybenzimidazole (PBI) polymer containing positively charged N groups as the membrane material. The porous membranes fabricated by the VIPS method also had spongy porous structures and positively charged groups (Fig. 20d).²¹² Therefore, the high selectivity originated in four aspects: (i) the unique spongy pore structures composed of thousands of micron-sized cells; (ii) the VIPS method was inclined to forming uniformly distributed

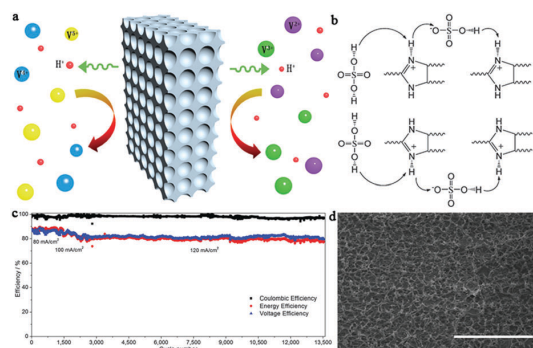


Fig. 20 (a) The schematic principle of the designed membrane with symmetric spongy structures in VFBs; (b) the proton conducting mechanism of the prepared membranes; (c) the long-term stability test of a VFB assembled with PBI-68 at current densities ranging from 80 to 120 mA cm⁻²; (d) a scanning electron microscopy morphology of the membrane cross section; scale bar: 5 μm.²¹² Reproduced from ref. 212 with permission, copyright the Royal Society of Chemistry, 2016.

and disconnected porous structures; (iii) the optimization of preparation parameters during VIPS could tune the pore structures; and (iv) the positively charged pore walls of all disconnected cells provided multiple barriers for vanadium ions. Meanwhile, the acids doped in PBI pores resulted in high proton conductivity, owing to the fact that nitrogen in the PBI ring could be easily protonated under acidic conditions (Fig. 20b).²¹³ Despite the charged groups, the intrinsically very high thermal, mechanical and chemical stability of PBI, and the optimized pore structure could still bring about excellent stability of porous PBI membranes in VFBs. Finally, the VFB assembled with the resultant membrane (PBI-68) showed a CE of 98.9%, a VE of 91.1% and an EE of 90.1%, which were overall much higher than that of commercial Nafion 115. And the most notable performance was its extremely high chemical stability. A VFB with PBI-68 could run for more than 13 000 cycles, with no obvious efficiency decay (Fig. 20c). This was the first time that a non-perfluorinated porous membrane had been fabricated with stability over 10 000 cycles. Therefore, a superior tradeoff between high ion selectivity and proton conductivity of porous membranes was realized. It must be worth noting that such an excellent balance is the coalescence of introducing the novel hydrophilic membrane material, introducing positively charged amine groups and optimizing preparation parameters during the process of phase separation.

In short, it is effective and available to combine the Donnan exclusion and pore size exclusion mechanism to improve the ion selectivity of porous membranes, by introducing positively charged groups into them. It is worth noting that materials containing positively charged groups (like amine groups) should own relatively good hydrophilicity to ensure proton conductivity. And the main aim of introducing negatively charged groups is to improve the hydrophilicity of porous membranes. The ion selectivity is usually ensured by adjusting the pore structure, on the basis of pore size exclusion, which can be realized by optimizing preparation parameters during the process of phase separation or the filling of inorganic

nanoparticles, *etc.* Thus, the utilization of charged groups in porous membranes is an efficient way to balance high ion selectivity and proton conductivity. Nonetheless, more stable membrane materials and tunable pore size must be applied to remedy the loss of chemical stability, or ion selectivity, or proton conductivity caused by charged groups.

3.1.3.4. The structure design and optimization. A great balance between high ion selectivity and proton conductivity can be realized by the aforementioned methods. But whichever methods are adopted, their purpose is structure design and optimization of the porous membranes. Hence, understanding the mechanism of ion transport through a porous membrane, the formation mechanism of porous membranes, the mechanism of capacity decay and so on is extremely important. To the best of our knowledge, investigations on these mechanisms are very rare. Until 2016, Zhao *et al.* proposed a model of ion transport through a porous membrane in a VFB.²¹⁴ They reveal that the mechanism of vanadium ion crossover through available separators is predominated by convection. Reducing the pore size can effectively minimize the convection-driven vanadium ion crossover. However, only when the pore size is reduced to a level close to the size of vanadium ions, can the reduction in migration- and diffusion-driven vanadium ion crossover be achieved. Moreover, operating conditions exert a significant influence on the vanadium ion crossover rate, like the electrolyte flow rate. Nevertheless, the porous membrane that they adopted is a commercially available one. The mechanism of ion transport through most of the porous membranes in the experimental level including the aforementioned membranes, is still in a black zone.

The formation mechanism of porous membranes is the most complicated and profound one. Explicit and deep cognition of this mechanism can help instruct the design and production of porous membranes minutely and precisely. As stated, the introduction of charged groups should be avoided as much as possible, in view of the commercial utilization of VFBs in the long term.^{19,20,215} Consequently, designing and developing high-performance porous uncharged membranes is considerably significant. But the controllability of the porous uncharged membrane morphology and performance in VFBs cannot be realized without a clear and thorough understanding of the formation mechanism of porous membranes. Thus, the lack of research studies on this mechanism must be made up.

Lately, Lu *et al.* carried out a preliminary investigation on the formation mechanism of porous membranes by a novel and simple solvent treatment method.¹⁰¹ By adjusting the solvent evaporation time during solvent treatment, the controllability of the pore structure and performance of porous membranes was realized. As a matter of fact, it was the adjustment of the cohesive and swelling force of the polymers that tuned the membrane morphology. The difference in the cohesive and swelling force served as the acting force to shrink the pore structure, in favor of improved ion selectivity and enhanced chemical stability (Fig. 21). Controlling the pore size to be larger than the size of hydrated protons (but smaller than that

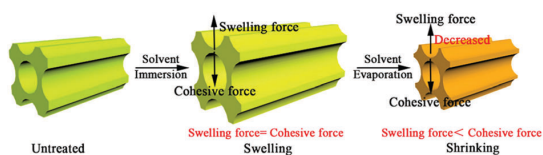


Fig. 21 The evolution of the pore during solvent treatment.¹⁰¹ Reproduced from ref. 101 with permission, copyright the Royal Society of Chemistry, 2016.

of hydrated vanadium ions) and simultaneously keeping the good pore interconnectivity of the original membranes led to well-maintained proton conductivity. The final membranes exhibited a CE of over 99% and an EE of over 90% in VFBs at 80 mA cm^{-2} .

Afterwards, studying the formation mechanism by the solvent treatment method was further conducted in order to better carry out the structure design and optimization of porous membranes. We used the interactions between solvents and charged groups in the membrane matrix to construct an ordered hydrophobic/hydrophilic phase separated structure. Polymer chains in the porous PES/SPEEK blend membrane were reorganized induced by polymer-solvent interactions during solvent immersion (Fig. 22). Hydrophilic ion-transport channels were thus formed during the process of solvent evaporation, including a number of aggregated hydrophilic groups on pore walls.²¹⁶ And these ion-transport channels could be controlled by changing solvent evaporation time. Such a phase separated structure is composed of a shrunk pore structure and hydrophilic pore walls, and a better tradeoff between high ion selectivity and proton conductivity was thereby achieved.

These primary research studies on the formation mechanism of porous membranes confirmed the feasibility and availability to design and control pore structure precisely. This expands a new view on how to easily obtain the ideal structure and performance of porous membranes in VFB applications.

In general, ion selectivity of porous membranes is ensured by the pore size sieving effect or the Donnan exclusion effect or their combination, while their proton conductivity is assured by

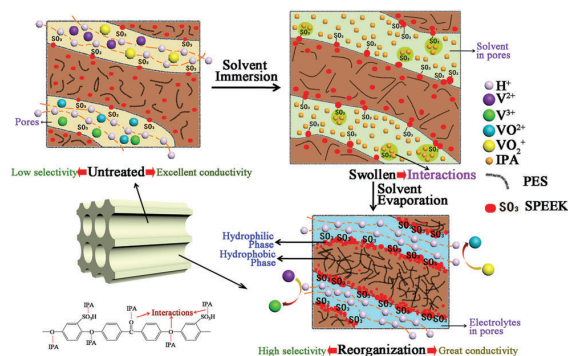


Fig. 22 The principle of the solvent-induced reorganization of polymer chains in the porous PES/SPEEK blend membrane.²¹⁶ Reproduced from ref. 216 with permission, copyright John Wiley and Sons, 2016.

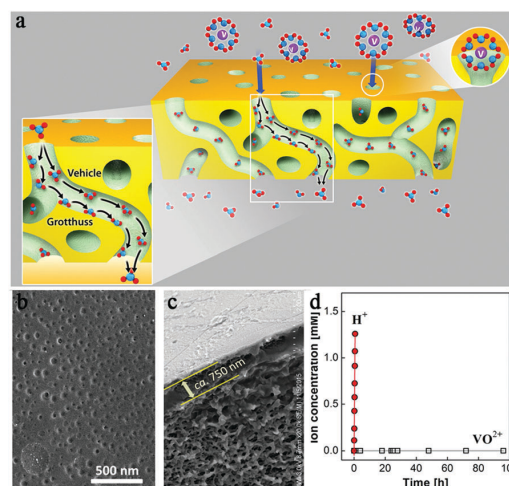


Fig. 23 (a) The principle of proton transfer based on the Grotthuss or convection mechanism, and the blocking of hydro-solvated vanadium ions by a subnano-sieving PIM-1 membrane during the redox process; (b) surface and (c) cross-section morphology of the PIM-1/PAN composite membrane; (d) the H^+/V selectivity of the prepared PIM-1 (0.75 μm)/PAN membrane.²¹⁷ Reproduced from ref. 217 with permission, copyright John Wiley and Sons, 2016.

the hydrophilicity of membrane materials. Nevertheless, Wessling *et al.* recently reported a fundamentally unprecedented concept of hydrophobic porous polymer membranes with ultra-high proton/vanadium selectivity.²¹⁷ The concept was based on PIM-1 coating and the PAN ultrafiltration membrane support (Fig. 23b and c). PIM-1 is a kind of hydrophobic polymer but with an intrinsic microporosity. The fact that hydrophobic PIM-1 did not swell in water led to confined water inside its pores, while the hydrophobic matrix remained changeless. Differently from porous membranes with charged groups, proton conductivity through this hydrophobic material was based on the vehicle mechanism, namely the convection mechanism. Hence, it was exactly that such confined water inside the microporosity of PIM-1 realizes the transport of protons (Fig. 23a). Their smaller pore size, the relatively little swollen and rigid polymer matrix prevented the crossover of bulky vanadium ions. Therefore, an infinite H^+/V selectivity was achieved using hydrophobic, non-ionic polymeric membranes for the first time (Fig. 23d). Sufficient proton transfer without vanadium ion crossover finally resulted in an unprecedented high EE of 98.7% or so at 1 mA cm^{-2} .

This concept confirmed the feasibility and applicability of hydrophobic materials in VFBs. Nevertheless, the proton conductivity of hydrophobic membranes is still poorer compared with that of hydrophilic ones. Some necessary modifications still need to be carried out for further improving their proton conductivity.

3.1.4. The upscale application of porous membranes. To date, the electrochemical performance of porous membranes in VFBs has been very high and there is actually relatively finite room for improvement in their efficiencies (Fig. 24). Currently,

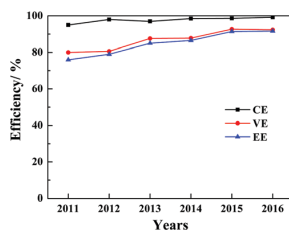


Fig. 24 The development of energy efficiencies of porous membranes at 80 mA cm^{-2} in VFBs.

the most important topic in the field of porous membranes should focus on their upscaled utilization in VFB applications. Considering the advantages and drawbacks of the aforementioned modification methods, Yuan *et al.* assembled a kW stack with PBI-68, because PBI-68 possessed great balance between high ion selectivity and proton conductivity together with excellent stability as mentioned before (Fig. 25a).²¹² A superior battery cell stack efficiency and high capacity retention were realized as current densities varied (Fig. 25b). Furthermore, the cell stack has continuously operated stably for more than 100 cycles at a current density of 120 mA cm^{-2} (Fig. 25c).

This research progress of porous membranes proved their reliability and practicality in VFBs. The low cost and high chemical stability are the keys in the upscaled application of porous membranes. This extraordinary demonstration elucidates that apart from carrying out modifications on traditional porous membranes, to seek and exploit novel membrane materials with high performance and stability is another feasible method.

Accordingly, optimizing preparation parameters or using more effective preparation methods, introducing different advanced modifying materials, studying various mechanisms of porous membranes deeply and in detail, and developing novel membrane materials can be potential ways to promote the upscaled use of porous membranes in VFBs (Table 1). It is very possible for porous membranes with high performance but low cost to replace commercial Nafion membranes in the near future. But whichever methods are adopted, the intrinsic pore size exclusion of porous membranes is their basis.

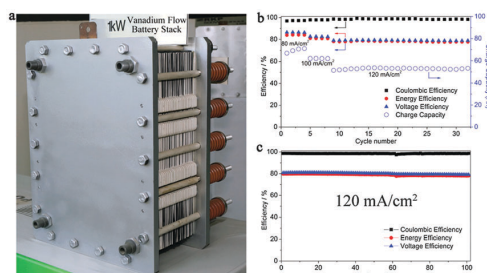


Fig. 25 (a) The kW VFB cell stack prototype using a PBI-68 porous membrane; (b) the kW VFB cell stack performance at current densities ranging from 80 to 120 mA cm^{-2} ; (c) the cycling performance of the cell stack assembled with a PBI-68 porous membrane under 120 mA cm^{-2} .²¹² Reproduced from ref. 212 with permission, copyright the Royal Society of Chemistry, 2016.

Even though the idea of using porous membranes in VFB applications was put forward in 2011, their performance has been dramatically improved in recent years. And the EE of the VFB assembled with the optimized porous membrane reached as high as 91% at 80 mA cm^{-2} after a series of deep and thorough investigations. Their first introduction into VFBs was due to their high stability of porous uncharged membranes without ion exchange groups. In addition, their unique pore size exclusion is promising to achieve high V/H selectivity. Since then, various modification methods have been adopted to optimize the porous membrane performance in VFBs. These methods consist of changing the preparation parameters during membrane formation, introducing hydrophilic inorganic based materials and charged groups into porous matrices, *etc.* Their conjunct aim is to carry out structure design and optimization, because the adjustment of pore size, porosity, pore size distribution, pore interconnectivity and pore charges is dominant for the performance optimization of porous membranes in VFBs. For instance, the spongy structure is better for the improvement in the ion selectivity and stability than the finger-like structure. Although negative charges on pore walls or in membrane matrices also contribute to the rapid transference of vanadium ions, the conditioning of pore size, pore interconnectivity and so on can improve the ion selectivity by pore size exclusion as well. Therefore, the mechanism of ion transport, the formation mechanism and the mechanism of capacity decay should be paid more and more attention to instruct structure design and optimization. And a better balance between ion selectivity and proton conductivity was indeed acquired by using the formation mechanism of porous membranes. The future target of porous membranes is to continue studying the relevant mechanism of porous membranes to further understand the preparation–structure–performance relationship, and finally successfully realizing their industrialization. Therefore, further reducing the cost and improving the stability of porous membranes will be the focus in the near future.

Except for VFBs, porous membranes (such as commercial Daramic membranes) can also be applied in other FBs, like iron–redox batteries and iron–vanadium (Fe/V) flow batteries.^{156,218,219} However, investigations concentrated on porous membranes in other FBs are very scarce, so we won't pay more attention to them in this review.

3.2 Lithium-ion batteries (LIBs)

3.2.1. Desirable properties for porous membranes in a LIB. LIBs have received very high attention due to their high volumetric as well as gravimetric energy storage capability, high energy density, long cycle life, low self-discharging, high voltage and no memory effect. In the past few years, LIBs have been extensively applied in powering portable electronic products and electric vehicles.^{28,34,220–225} Similar to VFBs, the membrane, which is often called as the separator, is a crucial component for a traditional LIB. It plays the role of separating the anode and cathode to prevent short circuits, while permitting the rapid and free transport of lithium ions to achieve a complete electric circuit.^{16,28,156,226–228} In addition, separators should possess the

Table 1 The summary of modification methods on porous membranes in VFBs

Modifying method	Membrane matrix	Parameters	Problems and requirements	Ideas	Results
To optimize preparation parameters	PES	Properties and contents of additives in the casting solutions (NIPS).	Tune porous membrane morphology effectively and simply.	Clarify the effects of additives on the membrane formation process, morphology and performance.	Obtain different structures; increase the stability; poor balance between selectivity and conductivity; ^{a,b} EE: about 76%. ⁸⁷
	PVDF	Composition of the casting solutions; the casting thickness (NIPS).	Choose suitable alternatives for commercial membranes in VFBs.	Tune the pore structures of porous membranes.	Excellent stability; lower cost; relatively lower selectivity; high hydrophobicity of PVDF; ^c EE: 78.6%. ²⁷
	PES	Contents of the polymer and hydrophilic SPEEK in casting solutions (NIPS).	Tune porous membrane morphology effectively and simply.	Adjust the membrane morphology by changing the polymer compositions and blending hydrophilic materials in the casting solutions.	Tune structures from finger-like to sponge-like pores; excellent oxidation stability; lower CE and VE; losing mechanical stability; ^c EE: 78%. ⁸⁹
	PVDF	Compositions of the coagulation bath (NIPS).	Tune porous membrane morphology effectively and simply.	Study the effect of coagulation medium on the PVDF membrane morphology to optimize their performance.	Tune the membrane morphology effectively; lower CE and VE; poor cycling performance; ^b EE: 80.1%. ⁸⁰
	PES/SPEEK	Content of the solvent and solvent template (solvent-template method).	Prepare ICMs with desirable porous structures.	Exploit a novel and efficient preparation method of porous membranes to easily control the membrane morphology along with the battery performance.	Controlled ion channel size of as-prepared membranes; good chemical stability; high battery efficiency (CE: over 99%); ^{b,d} EE: over 92%. ¹⁹⁶
To introduce hydrophilic inorganic based materials	PAN; PSF/SPEEK	Silica	Low selectivity and low conductivity of pure porous membranes.	Adjust pore size to improve the V/H selectivity and still keep a high conductivity.	Improved selectivity and chemical stability; lower conductivity; ^c EE: 79% (PAN) and 78% (PSF/SPEEK). ¹⁹⁷
	PTFE	Silica	Low selectivity and high cost of commercial membranes.	Combine the stability of PTFE and the submicron size as well as hydrophilicity of silica.	Low cost; excellent stability for long-term operation; not stable enough for the upscale application; ^{e,f,g} EE: 80%. ²⁰²
	PES/SPEEK	Silica	Serious conflict between high ion selectivity and proton conductivity.	Adjust pore size and pore size distribution by controlling the quantity of silica gels inside pristine pores by the solvent responsive sol-gel method	Higher CE; high oxidation stability through long-term battery operation; lower VE; ^c EE: 83%. ²⁰⁰
	PES/SPEEK	ZSM-35	Difficulty in tuning pore structures to effectively separate vanadium ions from protons.	Construct a selective layer to tune pore size between that of vanadium ions and protons to allow free transport of protons and enable pore size exclusion simultaneously.	Excellent balance between high selectivity and conductivity; high chemical stability; great cycling performance; low cost; relatively poor stability for the upscale application; ^c EE: 91.4%. ¹⁰⁹
To introduce charged groups	PSF	NaSS (negatively charged)	Conflict between high ion selectivity and proton conductivity of porous PSF membranes.	Carry out the hydrophilic treatment by grafting hydrophilic materials to improve conductivity and keep small pore size to retain selectivity.	More hydrophilic membranes; higher ions permeability; higher VE but lower CE; complicate and expensive method; ^b EE: 78%. ²⁰¹
	PES/SPEEK	Nafion (negatively charged)	Conflict between high selectivity and high ohmic polarization induced by smaller pores.	Introduce an ultrathin ion selective layer to ensure conductivity, and selectivity is assured by the pore size exclusion effect.	Improved ion selectivity; relatively high VE; low stability; more cross-mixing of vanadium ions; ^b EE: 87%. ⁸⁸
	PVDF	PVP (positively charged)	High hydrophobicity of PVDF.	Improve the hydrophilicity of PVDF membranes and construct well-connected ion transport networks by chemical cross-linking and grafting PVP on the membranes.	Better hydrophilicity; effective pore size adjustment; increased ion selectivity; lower CE; complex method; ^c EE: 83%. ¹⁹⁹
	CMPSF	Py (positively charged)	Serious conflict between high ion selectivity and proton conductivity.	Construct a spongy structure containing fixed positive charges to combine pore size and Donnan exclusion effect.	High selectivity and improved conductivity but still low VE; comparably high chemical stability; ^c EE: 85%. ¹¹⁰
	CMPSF	Imidazolium (positively charged)	Poor chemical stability of IEMs; conflict between selectivity and conductivity.	Construct internal positively charged cross-linked networks.	Ultra-high stability and selectivity; excellent cycling performance; lower VE; ^e EE: 86%. ¹⁹⁵

Table 1 (continued)

Modifying method	Membrane matrix	Parameters	Problems and requirements	Ideas	Results
	PBI	Imidazole (positively charged)	Choose suitable and high-performance alternatives for commercial membranes in VFBS.	Use the combination of introducing novel membrane materials, optimizing preparation parameters and Donnan exclusion effect to improve membrane performance.	Facile fabrication procedure; ultra-long cycle life; easy up-scaling and low cost; not stable enough for the industrial application; ^h EE: 90.11%. ²¹²
	PES	PPY (positively charged)	The conflict between high ion selectivity and proton conductivity.	Use PPY nanoparticles to decrease the pore size of membranes, while still maintaining high ion conductivity <i>via</i> the acid doped PPY.	High ion selectivity; excellent ion conductivity; high chemical stability; relatively poor stability for the upscale application; ^c EE: 87.2%. ²¹¹
To carry out structure design and optimization	PES	Solvent evaporation time	The unclear cognition on the formation mechanism of porous membranes.	Study the formation mechanism of porous membranes to realize the controllability on the membrane morphology and performance by solvent treatment.	Realization of the controllability on the pore structure and performance; excellent balance between selectivity and conductivity; low cost; relatively poor chemical stability; ^h EE: 90.19%. ¹⁰¹
	PES/SPEEK	Solvent evaporation time	The still unclear cognition on the formation mechanism of porous membranes.	Use interactions between the solvent and polymer to construct a hydrophobic/hydrophilic phase separated structure with a highly stable porous matrix and interconnected small pores to form proper ion-transport channels.	Creation of membranes with controlled ion-transport channels; excellent balance between selectivity and conductivity; relatively poor chemical stability; ^h EE: 91.62%. ²¹⁶

^a At 80 mA cm⁻² without special explanations. ^b The effective area of the electrode is unavailable. ^c The effective area of the electrode is 9 cm² without special explanations. ^d At 40 mA cm⁻². ^e At 50 mA cm⁻². ^f In the mixed-acid VFB system. ^g The effective area of the electrode is 40 cm². ^h The effective area of the electrode is 48 cm².

function of improving the performance and ensuring the safety of LIB application. An ideal separator used in LIBs should own the following features:^{16,28,63,226,229–231}

- (1) Electronic insulator to prevent an electric short circuit.
- (2) Excellent wettability to liquid electrolytes to obtain high lithium ion conductivity.
- (3) High thermal stability at high temperature.
- (4) Mechanical and chemical stability.
- (5) Other appropriate properties, like thickness, resistance, etc.

IEMs are unable to conduct lithium ions in electrolytes to complete an integrated circuit, due to the fact that LIBs normally use organic electrolytes. Thereby, porous separators are normally used in lithium-based batteries with organic electrolytes, including LIBs and Li-S batteries. In LIBs, microporous membranes (MMs) have been normally used as separators, because of their ability to absorb and retain ionically conductive liquid electrolytes. These electrolytes traditionally contain lithium salt to ensure ion conductivity, such as the frequently-used ethylene carbonate (EC) and propylene carbonate (PC).^{28,220} The current commercial microporous separators in LIBs are mostly made from polyolefin materials, including PE, PP, and their combinations such as PE/PP and PP/PE/PP (Fig. 26).^{16,28,156,222,232–234} More recently, a variety of polymers, like PVDF-based polymers,^{63,235–238} poly(vinyl alcohol) (PVA),²³² and polyimide (PI)²³⁹ have also been used as materials to prepare microporous separators for LIBs. Zhang *et al.* have made a detailed introduction on their research and development.²⁸ In this review we will more focus on membrane modification methods and their further development.

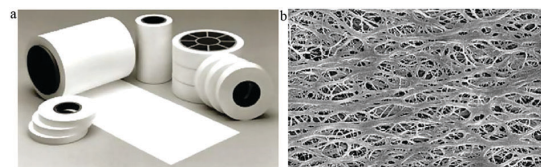


Fig. 26 (a) Microporous polyolefin separators used in LIBs; (b) surface morphology of the microporous PP separator.^{156,229} Reproduced from ref. 156 with permission, copyright American Chemical Society, 2004; and ref. 229 with permission, copyright Elsevier, 2007.

3.2.2. Microporous polyolefin separators. Polyolefin is among the most significant materials for separators in LIBs, as a result of its low price, high chemical resistance, high mechanical stability and so on.^{227–229,233,234,240,241} Nonetheless, the poor wettability to liquid electrolytes and serious thermal shrinkage of polyolefin at higher temperature limit its further application in LIBs. In general, the poor affinity of microporous polyolefin separators for liquid electrolytes results from their low polarity and low surface tension. In general, the common electrolytes, like EC and PC, own ether groups, ester groups and other polar groups. The lack of relevant polar groups results in a large difficulty in absorbing and holding enough liquid electrolytes including lithium ions. As a consequence, the ultrahigh electrolyte resistance constrains higher ionic conductivity and better rate capability of LIBs.^{223,227,229,242–244} Furthermore, the severe thermal shrinkage at higher temperature leads to internal short circuits and even to fire outbreak or explosion, particularly when the battery is over-charged or overheated.^{25,156,229,230,245–250} These phenomena

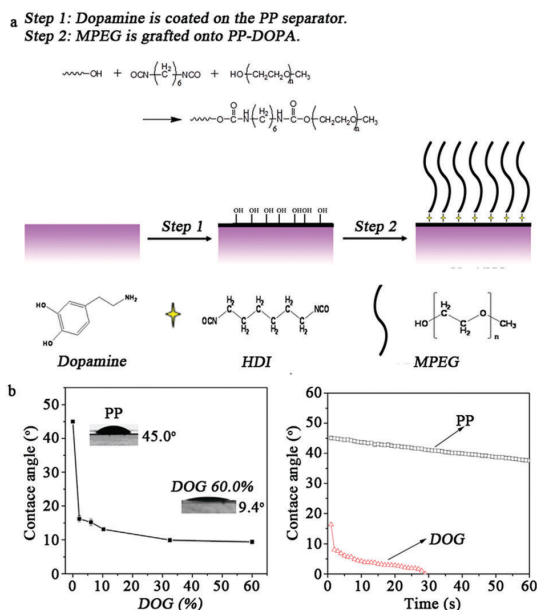


Fig. 27 (a) Schematic illustration of the immobilization of MPEG on the dopamine functionalized PP separator; (b) (left) static and (right) time dependent liquid electrolyte contact angle on PP separators and PP-g-MPEG separators (MPEG: methoxy polyethyleneglycol).²²⁷ Reproduced from ref. 227 with permission, copyright Elsevier, 2013.

seriously affect the rate performance and safety of LIBs assembled with microporous polyolefin separators. And safety is one of the most significant factors determining the practical application of LIB technologies. Hence, most modification methods on microporous polyolefin separators concentrated on solving the above two issues.

Surface modification, including surface grafting and surface coating is an effective method to optimize the pore structure and performance of polyolefin separators. The latter is usually used for improving the affinity for liquid electrolytes and the latter is generally applied to enhance the thermal stability of microporous polyolefin separators.

3.2.2.1. Surface grafting. The key to improving the wettability of microporous polyolefin separators lies in the introduction of adequate electrolyte-philic monomers, which can increase their polarity and surface energy. These electrolyte-philic monomers often contain polar functional groups, such as ester groups and ether groups. Because the electrolytes usually used in LIBs include the polar ester groups, ether groups, and sometimes sulphone groups. More electrolytes are thus absorbed to accelerate the transport of lithium ions, in favor of the improved rate capability.^{156,223,226–228,242,244,251–253} To date, polymers like polyethylene glycol (PEG), poly(ethylene glycol) borate acrylate (PEGBA), poly(methylmethacrylate) (PMMA), glycidyl methacrylate (GMA) and so on can be grafted onto polyolefin supports. And the grafting methods include radiochemical grafting, atom transfer radical polymerization, electron beam radiation-induced graft copolymerization, radiation-induced

graft polymerization and so on.^{227,242,244,251,252,254,255} Among them, radiation grafting is the most popular method, but the cost is too high and this method often decreases the stability of the porous matrix. As a consequence, some novel grafting methods were developed to overcome such problems.

Zhu *et al.* proposed a facile approach to introduce electrolyte-philic PEG chains (containing ether groups) onto the surface of PP separators. This approach was based on the mussel-inspired dopamine (DOPA) coating to build covalent bonds between the separator and PEG modification layer (Fig. 27a).²²⁷ PP separators coated by DOPA were firstly formed by directly immersing PP into a DOPA solution. PP-DPOA separators then reacted with methoxy polyethylene glycol (MPEG) to finally form PP-g-MPEG separators. The existence of the electrolyte-philic PEG chains on PP separators could facilitate liquid electrolyte penetration into the porous structure, resulting in the immediate wetting of modified separators (Fig. 27b). Better performance of LIBs was thus achieved.

3.2.2.2. Surface coating. Surface coating can help to suppress the thermal shrinkage of original polyolefin separators at higher temperatures, while not largely damaging their electrochemical properties. Besides, its simplicity, validity and processing versatility make it the most usual way to enhance the thermal stability of polyolefin separators in LIBs. Coating materials are also composed of electrolyte-philic ones, such as ceramic materials and polymers normally with polar functional groups. The common ceramic materials include 0D nanoparticles, such as Si, TiO₂, Al₂O₃, SiO₂ and ZrO₂, zeolite, and 1D nanotubes, like silica nanotubes. The frequently-used electrolyte-philic polymers include poly(ethylene oxide) (PEO), PI, cellulose-based polymers, PMMA, polydopamine (PDA), aramid nanofiber, PES, PVDF, and polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) co-polymer, *etc.* The intrinsic polar nature of coating materials can be directly used to improve the wettability of microporous polyolefin separators and ceramic materials can also suppress the growth of lithium dendrites.^{25,156,223,228,242,243,245,247,249,250,253,256–270}

As described above, ceramics are the most widely used coating materials, because of their intrinsically and thermally stable properties. Such properties can efficiently improve the heat resistance of polyolefin separators at high temperature, thus enabling the size of separators to be mechanically maintained at high temperature.^{25,247,271–276} Apart from these features, ceramic coatings with polar groups attached to their surface won't sacrifice the affinity of polyolefin separators for polar liquid electrolytes. It is notable that an appropriate polymeric binder is commonly necessary for inorganic ceramic materials, like PVDF-HFP copolymers and poly(lithium 4-styrenesulfonate). The purpose of using binders is in order to keep stable connection between the coating with the separator surface under the mechanical stress during assembly or operation.^{247,249,272,277} However, these polymeric binders normally suffer from more serious thermal shrinkage at higher temperatures, sacrificing the thermal stability of ceramic coatings, because polymeric binders can easily swell, gel, or even dissolve in non-aqueous liquid electrolytes.^{25,228,260,278} To solve this problem, one method is to develop more stable polymers to

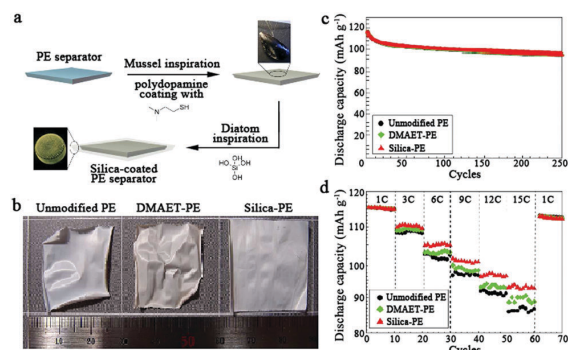


Fig. 28 (a) Schematic description of the on-surface silica growth on the PE separator; (b) digital photographs of the different separators after exposure to 140 °C for 1 h (DMAET: 2-dimethylaminoethanethiol); (c) cycling performance of the same cells (1C for both charge and discharge); (d) rate capabilities for the cells with the different separators (1C for charge and various C-rates for discharge).²⁷⁹ Reproduced from ref. 279 with permission, copyright American Chemical Society, 2012.

work as binders, such as PI-based polymers along with water-soluble binders.^{228,249,260,278} But then, a binder-free method is the most attractive way, because binders in the thick ceramic coating often block the pores of separators to reduce their ionic conductivity in LIBs.^{257,264,279} Choi *et al.* developed an environmentally friendly and cost-effective bio-inspired way to synthesize a diatom-inspired silica layer on the surface of a PE separator. This bond between the coating layer and the membrane support was based on the direct growth of ceramic materials not using binders. This approach could minimize the agglomeration of ceramic particles compared with the ceramic/binder slurry coating process (Fig. 28a).²⁷⁹ The blocking of pores can thereby be prevented to a large extent. Moreover, the robust adhesion was adjusted by the mussel inspired coating technique and could be well kept during the long-term operation of LIBs. As a consequence, the silica-PE separator exhibited better thermal stability (85.2% preservation after 140 °C for 1 h), compared with unmodified PE (70.4% preservation) (Fig. 28b). Finally, better rate performance and cycling performance of LIBs assembled with separators functionalized with silica layers were successfully achieved (Fig. 28c and d). To reduce the cost, tannic acid with lower cost was also used as the coating material to modify polyolefin separators.²⁵⁷

But then, the coating of ceramic materials will lead to increased thickness, partially blocked pores and reduced porosity, and even the heterogeneous distribution on the surface of separators.^{246,257,260,262,280} Moreover, the poor binding power between the coating and supporting layer makes the coating layer impermanent. This fact will result in the detachment of particles from the separators by mechanical stress generated during cell assembly and operation.^{242,252} To further promote the utilization of ceramic coatings on polyolefin separators, researchers have developed diverse solutions to the aforementioned problems. Introducing more stable binders or adopting binder-free methods can enhance the adhesion between coating layers and separators, namely improving the stability of coated

separators, such as the dip-coating method,²⁶⁰ and exerting molecular-level control over the thickness and surface characteristics of assembled layers, such as self-assembly. The adoption of binder-free methods can also reduce the effects on the pore structure exerted by surface coating, such as the combination of plasma activation and atomic layer deposition.^{230,269,281–283}

Moreover, polymers with high electrolyte uptake and thermal stability can also be treated as coating materials. Because, the distribution of polymers on the surface of polyolefin separators is more uniform, the thickness of polymer coatings is relatively thin and the adhesion between them and the separator supports is more robust.^{253,259,260,262,284,285}

In fact, robust enough adhesion is the most important factor to take full advantage of the coating materials and keep a stable performance of batteries. For example, PDA has versatile adhesion capability, good hydrophilicity and high compatibility with a simple dipping process.^{253,259,284,285}

Therefore, the utilization of PDA in LIBs is very widespread. Choi *et al.* developed a simple dipping process to produce PDA-coated PE separators (Fig. 29a).²⁵⁹ The exceptionally strong adhesion of PDA on the separator surface made the modified separators more robust for long-term battery operation. And the hydrophilicity (polarity) of PDA helped to generate an electrolyte-philic surface of PDA-coated PE separators, and the modified PE separators thus showed dramatically improved power performance (Fig. 29b). Besides, thin PDA coating did not block the pores, which was different from the ceramic coatings. Also, this dipping process was simple, effective and green to obtain high-performance composite porous separators in LIBs.

Recently, a composite coating consisting of a polymer (not the binder) and a ceramic material has been a promising method to realize enhanced thermal stability and increased wettability of separators simultaneously. The mechanically stable ceramic materials improve the thermal stability of polyolefin separators. And this will not bring about reduced affinity for liquid electrolytes thanks to the electrolyte-philic nature of polymers and ceramic materials. By far, polyethylenimine (PEI)/SiO₂, PMMA/SiO₂, cellulose diacetate (CDA)/SiO₂, poly(acrylic acid) (PAA)/ZrO₂ composite coating, *etc.* have been successfully introduced into microporous polyolefin separators.^{269,281,286,287} As for these composite coatings, the robust adhesion between coating layers and separators can also be strengthened. And the influence that they exert on pore structures must be as light as possible. These results are usually achieved by the innovation

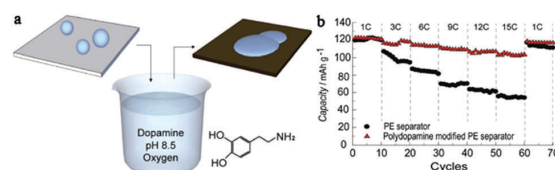


Fig. 29 (a) Schematic illustration of the mussel-inspired PDA surface treatment using a simple dip-coating process; (b) a comparison of discharging capacities for both types of cells at a series of current densities. The voltage range for these measurements was between 3.0 and 4.5 V.²⁵⁹ Reproduced from ref. 259 with permission, copyright John Wiley and Sons, 2011.

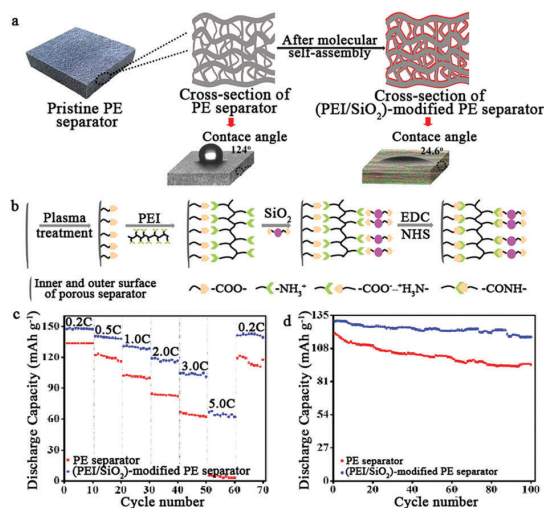


Fig. 30 (a) Self-assembly of PEI/SiO₂ on PE separators for LIBs with improved hydrophilicity; (b) experimental process; (c) comparison of discharge C-rate capabilities and (d) cycling performance of cells assembled with different separators.²⁸¹ Reproduced from ref. 281 with permission, copyright American Chemical Society, 2015.

of coating methods. For instance, Wang *et al.* developed a simple and green self-assembly process to construct an ultrathin layer of PEI/SiO₂ on the surface of PE separators (Fig. 30a).²⁸¹ Clean PE separators were treated by CO₂-plasma to give rise to a carboxyl-activated surface. Subsequently, the resultant PE separators were immersed into an aqueous solution of PEI and carboxyl functionalized SiO₂ colloid alternatively to complete the self-assembly process. The interlayer cross-linking was formed at the end through the imidization between carboxyl groups and amino groups (Fig. 30b). The most important advantage of this approach was its ability to exert molecular-level control over the thickness and surface characteristics of assembled layers. Nearly unchanged thickness and well-preserved pore structure of PE separators were thus achieved. The modified PE separator demonstrated significantly increased electrolyte uptake and superior electrochemical stability. The LIB with this modified PE separator thus showed excellent capacity retention at high C-rates and superior cycling performance (Fig. 30c and d).

It is worth noting that surface grafting can also suppress the thermal shrinkage of microporous polyolefin separators, while surface coating can improve their wettability as well.^{262,280} Therefore, enhanced thermal stability and increased wettability can also be realized simultaneously by surface modifications. Cao *et al.* lately reported a novel TiO₂ ceramic-grafted PE (TiO₂-grafted PE) separator fabricated by electron beam radiation.²⁸⁰ The high energy electron beam produced a large number of free radicals on the PE surface to initiate the grafting reaction with isopropyl triethyl titanate (IPTT). The grafted IPTT molecules were then hydrolyzed and reacted with titanium dioxide sol to complete the grafting process. The uniform distribution of TiO₂ nanoparticles brought about almost unchanged but rougher surface morphology. The surface electrolyte-philicity of separators

was thus improved. The results exhibited that the effects of TiO₂ grafting on the porosity and thickness of separators were little, obviously different from the results of ceramic coatings. Although the mechanical stability was reduced by electron beam radiation, the thermal stability of TiO₂-grafted PE separators was almost not affected. Consequently, such TiO₂-grafted PE separators finally showed highly enhanced dimensional properties together with thermal stability, and improved ionic conductivity.

Of course, surface modification has some drawbacks, such as that grafting is usually expensive and complicated. Nevertheless, various optimizations have been applied to solve such problems to make surface modification more simple and practical (Fig. 31).^{227,230,242,246,252,257,260,262,269,280–283}

Apart from surface modification, a microporous blend polyolefin membrane as the separator for LIBs was proposed for the first time.²⁸⁸ Li *et al.* blended high density polyethylene (HDPE) with methylcellulose (MC) to prepare electrolyte-philic blend membranes by the TIPS method. LIBs assembled with microporous HDPE/MC blend membranes demonstrated higher capacity performance and better discharge performance at various current densities.²⁸⁸

Recently, Cui *et al.* designed a novel separator by sandwiching ceramic materials between two commercial polyolefin membranes as shown in Fig. 32.²⁸⁹ In this sandwiched configuration, the porous structure created by the packing of spherical silica nanoparticles could improve the wettability of PE separators. And the electrical insulativity of silica nanoparticles could control the formation and growth of lithium dendrites. When lithium dendrites grew and penetrated the separator, they would contact each other. Silica nanoparticles would be lithiated by lithium dendrites, thus consuming lithium and stopping or slowing down their further growth. At the end, the time for lithium dendrites to penetrate through the separator was delayed, thereby extending the life of the battery. Different from ceramic coatings on the surface of polyolefin separators, nanoparticle-sandwich separators can avoid the undesired side reactions between ceramic nanoparticles and electrodes. Besides, this composite separator is more robust than that prepared by surface coating. This method can be not only used in LIBs but also in other lithium-based batteries.

3.2.3. Microporous PVDF-based membranes. Semi-crystalline PVDF polymer is known to be more compatible with liquid electrolytes than normal polyolefin separators, due to its higher polarity. And it owns high stability as a result of the intrinsic presence of a highly electronegative fluorine atom in its backbone.^{61,236,290–294} Therefore it is an attractive candidate for polyolefin in LIBs. Porous PVDF membranes can be prepared *via* simple phase inversion methods as mentioned above. It is worth noting that the ionic conductivity of porous PVDF membranes prepared by the TIPS method is generally higher than that by the NIPS one.^{59,61,231,236,293,295–297} Therefore, the TIPS method is more frequently-used to produce PVDF membranes for LIB applications. Similar to the case of microporous polyolefin separators, the relatively low ion conductivity derived from the high crystallinity of PVDF membranes is still one of the most significant restrictions on their application in LIBs.^{59,298} Therefore, reducing

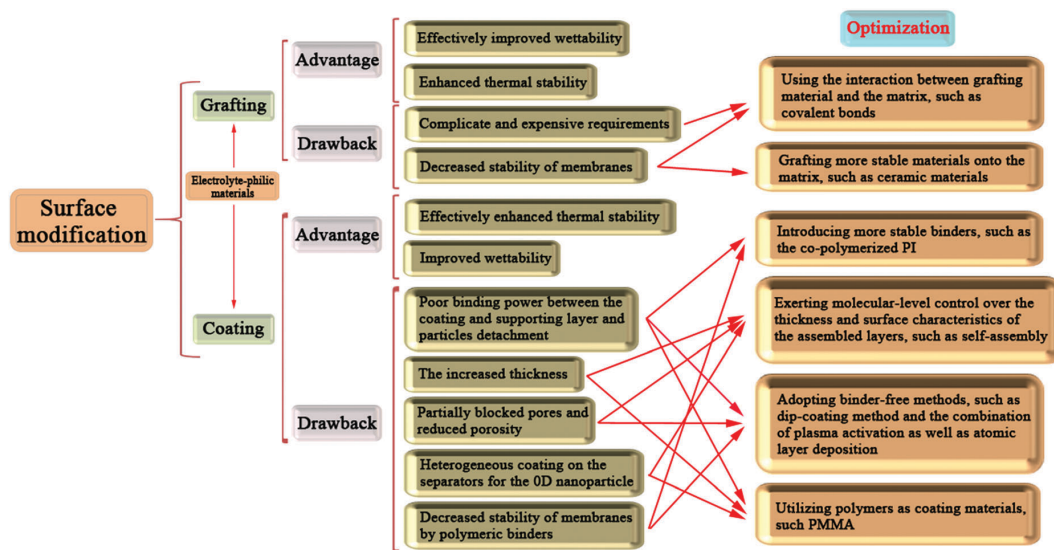


Fig. 31 The comparison of different surface modification methods on microporous polyolefin separators for LIB applications and their further optimization.

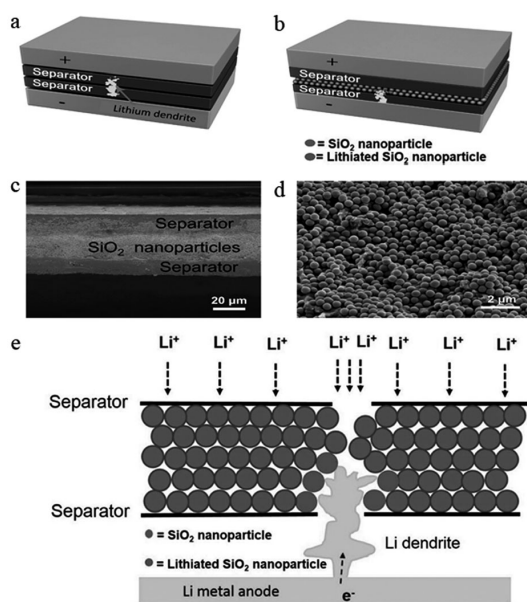


Fig. 32 The schematic diagram of (a) lithium dendrites penetrating through the inert polymer separator; (b) a layer of silica nanoparticles was sandwiched by two layers of commercial polymer separators; (c) SEM image of the silica nanoparticle sandwiched separator; (d) SEM image of the closely packed silica nanoparticles inside the sandwiched separator; (e) the mechanism for the extended battery life using silica nanoparticle-sandwich separators.²⁸⁹ Reproduced from ref. 289 with permission, copyright John Wiley and Sons, 2016.

their crystallinity, forming more open pore structures, introducing electrolyte-philic materials and so on are effective ideas to improve

the wettability of porous PVDF membranes. Apart from optimizing the preparation parameters during the process of phase separation, the simple and available blending method is the most universal method to increase the electrolyte uptake of PVDF membranes.^{59,236,295–300} Blending PVDF with electrolyte-philic polymers has been widely used over the years. These polymers generally possess a certain compatibility with PVDF, like PEO, PMMA, poly(dimethylsiloxane) (PDS), PAN, and PSF.^{59,236,293,295–298,301,302} These electrolyte-philic polymers are often hydrophilic, containing electrolyte-philic groups, like ether groups, ester groups and sulphone groups. Their addition will influence the process of phase separation, further tuning the pore structure of porous PVDF membranes. And the blending materials will also influence the properties of the resultant PVDF blend membranes. For instance, the addition of PEO can clearly alter the pore configuration, causing larger pore size, higher porosity, and better pore connectivity of microporous PVDF separators. The possible reason was that the stronger interaction between PEO and nonsolvent made the nonsolvent distribute better and the pore distribution thereby becomes denser.²⁹⁷ Besides, the electrolyte-philic PEO also improved the wettability of PVDF blend membranes to liquid electrolytes.

Cui *et al.* prepared PVDF/PSF blend membranes *via* the TIPS method for LIBs.³⁰² The considerably poor compatibility between PSF and PVDF caused weak interactions between PVDF and diluent. And the rigid segments of the benzene ring in PSF molecules could accelerate the nucleation for PVDF crystallization. As the PSF/PVDF weight ratio increased, the solution was inclined to undergo liquid–liquid demixing from solid–liquid demixing. Thus, the size of spherulites decreased and the shape of spherulites became irregular (Fig. 33). And this spherulic morphology was the traditional morphology of PVDF membranes prepared by the TIPS method (solid–liquid demixing).

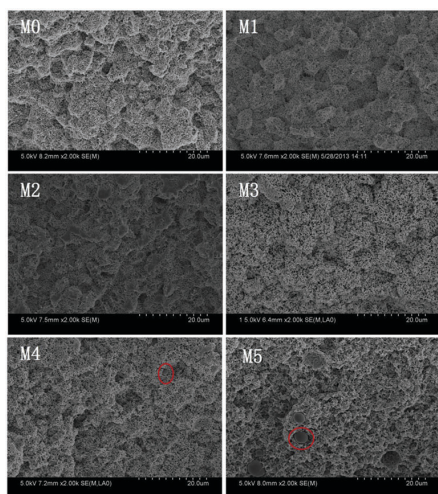


Fig. 33 Cross-section SEM micrographs of membranes with different PSF/PVDF weight ratios (M0–M5: increasing PSF content).³⁰² Reproduced from ref. 302 with permission, copyright Elsevier, 2014.

Therefore, the increased porosity, the more swelled amorphous domain and the more functional groups in blend membranes increased the electrolyte uptake of PVDF membranes.

Except for PVDF, copolymers based on PVDF and HFP can also obtain great electrochemical performance in LIBs. The amorphous HFP phase helps to capture and retain a larger amount of liquid electrolytes. And the PVDF crystalline phase keeps good mechanical stability. Hence, more and more research studies have focused on PVDF–HFP copolymers in LIBs recently.^{303–312} Moreover, to composite PVDF–HFP with some modifying materials is effective to further enhance the performance of microporous PVDF–HFP membranes in LIBs, such as ceramic materials (like SiO₂ and TiO₂) and polymers (like PMMA and PEG).^{304,305,308,310,311,313,314} These modifying materials can usually change the process of membrane preparation, improve the membrane electrolyte-philicity and reduce the crystallinity of the PVDF phase. More electrolyte uptake is thereby obtained. Liu *et al.* lately prepared a kind of composite porous membrane based PVDF–HFP and HDPE (PVDF–HFP/HDPE) *via* the NIPS method.³¹³ The introduction of HDPE particles led to the disorder of regular long chains in PVDF, resulting in lower crystallinity and expanded amorphous area of the composite membrane. Besides, the possible formation of cross-linked structures may favor strengthening of PVDF–HFP/HDPE membranes, which originated from the uniform dispersion of HDPE particles. The resultant membrane exhibited good rate capability and cycling performance that could be comparable to the commercial PP separator. Notably, PVDF–HFP based polymers are also fantastic materials to be the matrix of gelled polymer electrolytes used in LIB applications.

3.2.4. Other membrane materials for separators in LIBs. Developing suitable candidates as separators for LIBs is very necessary in the future, because commercial polyolefin membranes have limited electrolyte wettability as well as severe thermal

shrinkage at high temperature. In addition to PVDF-based materials, PAN, PEO, PI, glass fiber (GF), cellulose-based polymers, PVA based polymers, polybenzoxazine, aramid, poly(arylene ether ketone) (PAEK), polyethylene terephthalate (PET), polybenzoxazole (PBO), poly(phenylene oxide), and their composites with other materials have been applied. These materials normally own good wettability to liquid electrolytes and high thermal stability at an elevated temperature. Of course, their low cost is another important factor. To date, woven or nonwoven composite membranes, nano-fiber membranes and mesoporous membranes, *etc.* were fabricated as separators for LIB applications.^{32,153,232,239,315–329} Most of such separators were prepared by relatively straightforward, low-cost and environmentally friendly methods, like phase separation methods, the electrospinning technique, the stretching technique, filtration process, *etc.*^{232,239,315–318}

Liu *et al.* used a cross-linked polybenzoxazine electrospun fiber mat (CR-PBz-FbM) to prepare porous separators with high thermal stability for LIBs by the electrospinning process (Fig. 34),³²⁹ because the thermally cross-linked PBz polymers showed high mechanical as well as thermal stability, good film formability, high film flexibility, and flame resistance. When such a CR-PBz-FbM separator was used in a LIB, it demonstrated a higher ion conductivity than that of the commercial polyolefin separator and high thermal stability (near zero shrinkage at 150 °C) (Fig. 34b). Especially, the LIB with a CR-PBz-FbM separator only exhibited a capacity loss of 16% compared to a

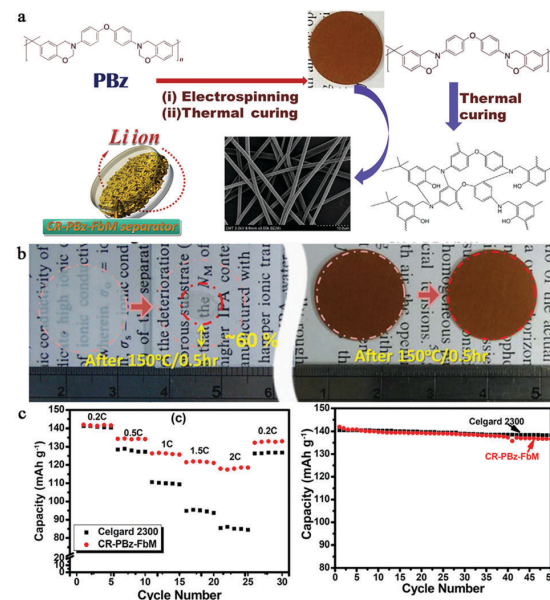


Fig. 34 (a) Chemical structure of the PBz precursor and the preparation of the CR-PBz-FbM electrospun fiber mat as a separator for LIBs; (b) photographs of the separators before and after thermal treatment at 150 °C for 0.5 h: (left) Celgard 2300 and (right) CR-PBz-FbM; (c) (left) rate capacity tests on the cells that employ the separators at different C-rates and (right) cycling performance of the cell with the CR-PBz-FbM separator.³²⁹ Reproduced from ref. 329 with permission, copyright John Wiley and Sons, 2016.

40% capacity loss for the battery based on a Celgard separator (Fig. 34c).

But then, it is indeed hard to achieve high-performance porous separators in LIBs by only using novel membrane materials. Some modification methods similar to that used for microporous polyolefin and PVDF-based separators are indispensable sometimes.^{32,153,318,319,321,326,328} For instance, coating SiO₂/PVDF-HFP on poly(ethylene terephthalate) non-woven membranes could prepare composite separators with high ion conductivity and thermal stability in LIBs.³²⁸ As a consequence, no matter whether commercial polyolefin separators or other kinds of separators are used, modifications are indispensable in most cases, even dominant for their ultimate high performance in LIBs.

In summary, the poor affinity of commercial polyolefin separators for liquid electrolytes and their poor thermal stability urgently need to be solved. Surface modification is one of the most effective and universal methods for modifying microporous polyolefin separators in LIB applications. The introduction of highly electrolyte-philic and thermally stable coatings can not only enhance the thermal stability but also improve the wettability of microporous polyolefin separators. Although, there are disadvantages for surface modifications, various methods have been used to solve these limitations (Fig. 31). Consequently, surface modification is still by far the most widely used method for the improvement in the performance of microporous polyolefin separators in LIB applications.

Apart from polyolefin, PVDF-based polymers can also be used in LIBs, due to their higher electrolyte uptake. Blending them with suitable materials can not only adjust the process of phase separation but also enhance the wettability of the resultant porous membranes, making them more suitable for the utilization in LIBs. As for other kinds of porous separators, similar modifications can be used to improve their wettability and enhance their thermal stability as well.

3.3 Lithium-sulfur (Li-S) batteries

3.3.1. Desirable properties for porous membranes in a Li-S battery. Li-S batteries have been one of the most promising next generation batteries, considering their features like high theoretical capacity along with energy density, the abundance of the required elements in nature, good environmental protection and low cost.^{35,330–334} However, the main restriction on the further commercial use of Li-S batteries is their dramatic capacity fading. Their capacity fading is caused by various factors, such as high resistance of intermediate products of sulfur, the solubility of polysulfide species, the passivation of both electrodes and the shuttle effect of dissolved polysulfide species.^{35,331,332,335–339} Except for optimizing electrodes and electrolytes, the improvement in the separator performance of Li-S batteries can effectively overcome the aforementioned problems as well. The separator of Li-S batteries normally possesses a microporous functional polymeric membrane to separate the positive and negative electrode so as to avoid a short circuit. Besides, it plays an extremely important role in inhibiting the diffusion and migration of polysulfide species.³⁵

The most appropriate separator should own such characteristics as follows:^{35,333,340–342}

- (1) Electronically insulating but ionically conducting.
- (2) Excellent mechanical flexibility and chemical stability.
- (3) The ability to shut off the diffusion of polysulfide species while allowing facile lithium ion diffusion or high selectivity.
- (4) Appropriate pore structure (pore size, porosity, *etc.*) to achieve good affinity for liquid electrolytes.
- (5) Low cost.

The common commercial separators are microporous polyolefin membranes, such as PP, PE and their hybrids (referred to as Celgard).^{35,331,333} However, to suppress the capacity decay, modifications on microporous polyolefin membranes, developing novel alternative membrane materials and so on are also needed. These methods can not only absorb and hold liquid electrolytes to accelerate lithium ion conduction, but also inhibit the shuttle effect of polysulfide species, hence meeting the requirements of Li-S batteries.

3.3.2. Modifications on porous membranes for Li-S batteries.

Research studies of modifications on microporous polyolefin separators in Li-S batteries mainly occurred in recent years.^{343,344} One of the most widely used modification methods is to introduce conductive materials onto them to overcome the restrictions caused by the poor electronic conductivity of sulfur, like conductive carbon materials and conductive polymers. Conductive polymers, such as PPY and polyaniline (PANI), are able to absorb and hold sulfur, thereby inhibiting the transport of lithium polysulfide species.^{345–347} Wu *et al.* have studied the performance of PPY modified separators in Li-S batteries and found that their wettability to liquid electrolytes was improved greatly. Their capability of hindering the transport of lithium polysulfide species was increased as well. As a result, a better electrochemical performance than that modified with conductive reduced graphene oxide (rGO) was realized.³⁴⁶ Nevertheless, the most commonly used conductive materials are still conductive carbon. To date, various conductive carbon materials have been designed and developed to modify microporous polyolefin separators, such as carbon black (like Super P and acetylene black), multi-walled carbon nanotubes (MWCNTs), graphene, nitrogen-doped conductive carbons, activated-carbon nanofiber-filters, active metal oxide nanoparticle-decorated porous carbon and their composites with each other or other materials, because conductive carbon materials possess high conductivity, adjustable porous structure and light weight. They can also reduce impedance, and adsorb and trap soluble polysulfide species in electrolytes. Therefore, conductive carbon materials can serve as an effective barrier for the shuttle effect of polysulfide species in Li-S batteries. The introduction of conductive carbon materials can thus lead to enhanced utilization of sulfur, stable cycling performance, and low capacity decay rate. Besides, such materials often work as coating materials on the one side or both sides of a separator and usually facing the sulfur cathode.^{343,344,348–361} For example, Manthiram *et al.* proposed a C-coated bi-functional separator, whose architecture consists of a conductive Super P thin film coated on one side of the Celgard separator (Fig. 35a).³⁴⁸ The bi-function of separators means that the C-coating functioned as a conductive upper current collector

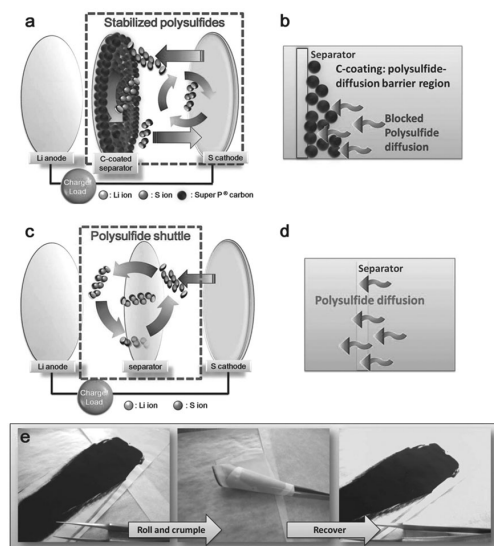


Fig. 35 (a) Schematic configuration of a Li-S battery with the C-coated separator; (b) the polysulfide species-diffusion barrier region; (c) schematic configuration of a Li-S battery with the Celgard separator; (d) the typical severe polysulfide species diffusion; (e) demonstration of the flexibility and mechanical strength of the C-coated separator.³⁴⁸ Reproduced from ref. 348 with permission, copyright John Wiley and Sons, 2014.

as well as a barrier region for the diffusion of polysulfide species. And the Celgard separator served as the electrically insulating membrane (Fig. 35b and d). As a result, the C-coated separator owned high flexibility and mechanical strength (Fig. 35e). The Li-S battery assembled with the coated separator showed a high initial discharge capacity near 1400 mA h g^{-1} , and a reversible capacity of 828 mA h g^{-1} after 200 cycles at a C/5 rate. Moreover, an excellent rate capability, a high CE of about 98% and a lower self-discharge rate of 0.19% per day were also exhibited. These results indicated that utilizing such low-cost materials and simple processing techniques to introduce a C-coated separator into Li-S batteries could greatly enhance their dynamic and static performance.

Besides, to improve the chemical affinity of polyolefin separators for dissolved lithium polysulfide species, a functional RuO_2 nanoparticle-decorated mesoporous carbon ($\text{RuO}_2\text{-MPC}$) was coated on PP separators for the first time.³⁵⁴ That was on account of the high conductivity and high chemical stability along with the catalytic activity of RuO_2 . The high catalytic activity of RuO_2 enhanced the redox reaction rate of the active sulfur-based material and further improved sulfur (re)utilization. As a result, a better overall electrochemical performance (a higher initial discharge capacity, a better cycling stability, a higher CE and better capacity retention) of Li-S batteries was demonstrated.^{354,362,363} But the precondition of accelerating the employment of active metal oxides in Li-S batteries is to understand their catalytic effect on the improved sulfur-based redox reaction kinetics.

Nevertheless, the amount of conductive carbon materials in coatings must be appropriate, because too much carbon on

separators will damage the energy density of batteries. Notably, apart from conductive materials, titanium oxide, black-phosphorus (BP), Nafion, polymers (like poly(3,4-ethylenedioxythiophene) together with poly(styrene sulfonate)), and Al_2O_3 have also served as coating materials on porous polyolefin matrices, thanks to their effects of electrostatic repulsion or steric hindrance for polysulfide species-diffusion.^{345,364–368}

3.3.3. Development of novel membrane materials for Li-S batteries. Although the coating of conductive materials is very effective to improve the performance of polyolefin separators, their poor wettability and serious thermal shrinkage will still restrict their electrochemical performance in Li-S batteries.^{333,342,365} Therefore, developing new membrane materials is in need to further improve the performance of Li-S batteries. By far, composite porous PAN/ SiO_2 separators, porous cellulose-based separators, porous glass fiber (GF) separators, zinc-organic framework based separators, PIM separators, PVDF, and so on have been designed and successfully used in Li-S batteries.^{333,342,369–373} In general, the main reasons for utilizing such materials are their high electrolyte-philicity and good thermal stability.^{333,369} B. Goodenough *et al.* applied a porous cellulose-based separator, whose pore size in the nanometer range was significantly smaller than that of the Celgard separator (Fig. 36).³⁴² But their electrolyte uptake was better than that of the Celgard separator (Fig. 36b). Their purpose was to suppress the formation as well as the growth of lithium dendrites,

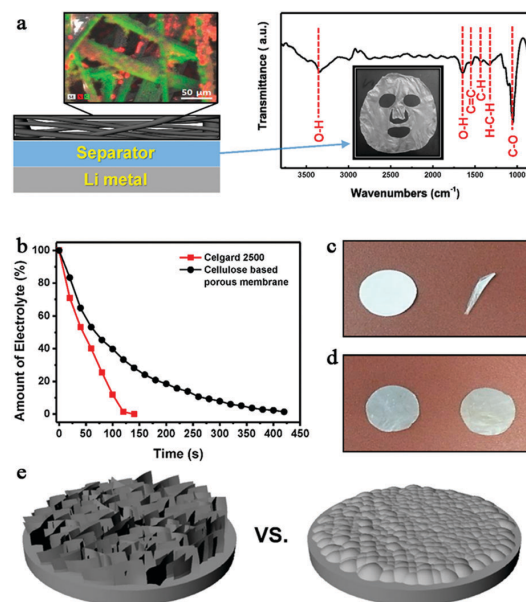


Fig. 36 (a) Configuration of a Li-S battery with used cellulose-based membrane (upper) EDS mapping images of carbon paper/S cathode, (right) FTIR of cellulose-based porous membrane; (b) electrolyte storage capacities of Celgard 2500 and porous cellulose-based membrane; (c) Celgard 2500 at (left) 25°C and (right) 150°C for 12 h; (d) porous cellulose-based membrane at (left) 25°C and (right) 150°C for 12 h; (e) schematic images of Li metal after cycling with (left) Celgard 2500 and (right) cellulose-based porous membrane after many cycles.³⁴² Reproduced from ref. 342 with permission, copyright American Chemical Society, 2016.

and block the diffusion of polysulfide species (Fig. 36e). Finally, the CE with the porous-cellulose separator was close to 100%, showing high selectivity on soluble polysulfide species. The nanosized pores of the cellulose separator may be critical for suppressing dendrite formation to generate a uniform current density across the anode–electrolyte interface during cycling.³⁷⁴ Besides, the thermal stability of porous cellulose-based separators was better than that of commercial Celgard separators (Fig. 36c vs. Fig. 36d). Therefore, higher capacity retention was realized for such membranes in Li–S batteries.

Using appropriate separators to maintain the high capacity of Li–S batteries is still an effective way to improve the battery performance. However, efficient modification methods are still needed to enhance their performance, similar to porous polyolefin separators in Li–S batteries and LIBs. For instance, Zhang *et al.* introduced an integral ultra-light and thin MWCNT sheet into the PAN/SiO₂ membrane to prepare a multi-functional composite separator for Li–S batteries.³³³ PAN and SiO₂ owned great ability for the adsorption of Li₂S or lithium polysulfide species, consequently inhibiting their diffusion effectively. The role of MWCNTs was offering electron pathways through the insulating S/Li₂S and preventing the migration of polysulfide species. Therefore, Li–S batteries with these multi-functional separators realized highly improved cycle stability and rate capability. And the practicality of Li–S batteries was thus further enhanced.

In short, introducing conductive materials into microporous polyolefin separators can take full advantage of their merits, mainly including their ability to absorb and trap soluble polysulfide species, consequently alleviating the shuttle effect effectively. Nevertheless, finding novel membrane materials with high performance is also an efficient and promising way to promote the commercial use of Li–S batteries. Modifications of commercial separators or other novel separators will still be the research emphasis in the future.

3.4 The universality of modification methods and membrane materials in different secondary batteries

As a matter of fact, one modification method on porous membranes and one kind of membrane material can be versatile and be used in different secondary batteries. But the properties of as-prepared porous membranes must conform to the desirable requests of different secondary batteries. For example, a zeolite can be coated onto the surface of a porous membrane support and achieve excellent performance in VFBs.¹⁰⁹ Similarly, Lin *et al.* also reported a kind of zeolite-coated PP separator with tunable surface properties for LIBs.²⁵⁶ Their main aim was to improve the wettability of PP separators through using the electrolyte-philic nature of zeolites. And the electrolyte-philicity of zeolites could be adjusted by tuning their Si/Al ratio. The modified PP separators with a zeolite layer, which had an appropriate Si/Al ratio, owned much higher wettability to the electrolyte than the pristine PP separator. Differently, silica could also be used in both VFBs and LIBs. But then, silica was used as the blending material in the former while it was used as the coating material in the latter. For the

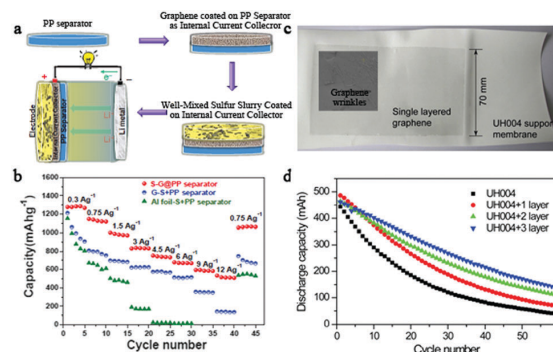


Fig. 37 (a) Schematic diagram of the electrode configuration using an integrated structure of sulfur and G@PP separator and the corresponding battery assembly; (b) rate performance of the S-G@PP separator, G-S + PP separator, and Al foil-S + PP separator cells at different current densities; (c) photographs of the graphene/UH004 membranes with one graphene layer; (d) the discharge capacity decay of VFB single cells with different composite graphene membranes at a current density of 80 mA cm⁻².^{350,375} Reproduced from ref. 350 with permission, copyright John Wiley and Sons, 2014; and ref. 375 with permission, copyright Elsevier, 2017.

VFB, the silica was introduced into a membrane to improve the ion selectivity, while the silica layer on the surface of the membranes can improve the thermal stability and safety of a LIB. This discrepancy largely results from different demands for the performance of porous membranes in VFBs and LIBs, respectively. Moreover, PIM with intrinsic microporosity can also be utilized in VFBs and Li–S batteries. However it serves as a coating material in VFBs, while as the membrane material in Li–S batteries.

Besides, conductive carbon materials, which were widely used in Li–S batteries, also were investigated in VFBs (Fig. 37). Zhang *et al.* prepared graphene/UH004 (a kind of PES ultrafiltration membranes) composite membranes with different graphene layers on the membrane supports for VFBs.^{350,375} The resultant membranes achieved enhanced selectivity and improved battery performance in VFBs (Fig. 37c and d). Although, their overall performance in VFBs is poorer than that of porous membranes reported previously, this research provided a novel ideal to further expedite the process of VFBs.

Moreover, the layer-by-layer technique could be also utilized in the preparation of novel composite porous membranes for VFBs and LIBs.^{281,376} And blending is actually very universal in different secondary batteries (Table 2). Therefore, using the modification methods or membrane materials for lithium-based batteries in VFBs or other secondary batteries and *vice versa* is a facile and applicable way to enhance the performance of secondary batteries. This method is worth trying to open up a novel idea to improve the performance of porous membranes. However, the desirable properties for porous membranes in different secondary batteries must be considered firstly. As an illustration, modifying materials should own the ability to keep their integrated properties in the strong acid and oxidizing operating environment of VFBs. Therefore, the hydrolysis, oxidation and decomposition of modifying materials or

Table 2 The summary of common modifying materials in different secondary batteries

Modifying material	Property	Method	Function	Membrane matrix	Further improvement
SiO ₂	Hydrophilicity; mechanical stability.	<i>In situ</i> hydrolysis of TEOS or the sol-gel method. ^a	Improve the hydrophilicity; and tune the pore size of porous membranes.	PAN; PES (VFBS) ^{197,200}	Uniform distribution.
	Adsorb polysulfide species.	Surface coating	Enhance the mechanical and thermal stability; improve the wettability to liquid electrolytes.	Polyolefin (LIBs) ^{246,264,377}	Uniform distribution; robust bond; controlled thickness.
		Mixing with other materials as composite coating (PEI, PMMA, PVDF, and so on)	Inhibit the diffusion and migration of polysulfide species; improve the stability of porous separators.	PAN (Li-S batteries) ³³³	Uniform distribution; robust adhesion; controlled thickness.
	Able to form hydrogen bonding between it and some solvents.	Blending	Avoid forming cellular pores; cause a well-interconnected porous structure; help to absorb the electrolytes immediately.	PPO (LIBs) ³²¹	Uniform distribution; preparation parameters.
	Electrical insulativity; react with lithium dendrites.	Interlayer	Own robust adhesion with the membrane; delay the penetration of lithium dendrites through the separator to expand the battery life.	Polyolefin (LIBs and Li-S batteries) ²⁸⁹	Uniform distribution; creation of pore structure; relatively poor stability of binders.
Al ₂ O ₃	Electrolyte-philicity; mechanical stability; can use a water-soluble binder.	Surface coating	Realize wonderful thermal stability and higher uptake of liquid electrolytes; own the economic and environmentally friendly coating process.	Polyolefin (LIBs) ²⁷⁸	Uniform distribution; robust bond.
	No need to use binders.	Surface coating	Improve the wettability with liquid electrolytes; the formation of pore structures in microporous membranes is not inhibited by polymeric binders.	Polyolefin (LIBs) ²⁷¹	Uniform distribution; controlled properties.
	Heat resistant; high surface area.	Surface coating	Exhibit good thermal stability and wettability in non-aqueous liquid electrolytes.	Polyolefin (LIBs) ²⁴⁷	Uniform distribution; relatively poor stability of binders.
	Adsorb and trap polysulfide species; mechanical stability.	Surface coating	Reduce the shuttle effect and enhance the stability of the sulfur electrode.	Polyolefin (Li-S batteries) ³⁶⁴	Uniform distribution; relatively poor stability of binders.
	Composite with other materials (Co-PI, poly(vinyl alcohol-co-ethylene) and so on) (LIBs). ^{228,319}				
PVP	Own high hydrophilicity and dissolve in water; containing positively charged amine groups.	Blending	Work as the pore-forming material to tune the pore structure of porous membranes.	PES (VFBS) ⁸⁷	Uniform distribution; preparation parameters.
	Easy grafting.	Surface grafting	Improve the hydrophilicity of hydrophobic PVDF; tune the pore size and pore size distribution.	PVDF (VFBS) ¹⁹⁹	Grafting conditions.
Zeolite	High mechanical stability; containing negatively charged sites; its pore size is exactly between that of hydrated vanadium ions and protons. Tuned electrolyte-philicity; well-ordered microstructure and unique framework; high surface area.	Surface coating	Improve the V/H selectivity, the hydrophilicity and the stability of membranes.	PES/SPEEK (VFBS) ¹⁰⁹	Uniform distribution; robust bond.
		Surface coating	Achieve tuneable surface properties and much higher wettability to electrolyte solvents.	Polyolefin (LIBs) ²⁵⁶	Uniform distribution; robust bond.
Nafion	High hydrophilicity; containing negatively charged groups; high chemical stability.	Surface coating	Improve the membrane conductivity and maintain ion selectivity. Serve as the retarding layer to suppress polysulfide species crossover through electrostatic repulsion.	PES/SPEEK (VFBS) ¹⁰⁹ Polyolefin (Li-S batteries) ^{367,368}	High cost; robust bond. Uniform distribution; controlled thickness.
PI	Co-polyimide: heat resistant; high solubility in polar aprotic solvents; easy controlled thicknesses and morphology of the coating layers.	Surface coating	Significantly decrease the thermal shrinkage of separators at higher temperatures; improve the safety of batteries.	Polyolefin (LIBs) ²⁶⁰	Relatively poor stability of PI.
	Thermally stable at high temperature; good wettability to liquid electrolytes.	Phase separation	Exhibit excellent thermal and dimensional stability; own more electrolyte uptake.	Membrane matrix (LIBs) ²³⁹	Preparation parameters.

Table 2 (continued)

Modifying material	Property	Method	Function	Membrane matrix	Further improvement
	Own outstanding mechanical properties, high radiation resistance and high inertness to solvents.	Work as the polymeric binder for ceramic coatings.		Polyolefin (LIBs) ²²⁸	Controlled thickness; blocked pores; thermal shrinkage.
PMMA	Electrolyte-philicity; PMMA nanoparticles own well-ordered, close-packed arrays. Have better affinity for liquid electrolytes and better interfacial stability towards lithium. High compatibility with PVDF-based polymers.	Surface coating	Obtain favourable wettability to liquid electrolytes and facile ionic conduction.	Polyolefin (LIBs) ²⁶²	Uniform distribution; robust bond.
		Surface coating	Enhance thermal resistance and improve affinity for liquid electrolytes as well as electrodes.	Polyolefin (LIBs) ^{234,242,379}	Poor mechanical strength of PMMA.
		Blending	Changing the process of membrane forming to tune the pore structure; increase the electrolyte-philicity of membranes.	PVDF (LIBs) ⁵⁹	Preparation parameters.
	Great affinity for liquid electrolytes.	Surface coating	Provide higher electrolyte uptake.	PVDF-HFP (LIBs) ³⁸⁰	The flammability of PMMA.
Cellulose-based polymers	MC: have high electrolyte-philicity.	Blending	Be used as a structure and performance regulator; improve the affinity for liquid electrolytes.	Polyolefin (LIBs) ²⁸⁸	Uniform distribution; preparation parameters.
	Ethylcellulose: own high thermal stability and polarity.	Surface coating	Remarkably decrease the thermal shrinkage and improve electrolyte wettability of separators.	Polyolefin (LIBs) ²⁶¹	Uniform distribution; robust bond.
	Cellulose: its pore size in nanometer range is significantly smaller than that of the Celgard separator; low cost.	Commercial	Nanosized pores of the cellulose membrane help suppress the formation of lithium dendrite; realize increased thermal stability.	Membrane matrix (Li-S batteries) ³⁴²	Controlled pore size of membranes.
	<i>Cladophora</i> cellulose: possess high crystallinity and good electrolyte-philicity; simple preparation method.	Vacuum filtration process	Achieve thermal stability and electrochemical inertness; improve wettability to liquid electrolytes.	Membrane matrix (LIBs) ³¹⁷	Inherently fragility of <i>Cladophora</i> cellulose.
PVDF-HFP	Capture and retain a larger amount of electrolytes and keep good mechanical stability due to the amorphous HFP phase and the PVDF crystalline phase; own chemical resistance and a large dielectric constant.	Work as the binder for ceramic coatings		PCM, polyolefin (LIBs) ^{c 246,276,322}	Relatively poor stability.
		Phase separation	Obtain highly porous structure and relatively good performance.	Membrane matrix (LIBs) ^{238,381}	Preparation parameters.
PVDF	Have better compatibility with liquid electrolytes; pore structure can be adjusted during phase separation.	Surface coating	Achieve high ion conductivity, better thermal and electrochemical stability.	Polyolefin (LIBs) ²⁶⁵	High crystallinity of PVDF; preparation parameters during preparing PVDF coating.
	High thermal, mechanical and chemical stability; low cost.	Phase separation	Offer good performance and excellent stability.	Membrane matrix (VFBs, LIBs) ^{199,301}	Hydrophobic nature; preparation parameters.
PDA	Own versatile adhesion capability and compatibility with a simple dipping process; electrolyte-philicity.	Surface coating	Achieve the electrolyte-philic surface; be more robust for long-term battery operation.	Polyolefin (LIBs) ²²⁶	High cost of PDA; controlled thickness of PDA coating.
TiO ₂	Electrolyte-philicity; mechanical stability.	Surface grafting	Realize uniform distribution and rougher surface; enhance dimensional and thermal stability; almost not affect the pore structure of membranes.	Polyolefin (LIBs) ²⁸⁰	Grafting conditions; high cost.
		Phase separation and <i>in situ</i> hydrolysis of Ti(OC ₄ H ₉) ₄	Improve mechanical properties and ionic conductivity of the resultant membranes.	PVDF-HFP (LIBs) ³⁰³	Preparation parameters.
PPY	Hydrophilicity; containing positively charged groups.	Polymerizing PPY in substrates	Restrain the vanadium ion passage through the Donnan exclusion and facilitate the improvement in selectivity.	PES/SPEEK (VFBs) ²¹¹	Even distribution.

Table 2 (continued)

Modifying material	Property	Method	Function	Membrane matrix	Further improvement
	Own good electronic and ionic conductivity; own strong adsorption effect to dissolved polysulfide species.	Interlayer	Inhibit the migration of the polysulfide species; improve the cathode conductivity and enhance the rate capability of the cell.	Polyolefin (Li-S batteries) ³⁴⁶	Uniform distribution; robust adhesion.
Graphene	Appropriate atomic thickness and excellent stability; high molecular selectivity; chemical inertness.	Surface coating	Enhance the membrane proton selectivity and the overall battery performance.	PES (VFBs) ³⁷⁵	Robust adhesion. The conductivity of graphene.
	Own high conductivity, adjustable porous structure and light weight.	Surface coating	Work as a current collector to offer a continuous electron transfer pathway; act as a good barrier and an effective reservoir for dissolved polysulfide species.	Polyolefin (Li-S batteries) ³⁵⁰	Controlled thickness of graphene membrane; robust adhesion.
PIM	Intrinsically microporosity; high surface area; limited swelling in aqueous solutions.	Surface coating	Rely on pore size exclusion to realize an ultra-high (infinite) H/V selectivity. Dramatically reduced polysulfide species crossover.	PAN (VFBs) ²¹⁷	High hydrophobicity of PIM-1. Pore size, pore chemistry, and overall porosity of membranes.
				Membrane matrix (Li-S batteries) ³⁷²	

^a TEOS: tetraethylorthosilicate. ^b PPO: poly(phenylene oxide). ^c PCM: ZrO₂-based porous ceramic membrane.

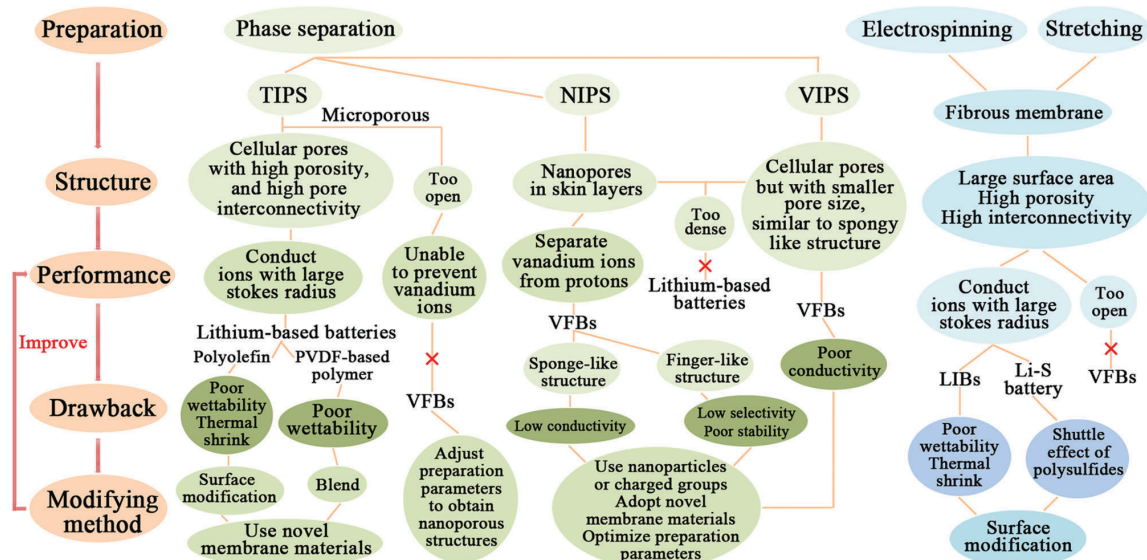


Fig. 38 The preparation-structure-performance relationship of porous membranes in different secondary batteries and corresponding modification methods.

membrane materials must be avoided in order to take full advantage of their original properties. In view of these requirements, PDA utilized in LIBs with phenolic hydroxyl groups may not be suitable for the utilization in VFBs, because PDA can be easily oxidized by the highly oxidizing VO₂⁺. Besides, sulfonic acid groups of SPEEK, which are commonly used in VFBs, cannot disassociate in non-aqueous LIBs. Therefore, SPEEK may not be used in such kinds of batteries as well.

According to the investigations of the application of porous membranes in different secondary batteries, the relationship

between the membrane structure and its performance in secondary batteries can be illuminated clearly. Therefore, the preparation-structure-performance relationship becomes more explicit.

The preparation methods of porous membranes in different secondary batteries are mainly the phase separation methods, the electrospinning technique and the stretching technique (Fig. 38). As for phase separation methods, the TIPS method is in favor of the formation of microporous membranes with cellular pores. Pore structures with higher porosity and high pore interconnectivity help conduct ions with relatively large

Stokes radius, such as lithium ions and vanadium ions. Therefore, membranes with such pore structures can be utilized in lithium-based batteries but not VFBs. However, the commonly used commercial polyolefin separators and the PVDF-based separators in lithium-based batteries possess drawbacks of poor wettability to liquid electrolytes and serious thermal shrinkage. Requisite modifying methods, such as surface modification on microporous polyolefin separators and blending for porous PVDF-based separators, need to be conducted for further improvement in the membrane performance. It is worth noting that adjusting the preparation parameters during the TIPS process to produce nanoporous membranes can probably be applied in VFBs.

The porous membranes prepared by the NIPS method often own nanopores in the skin layers, which determine their selectivity (Fig. 38). Such a porous structure is in favor of separating vanadium ions from protons in VFBs, but too dense to allow the free transference of lithium ions. Therefore, membranes fabricated *via* the NIPS method are often utilized in VFBs. Different mechanisms during NIPS bring about various pore structures, the sponge-like structure and finger-like structure included. The former often owns high selectivity and stability but poor conductivity, while the latter usually possesses high conductivity but low selectivity and stability. To optimize the preparation parameters, introducing hydrophilic inorganic based materials or charged groups and adopting novel membrane materials are effective ways to overcome such drawbacks.

As for the VIPS method, although cellular pores are formed, this structure has smaller pore size, similar to the spongy like structure (Fig. 38). Therefore, porous membranes prepared by this method are commonly used in VFBs. Poor conductivity of membranes can also be overcome by modification methods analogous to that of the membranes prepared using the NIPS method.

Compared with different phase separation methods, the electrospinning technique and the stretching technique are relatively simple. The two methods are used to fabricate fibrous membranes often with a large surface area, high porosity and high interconnectivity (Fig. 38). Thus, these fibrous membranes are utilized in lithium-based batteries, commonly with polyolefin and PVDF-based polymers as the membrane materials. When used in LIBs, poor wettability to liquid electrolytes and thermal shrinkage are the main drawbacks that need to be solved. And when used in Li-S batteries, it is hard for the too open pore structure to inhibit the diffusion and migration of lithium polysulfide. Surface modifications are the most commonly used method to improve the membrane performance as well.

The full and clear understanding of the preparation–structure–performance relationship favors the structure design and optimization of porous membranes in different secondary batteries. Beginning with the requirements of a secondary battery, the appropriate membrane material is firstly selected. And the requisite structure of a porous membrane is then designed. A suitable preparation method is utilized to form such porous structures, according to their relevant characteristics. When the as-prepared porous membrane is utilized in

the secondary battery, the results of the battery performance will determine whether the selected membrane materials and designed structure are appropriate or not. If not, choosing other membrane materials, or designing the membrane structure again, or selecting other preparation methods, or carrying out different modifying methods as mentioned above to optimize the membrane structure are necessary. After which, the battery performance of the resultant membrane should be detected to verify the availability of membrane structures. Therefore fully understanding the preparation–structure–performance relationship is extremely important to improve the performance of porous membranes in different secondary batteries.

4. Summary and prospects

Porous membranes fabricated by different preparation methods own various pore structures, and thus can satisfy diverse demands of different secondary battery technologies. Their abilities to conduct charge carriers to complete an electric circuit and separate active species from charge carriers are significant for secondary battery technologies.

The desirable requirements for porous membranes in different secondary batteries are quite variable. Consequently, different modification methods and membrane materials are adopted to further improve the performance of porous membranes. For instance, the purpose of modifications on porous membranes in VFBs is to improve their selectivity and conductivity, simultaneously. Differently, modifications on commercial polyolefin separators are to improve their wettability to liquid electrolytes and enhance their thermal stability at high temperature in lithium-based batteries.

Relying on the mechanism of pore size exclusion, porous membranes own much better chemical stability than traditional IEMs. This mechanism is especially important for VFBs to separate vanadium ions from protons with different Stokes radius and charge densities. Although high efficiencies have been obtained in VFBs after a series of modifications on porous membranes, there are still some challenges to be further overcome. The mechanism of ion transport through a porous membrane, the formation mechanism of porous membranes, the mechanism of capacity decay and so on are still not clear enough. And these relevant mechanisms are significantly important for the structure design and optimization of porous membranes in VFBs. Besides, the upscaled application of porous membranes must be emphasized to accelerate their further commercialization. As for lithium-based batteries, there have been various modification methods on commercial polyolefin separators. The safety issue, which is normally induced by the serious thermal shrinkage of separators at high temperature, is still one of the most significant challenges to be solved. Developing more stable membrane materials or designing more stable porous structures may be an effective and promising method to improve the safety of lithium-based batteries.

Carrying out modifications on porous membranes and exploring new membrane materials are highly needed for the improvement in the performance of secondary battery technologies. However, the deep and comprehensive cognition and

elucidation of the desirable requirements of different secondary batteries for porous membranes, the principles of different modification methods, the properties of diverse modifying materials or membrane materials, and the preparation–structure–performance relationship are extremely significant. In other words, deeply understanding the process of battery operation, continuously designing new modification methods for porous membranes, exploiting more appropriate membrane materials, and continually studying the preparation–structure–performance relationship are extremely pivotal for the successful commercialization of secondary battery technologies. And the successful upscaled application of these modified membranes and novel kinds of membranes will be of significance as well.

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