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Recent advances in the selective membrane for aqueous redox flow batteries

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ABSTRACT

Redox flow batteries (RFBs) have gained intensive attention and are regarded as the ideal choice for large-scale energy storage owing to their attractive features such as excellent electrochemical reversibility, long life, high efficiency, and decoupling of energy and power density. Ion-exchange membranes in the flow battery act as a physical barrier to separate the positive and negative half-cell and allow migration of charge-balancing ions from one side to the other to complete the internal circuit of the cell. Certainly, the overall performance of the RFBs heavily depends on the properties of the ion-exchange membranes. To prevent power loss and minimize the crossover of the active species, it is essential for the ion-selective membrane to acquire high ionic conductivity to ensure low area specific resistance and high selectivity. This review summarizes recent research advances on improvement methods to enhance the selectivity of membranes in RFBs, mainly including the modifications on the pore size, hydrophilicity, and some other aspects. The relationship between performances and structures of these membranes is analyzed, and the advantages and limitations are discussed. Based on the recent advances, corresponding perspectives on future development in this field are also discussed.

1. Introduction

In recent years, energy and environmental problems have been challenging people all the time, requiring urgent exploitation and utilization of clean energy [1]. However, most categories of clean energy supply, such as solar energy, wind energy, and tidal energy, are discontinuous so that peak load shaving is needed to be implemented by large-scale energy storage devices [2,3]. Among several energy storage technologies, low energy density in supercapacitors, short cycling life in lead-acid cells, poor security in sodium-sulfur cells, and high cost in lithium-ion batteries limited their applications for large-scale energy storage [4,5].

In the redox flow battery (RFB), the energy-carrying redox-active materials are stored in two separate external tanks and are pumped to the cell stack during its operation [6]. The cell itself consists of two sets of porous carbon electrodes separated by a membrane. The electrodes provide the active sites to facilitate the redox reaction of the electrolytes but do not participate in the redox reaction. The unique mechanism of RFBs enables disintegration of the energy and power, allowing them to scale independently from one another and enabling flexible design, extremely long lifetime, extensive scalability, and safety [7,8]. Therefore, RFBs are regarded as the most promising choice as they can improve the efficiency of the existing grid infrastructure by providing safe and cost-effective stationary storage at an acceptable cost together with a long life.

In recent decades, several systems of inorganic redox chemistries, such as bromine/polysulfide [9], all-vanadium [10–12], vanadium/bromine [13–15], zinc/polyhalide [16–18], zinc/nickel [19,20], zinc/iodine [21], vanadium/cerium [22], vanadium/manganese [23], cobalt/vanadium [24], all-iron [25], lead/acid [26], hydrogen/bromine [27], and polysulfide/polyiodide [28], have been considered as the active materials for traditional and hybrid RFBs. Among these available redox chemistries, the all-vanadium redox flow battery (VRFB) is by far the most studied and most commercialized redox chemistry owing to its long life [10–12]. However, despite this remarkable success of RFBs as a viable technology for large-scale energy storage, the extensive utilization of the RFBs has been hindered by the high cost of the commonly used proton-exchange membrane [29].

The membrane in RFBs not only separates the positive and negative electrolytes to avoid short circuit but also conduct ions to realize the current loop, which plays a decisive role in coulombic

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efficiency (CE) and energy efficiency (EE) of RFBs [30,31]. The function of the membrane in RFBs and the important indicators are illustrated in Fig. 1. As a kind of perfluorosulfonic cationic membrane, a series of Nafion membranes produced by the Dupont company provides high proton conductivity, and high chemical and electrochemical stability, which is a common membrane for RFBs [32–34]. However, the exorbitant price of Nafion membranes hindered their extensive utilization in RFBs [35]. Thus, developing more advanced membranes with both superior performances and low cost always attracts the attention of researchers. This review aims to summarize recent research advances on categories of the improvement method on membranes to enhance the performance of RFBs, mainly including the controlling of the pore size, hydrophilicity, and some other aspects. By providing an overview of the developments of membrane materials in RFBs, we hope to inspire various ways to explore more advanced membranes with both high performances and low cost.

2. Pore size modification

The porous membranes differ from traditional ion-exchange membranes in a sense that the ion selectivity in porous membranes is obtained either by size sieving or by Donnan's exclusion because the stoke radii of vanadium ions are much larger than those of the hydronium ions. The elimination of the ion-exchange groups from the porous membrane overcomes the limitation caused by the ion-exchange groups and significantly enhances the stability of the membrane under harsh operating conditions of VRFBs. The first ever porous membrane for VRFB application was reported by Zhang et al. [36] using a hydrolyzed polyacrylonitrile nanofiltration (NF) membrane with finger-like pores with an ultrathin top layer prepared by the phase inversion method (Fig. 2a). The main concept lies in tuning the porosity of the membrane to obtain higher selectivity between the protons and the vanadium ions. The membrane demonstrated an efficiency of 95% at 80 mA cm^{-2}, which remains stable for around 200 cycles, demonstrating excellent chemical stability of the membrane. To further improve the selectivity of the NF membrane, an idea of introducing a thin layer of filler onto the membrane to reduce the pore size was introduced by the same group [37]. The silica was introduced onto the NF membrane to decrease the pore size and thereby to enhance the selectivity by almost four times via in situ hydrolysis of tetraethyl orthosilicate. The silica-modified NF membranes exhibited a much higher CE of 98% at 80 mA cm^{-2}, which is even higher than the commercial Nafion 115. Besides, the versatility of the concept was also verified by using the polysulfone (PSF)/sulfonated poly(ether ether ketone) (SPEEK) blend that obtained a CE of 97% at 80 mA cm^{-2} and an EE of 80% at 40 mA cm^{-2} (Fig. 2b) [37]. Overall, the silica-modified NF membranes demonstrated better performance, but the stability of the membrane remained unknown. The commercial Daramic polyethylene/silica microporous membranes with an average pore size of 0.15 μm and 57% porosity were also used in an iron-vanadium RFB that yielded an EE of ~70% [38,39].

Later on, a hydrophilic separator composed of agglomerated silica particles enmeshed in a fibril polyvinyl chloride matrix that possesses a unique porous structure with an average pore size of 45 nm (Fig. 2c) and a porosity of 65% (Fig. 2d) was incorporated in the VRFB by Wei et al. [40]. These pores serve as ion transport channels resulting in lower ohmic overpotential. Nevertheless, the large pore size allows protons and hydrated vanadium ions to diffuse through with greater freedom, causing poor selectivity and high self-discharge. Consequently, the cell can only acquire a CE of 89.2%, a voltage efficiency (VE) of 87.0%, and an EE of 78.1%, which are significantly lower than the commercial Nafion 115 at the same current density of 50 mA cm^{-2}. Therefore, to enhance the selectivity of ion permeation and realize improved performance in the flow cell than the traditional ion-exchange membranes, fundamental factors affecting the performance of the porous membranes such as the morphology, preparation technique, additives, and so on were researched extensively over the years. After the successful implementation of the NF membrane in the VRFB, many researchers optimized the fundamental aspects of the porous membranes to achieve even better performance than the ion-exchange membranes.

Polyethersulfone (PES) has also been widely studied as a membrane material for the flow battery owing to its excellent mechanical and chemical stability and tunable morphology. PES membranes created by phase inversion methods usually hold an asymmetric structure composed of a skin layer that defines the selectivity and a porous support layer, which governs the ion transport resistance. Although the large pore size of the skin layer is preferred to reduce the ion transport resistance, it also leads to a higher amount of active ion crossover. The asymmetric morphology arising from the kinetic properties is usually driven by the concentration distribution, viscosity of the casting solution, activity gradients of non-solvents, evaporation time, and humidity [41–45]. In general, increasing the porosity increases the proton conductivity, but the selectivity of the membranes is still a major challenge. Two different mechanisms of phase separation by immersion precipitation and instantaneous and delayed demixing are usually used to tune the morphology of the PES matrix. In a ternary system, instantaneous phase separation occurs when the precipitation path crosses the bimodal phase and forms two distinct phases immediately after immersion, leading to the porous top layer, whereas in delayed demixing, the phase separation does not occur for a considerable amount of time after immersion because the precipitation path does not cross the binodal immediately, resulting a dense skin layer [46].

Xu et al. [47] showed that the finger-like pores become larger and the appearance of macrovoids decreases, as shown in the scan electron microscope (SEM) images in Fig. 3a, owing to the delayed demixing caused by the higher viscosity of the concentrated polymer solution with increasing concentration of SPEEK in the cast solution. SPEEK is highly hydrophilic and possesses excellent proton conductivity and miscibility with a large range of polymers [48–50]. The porous skin layer obtained by the addition of SPEEK to PES facilitates the diffusion of solvent molecules into the cast solution transforming the finger-like pores to sponge-like pores by changing the thermodynamic properties of the cast solution and affecting the phase inversion method [51]. However, the CE and EE obtained by the membrane in the full cell is only 92.8% and 78.4%, respectively, which are lower than the traditional Nafion 115 membrane. Similarly, Chen et al. [52] reported a porous hierarchical PES/SPEEK membrane obtained through the hard template method using phenolphthalein as the template. They removed phenolphthalein from the pore walls of the PES/SPEEK/phenolphthalein composite membrane, leading to well-defined nanoscale hierarchical pores on the selective layer. In addition, the increase in viscosity of the casting solution owing to the incorporation of phenolphthalein promotes the formation of a spongy structure, as shown in Fig. 3b. However, with the increasing phenolphthalein concentration, a decrease in the CE was observed owing to the high vanadium permeability resulting from the larger and interconnected pores. The VRFB cell performance of the SPEEK/PES composite was further improved by Li et al. [53]. They increased the selectivity of the porous PES/SPEEK composite membrane by adding double ion-selective layers (skin layer and top layer) by coating an ultrathin layer of Nafion on top of the PES/SPEEK membrane (Fig. 3c) created by the phase inversion method.

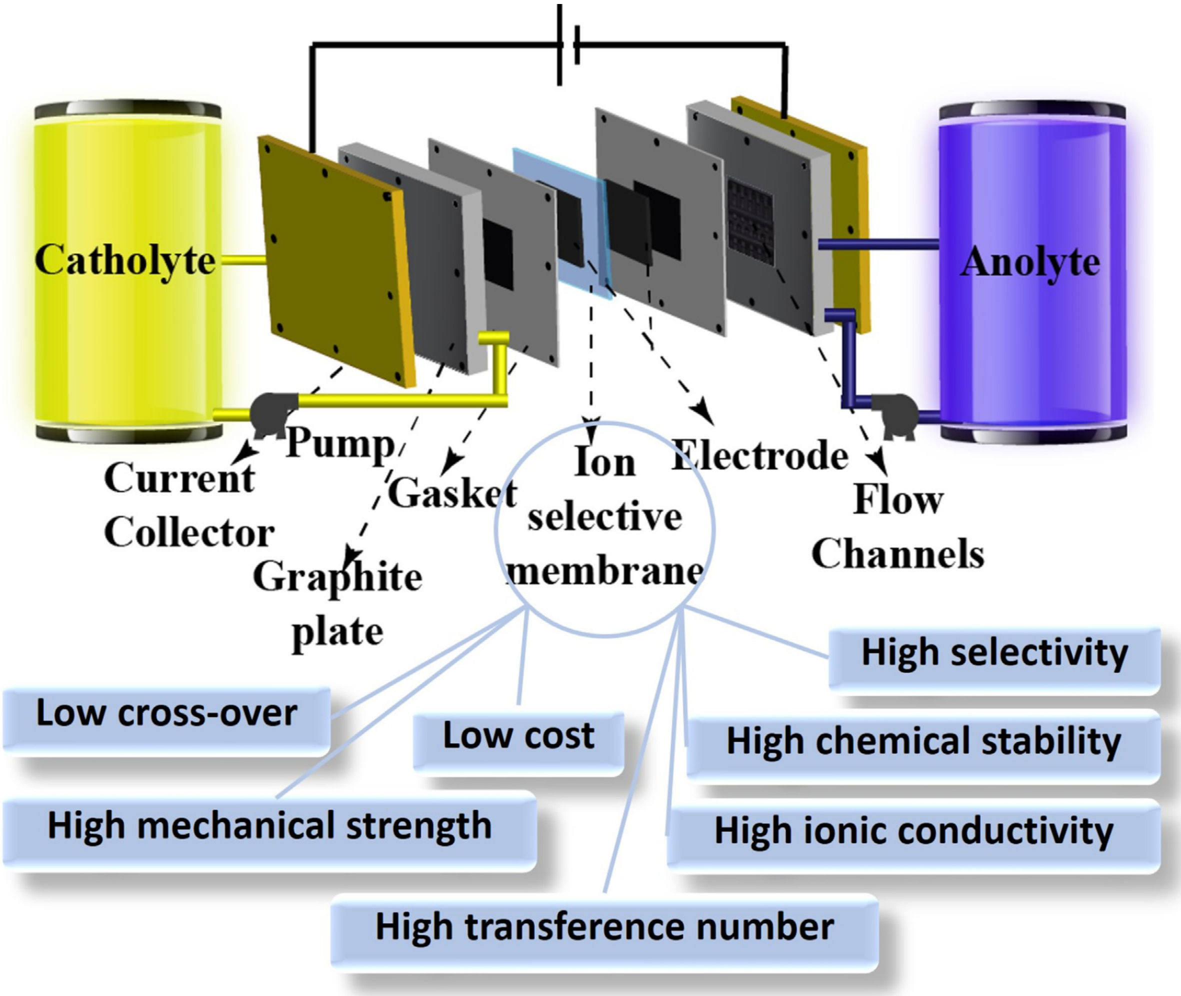

Fig. 1. Schematic diagram of redox flow batteries and important indicators of the membrane.

The role of additives in the membrane morphology and thus on the performance of the VRFB is explored by the aforementioned work. They showed that with the increasing poly(vinylpyrrolidone) (PVP) content and the increased molecular weight of PVP, it leads to enlarged and more interconnected pores in a series of asymmetric PES/PVP membranes. PVP causes thermodynamic enrichment and kinetic hindrance during the phase separation process by reducing the miscibility of casting solutions and simultaneously weakens the interaction between the solvent and non-solvent by increasing the viscosity of the casting solution [54,55]. As a result, the dramatic upsurge of vanadium permeability and the membrane with the highest PVP content displayed a poor CE of 66.8% and a VE of 81.6%, and the EE first reaches a peak at 76.1% and declines to 54.6%. However, additional optimization in the PVP content was able to achieve a decent CE of 92.4% and an EE of 76.1%, which is similar to the previously reported NF membranes. Furthermore, Yuan et al. [56] proposed a highly stable composite PES-based membrane doped with the corresponding salts of acidic phosphotungstic acid (TPA) and alkaline PVP, created through acid-base interaction by partially substituting the proton of TPA with alkaline nitrogen of PVP (Fig. 3d), which provides well-connected cross-linking networks that enhance the selectivity of the stable PES matrix. The rapid proton conduction occurs owing to the hopping of the protons from the TPA cluster to either the adjacent TPA or to the alkaline nitrogen in the PVP, resulting a high VE and EE of 88% and 87% at a current density of 80 mA cm^{-2}, respectively.

3. Hydrophilic modification

Among the different methods, hydrophilic modification is another effective way to improve the conductivity of PES membranes. To improve the ion conductivity of PES membranes, photoinitiated adsorption was proposed by Li et al. [57]. They grafted a vinyl monomer (sodium p-styrenesulfonate) on phase-separated PSF membranes by UV-assisted polymerization that enhances the hydrophilicity of PSF membranes. Initially, a photo initiator called benzophenone was coated on the PES surface and excited to a short lifetime single state by the irradiated photons. As a result, benzophenone forms a radical site at PES to relax its triplet state by extracting the primary hydrogen from the side methyl groups of PES and initiates polymerization of vinyl monomers (Fig. 4a). The grafted PES consists of a typical asymmetric structure made of a thin skin layer and a spongy sublayer, but the pore size after grafting decreases to 1.75 nm from 3.65 nm. Although the reduced pore size provides a steric hindrance to vanadium ions, the increasing hydrophilicity resulting from the polymer grafting facilitates the diffusion of the vanadium ions along with protons. In addition, the UV irradiation during the polymerization process could possibly escalate the structural degradation and reduce the chemical stability of the membrane. Thus, to retain the structural integrity, polymer blends were introduced to enhance the hydrophilicity, thereby increasing the proton conductivity [47,58].

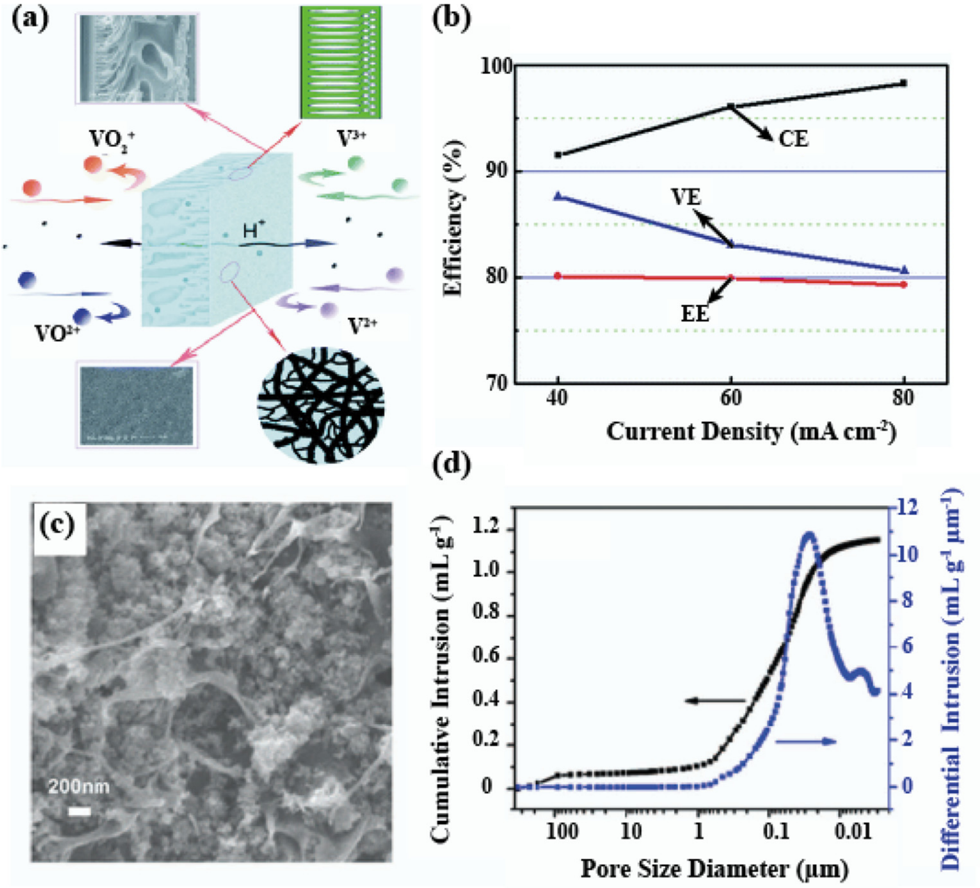

Fig. 2. (a) Schematic principle of nanofiltration membranes in the VRFB. Reproduced from Zhang et al. [36] with permission from the Royal Society of Chemistry. (b) VRFB single-cell performance of the tetraethyl orthosilicate−treated membrane under different current densities. Reproduced from Zhang et al. [37] with permission from the Royal Society of Chemistry. Cross-sectional field emission scanning electron microscope (FESEM) image (c) and pore size distribution obtained using mercury intrusion porosimetry (d) of the PVC/silica separator. Reproduced from Wei et al. [40] with permission from The Electrochemical Society. CE, coulombic efficiency; VE, voltage efficiency; EE, energy efficiency; PVC, polyvinyl chloride.

Furthermore, Yuan et al. [59] proposed a highly ion-selective membrane created by coating an 8-μm thick layer of zeolites, which are crystalline and microporous aluminosilicates with periodic cage-like arrangements on a porous PES substrate (Fig. 4b). Zeolites possess high proton conductivity owing to the existence of large numbers of exchangeable cation sites that can be exchanged for protons at the interlinked SiO_4 and AlO_4 tetrahedra (Fig. 4c). The high selectivity was obtained by incorporating ZSM-35 as the zeolite scaffold that contains pores of 0.42 nm × 0.54 nm, which is smaller than the stoke radii of protons (0.24 nm for $H_5O_2^+$) but larger than the hydrated vanadium ions (0.6 nm). The composite membrane demonstrated high chemical stability and a low area specific resistance of 0.98 Ω cm^2, leading to a current efficiency of 98.82% and an EE of 91.41% at a current density of 80 mA cm^{-2}. On the contrary, the battery using the Nafion 115 membrane can only achieve a current efficiency of 93.19% and an EE of 82.30%, simply owing to the higher vanadium ion permeability of Nafion 115−containing hydrophilic water channels of 2.5-nm diameter. The zeolite-coated membrane has also displayed higher efficiencies than Nafion 115 and a stable cycling performance for 100 cycles. Meanwhile, Lu et al. [60] reported an uncharged highly selective porous membrane by tuning the pore size and pore distribution of the PES membrane using solvent treatment, as illustrated in Fig. 4d. PES membranes with large and well-interconnected pores were created by the phase inversion method and further adjusted by introducing PVP into the casting solution. They further treated the porous membranes by immersing into isopropyl alcohol (IPA), followed by a controlled solvent evaporation process. During the solvent treatment, a swelling force acts on the membranes causing a reorganization of the polymer chains owing to the enhancement in their mobility, whereas during the controlled evaporation process, a cohesive force initiates the pore shrinkage. These two forces are equal at equilibrium, but the balance disrupts owing to the solvent treatment causing relatively higher shrinkage in the pores than the starting states of the membranes. This unique concept of achieving higher ion selectivity and the tuned morphology of the PES matrix is chemically more stable than Nafion 115, and the obtained CE and EE is higher than Nafion 115. However, the membrane only exhibited stable cycling for 120 cycles, and further improvement is needed to increase the lifetime of the membrane.

Similar perception of increasing the viscosity to limit the mass exchange rate and allow crystallization much earlier to gain higher crystallinity in the polyvinylidene fluoride (PVDF) ultrafiltration membrane with hydrophobic pores (Fig. 5a) was reported by Wei et al. [61]. PVDF is a semicrystalline polymer with at least four distinctive phases α, β, γ, and δ, and the crystallization together with the liquid-liquid demixing plays a crucial role in the obtained morphology of the phase-separated membranes. Li et al. [62] reported a membrane configuration by mixing PVDF and sodium allylsulfonate, where the pore size was controlled by the temperature and the time of polymer crystallization, as demonstrated in Fig. 5b. In this case, the morphology of the membranes was

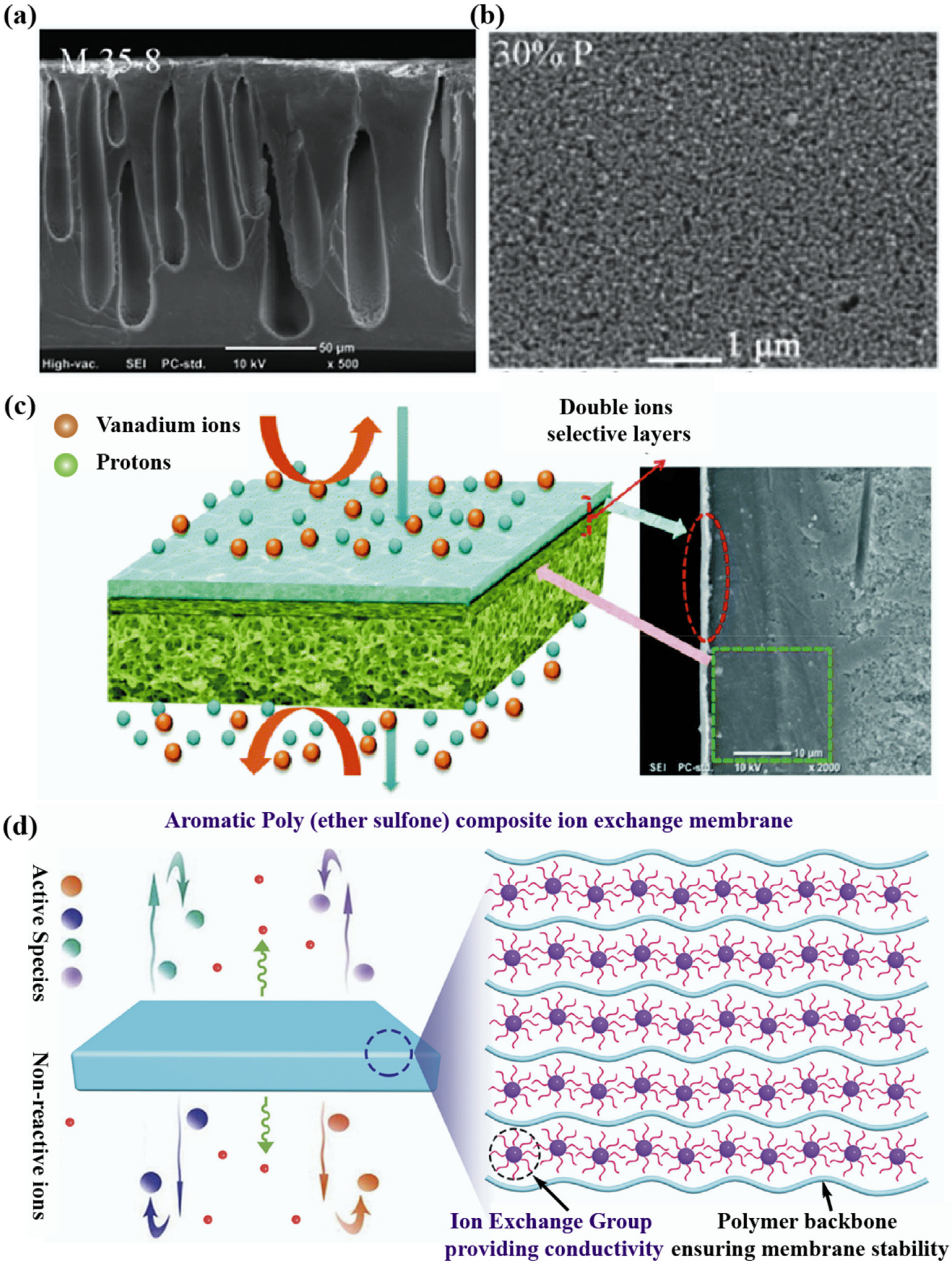

Fig. 3. (a) Cross-sectional morphology of the PES porous membrane prepared with different SPEEK contents. Reproduced from Xu et al. [47] with permission from the Royal Society of Chemistry. (b) Cross-sectional morphology of the prepared membrane with the 30% phenolphthalein template. Reproduced from Chen et al [52] with permission from the Elsevier. (c) The design of the porous PES/SPEEK composite membrane. Reproduced from Li et al. [53] with permission from the Royal Society of Chemistry. (d) The design of the aromatic polymer-based composite ion-exchange membrane. Reproduced from Yuan et al. [56] with permission from the Elsevier. PES, polyethersulfone; SPEEK, sulfonated poly(ether ether ketone).

dominated by the solid-liquid demixing during solvent evaporation rather than the liquid-liquid phase inversion. The gradual growth of crystals in the polymer solution forms globular grains that form a nanoscale-sieved network by approaching each other. They have also shown that the increased crystallization temperature and time significantly enhance the crystallization rate because it promotes polymer segment motion that generates more α phase, and part of the β phase also converts into the α phase through rearrangements, leading to a larger grain size and smaller pore size.

Owing to the high crystallinity and hydrophobicity, the PVDF-based membrane possesses outstanding thermal, mechanical, and chemical stability and higher selectivity owing to the intrinsically high resistance to the mass transfer caused by the repulsion between the water molecules and hydrophobic wall surface. However, this high hydrophobicity caused from the low surface energy can cause fouling owing to the strong repulsion between the PVDF and aqueous electrolytes. Therefore, several studies have been conducted to reduce the hydrophobicity of PVDF-based membranes. In achieving this, PVDF was grafted with various hydrophilic agents such as styrenesulfonicacid [63], sulfonated poly(ethersulfone) and TPA [64], and SPEEK [65,66] to improve proton conductivity. In addition, Zhou et al. [67] reported another interesting strategy to overcome the defects of the polymeric material by blending PVDF with ferroelectric ceramic such as barium

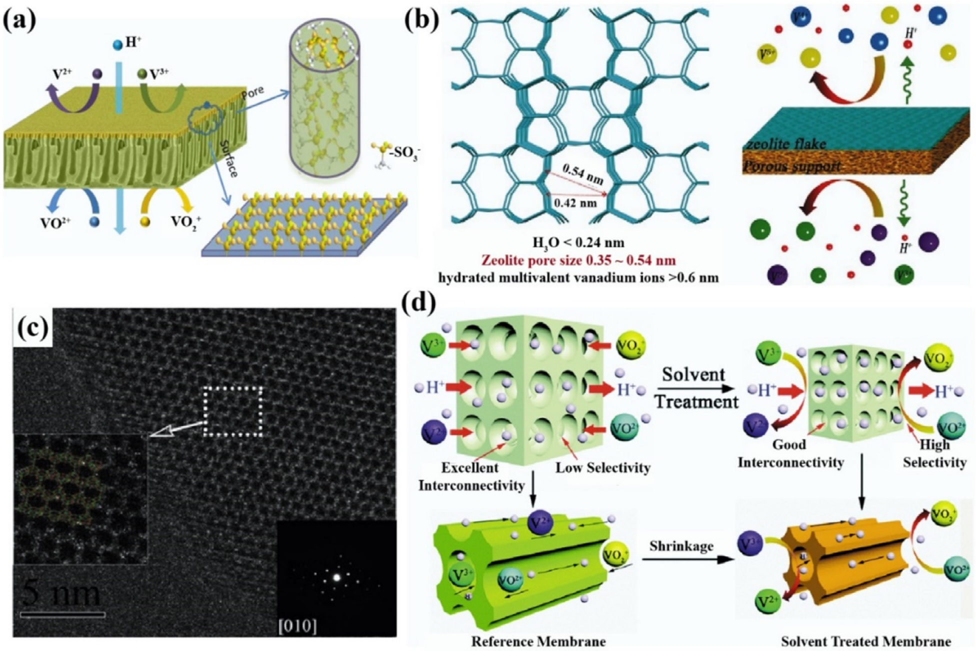

Fig. 4. (a) Schematic of modified polysulfone membranes used in the VRFB. Reproduced from Li et al. [57] with permission from the Elsevier. (b) Design principles of a VRFB with a porous membrane bearing a zeolite flake layer. (c) High-resolution transmission electron microscopy (HRTEM) image of ZSM-35 zeolite viewed in the [010] direction. The inset shows that a ZSM-35 framework drawn by diamond 4.0 (section in color: viewed in the [010] direction) fits perfectly with an HRTEM image viewed in the [010] direction. Reproduced from Yuan et al [59] with permission from the John Wiley & Sons, Inc. (d) The influence of the solvent treatment on the morphology and performance of the porous PES membrane. Reproduced from Lu et al. [60] with permission from the Royal Society of Chemistry. VRFB, all-vanadium redox flow battery; PES, polyethersulfone. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

titanate (BT) and grafting the blend with grafted polystyrene sulfonated acid. As the BT content in the membrane increased, more oxygen vacancies were created that cause more F^- to enter into the oxygen octahedron of BT, leading to the reduction in the degree of hydrophilic sulfonic acid grafting on the branched chain. Although this phenomenon decreases the ion conductivity, occurrence of microphase separation provides favorable channels for proton conduction between the highly hydrophobic C—F skeleton and sulfonic acid group. Similarly, to obtain connected ion transportation channels, Cao et al. [68] grafted hydrophilic PVP in the pores and on the surface of PVDF-based porous membranes first by immobilization of PVP on the PVDF substrate via cross-linking reaction using potassium persulfate as a cross-linking agent, followed by a solvent preswelling treatment using ethanol as the solvent, as depicted in Fig. 5c. Owing to the decrease in porosity and the pore size owing to PVP immobilization, the membrane can obtain a CE of 94.3% at 80 mA cm^{-2}. However, the firm immobilization of PVP on the pores tends to block the pores and increases the area specific resistance of the flow cell, and a solvent preswelling treatment is needed to enlarge the pores. In addition to PVDF, poly(vinylidene fluoride-*co*-hexafluoropropylene) was also used owing to its high hydrophobicity [69].

The polybenzimidazole (PBI)-based membrane, as another type of well-investigated membranes, exhibited chemical stability and good mechanical property. The drawback of this kind of ion-exchange membranes is their moderate proton conductivity, which usually manifested in unsatisfied VE. Recently, Ding et al. [70] used a polycondensation method to obtain the sulfonated polybenzimidazole (SPBI) membranes, enhancing the water uptake capability. The SPBI membrane shows higher average CE, VE, and EE values than that of the Nafion 115 membrane. Peng et al. [71] tried to graft non-ionic N-substitution hydrophilic side chains into the PBI membranes, forming hydrophilic clusters, which make the proton transfer more efficient.

4. Other modifications

Apart from introducing hydrophobic polymers, another interesting strategy to enhance the selectivity is to exploit Donnan's exclusion mechanism by introducing positively charged groups on the pore walls to restrict the permeability of vanadium ions through the pores and thereby increase the membrane's selectivity. In 2013, Zhang et al. [72] created a porous membrane with chloromethylated polysulfone resin and pyridine by the vapor-induced phase inversion method that looks similar to a bulk sponge with thousands of highly symmetrical micron-sized pores separated by ultrathin walls. All pores are grafted with weak alkaline groups and possess a uniform positive charge. As a result, protons can travel freely, but the large vanadium ions are rejected owing to Donnan's exclusion and the size sieving effect. By loosening the pore walls, the membrane can achieve proton conductivity similar to an aqueous sulfuric acid solution, and at the same time, it acts as a multilayered barrier to the vanadium ions, leading to an EE higher than 81% at 120 mA cm^{-2}. This specially designed membrane morphology provides an excellent solution for increasing the ion permeation selectivity while achieving a high VE and thus a higher EE.

Except for the size sieving and Donnan's exclusion, another strategy to enhance the selectivity is layer-by-layer (LBL) self-assembly [73–75]. A composite membrane possessing high selectivity for the vanadium ions was demonstrated by leaching out low-molecular-weight imidazole from a composite membrane of imidazole and SPEEK, followed by assembling two oppositely charged polyelectrolytes, poly(diallyldimethylammonium chloride) (polycation) and poly(sodium styrene sulfonate) (polyanion), on the obtained porous substrate. Although the membrane exhibited higher proton conductivity and high selectivity compared with the commercial Nafion membrane, the coulombic efficiencies obtained by the membrane at various current densities are much lower

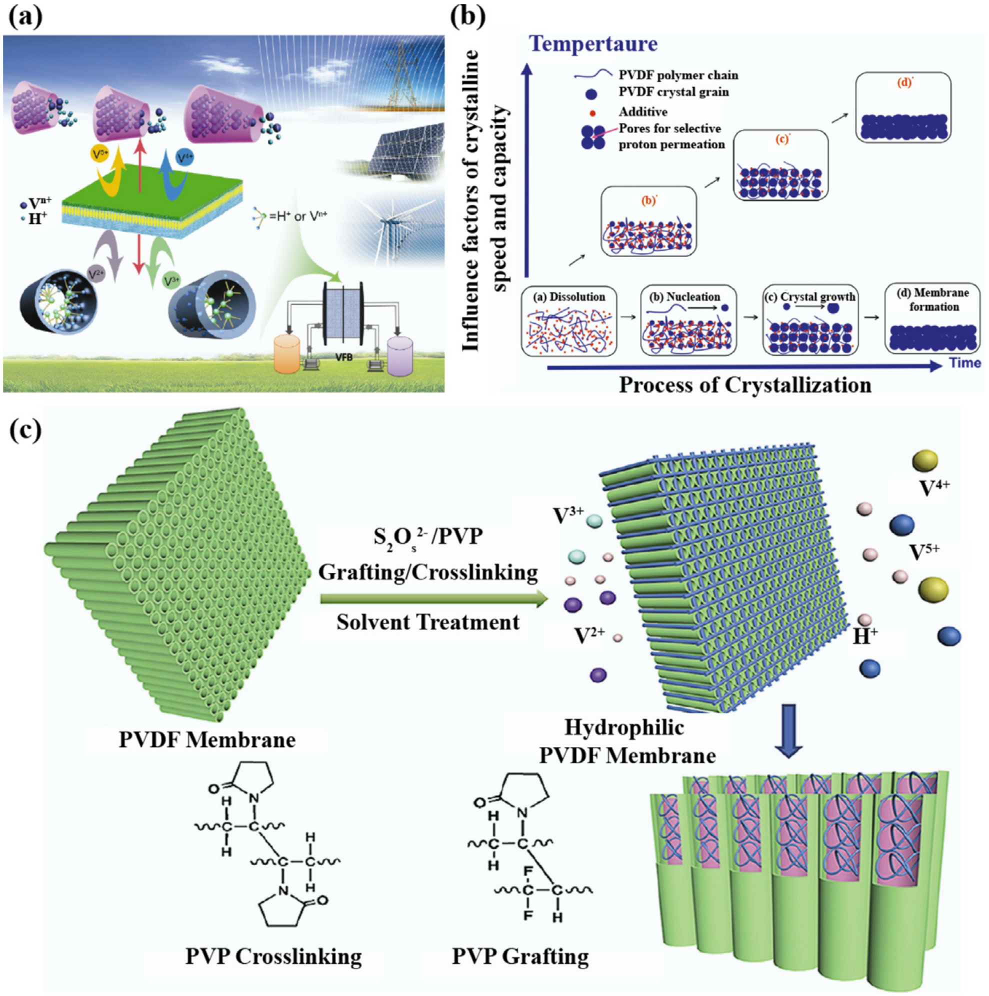

Fig. 5. (a) Proposed membrane transport mechanism. Reproduced from Wei et al. [61] with permission from the Royal Society of Chemistry. (b) The mechanism of membrane formation by controllable crystallization processes. Reproduced from Li et al. [62] with permission from the Elsevier. (c) Hydrophilic ion transport networks and the chemical reaction between PVP and PVDF by $K_2S_2O_8$ radical initiation. Reproduced from Cao et al. [68] with permission from the Elsevier. PVP, poly(vinylpyrrolidone); PVDF, polyvinylidene fluoride.

compared with Nafion 115 [75]. There are still other methods existing or being explored to improve the membrane performances not exhibited in this review. More effective strategies will be developed constantly, and the large-scale application of RFBs is being realized gradually. Part of the typical membrane materials and their properties are listed in Table 1 for brief comparison.

Table 1
Comparison of properties of typical membrane materials.

Material	Electrolyte	CE	EE	VE	Current Density	Ref
PAN	All-vanadium	95%	76%	–	80 mA cm^{-2}	[36]
PVC/Si	All-vanadium	89.2%	78.1%	87.0%	50 mA cm^{-2}	[40]
PES	All-vanadium	92.8%	78.4%	–	80 mA cm^{-2}	[47]
PES/SPEEK	All-vanadium	91.12%	–	86.10%	80 mA cm^{-2}	[51]
PES/PVP	All-vanadium	99%	81%	82%	140 mA cm^{-2}	[56]
PSF	All-vanadium	90.3%	78.4%	86.8%	80 mA cm^{-2}	[57]
PES	All-vanadium	98.63%	91.41%	92.68%	80 mA cm^{-2}	[59]
PES	All-vanadium	98.95%	89.69%	90.65%	80 mA cm^{-2}	[60]
PVDF	All-vanadium	95%	78.6%	82.7%	80 mA cm^{-2}	[61]

CE, coulombic efficiency; EE, energy efficiency; VE, voltage efficiency; PSF, polysulfone; PVP, poly(vinylpyrrolidone); PVDF, polyvinylidene fluoride; PES, polyethersulfone; PVC, polyvinyl chloride; SPEEK, sulfonated poly(ether ether ketone); PAN, polyacrylonitrile.

5. Conclusions and outlook

Improving the properties of the membrane materials is the key point to obtain high performances in RFBs. There is significant progress in developing the effective modifying method of the membranes in recent decades. One of the main strategies is controlling the pore size to change the ion selectivity, using the different radii between protons and transition metal cations and satisfying the results have been achieved. This strategy is limited by the great dependence on choosing the electrolyte containing the ions whose radius meets the requirement. Hydrophilic modification as another strategy is an effective way to improve proton conductivity of the membranes, but it is also facile to lead to the crossover of transition metal cations. Other methods such as introducing charge groups on the membranes and constructing LBL structures are also summarized in this review.

To realize the wide application of RFBs, there is still a long way to go by exploring membrane materials with more superior properties. First, the cost of the membrane materials should be reduced so that the competitiveness of RFBs could be promoted compared with other electrochemical systems for large-scale energy storage. Then, ion selectivity needs to be improved to ensure the long cycling life of RFBs. Besides, the pore size should not be too large and ion selectivity should be kept within a reasonable range to reduce the crossover of active ions. Moreover, the chemical stability of the membranes is the basic guarantee for stable operation of RFBs, requesting the membrane material to be kept stable under harsh chemical conditions. Finally, the mechanical strength of the membrane needs to be high enough to withstand the squeeze from the assembling of the battery and the pressure from proton diffusion during cycling.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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References

[1] M. Armand, J.M. Tarascon, Building better batteries, Nature 451 (2008) 652–657.
[2] J. Winsberg, T. Hagemann, T. Janoschka, M.D. Hager, U.S. Schubert, Redox-flow batteries: from metals to organic redox-active materials, Angew. Chem. Int. Ed. 56 (2016) 686–711.
[3] U. Mani, A. Vanchiappan, Y. Qingyu, M. Srinivasan, S.-K. Maria, L.T. Mariana, Recent advancements in all-vanadium redox flow batteries, Adv. Mater. Interfaces 3 (2016) 1500309.
[4] D. Larcher, J.M. Tarascon, Towards greener and more sustainable batteries for electrical energy storage, Nat. Chem. 7 (2014) 19.
[5] B. Dunn, H. Kamath, J.-M. Tarascon, Electrical energy storage for the grid: a battery of choices, Science 334 (2011) 928–935.
[6] J.D. Milshtein, J.L. Barton, T.J. Carney, J.A. Kowalski, R.M. Darling, F.R. Brushett, Towards low resistance nonaqueous redox flow batteries, J. Electrochem. Soc. 164 (2017) A2487–A2499.
[7] X. Wei, W. Pan, W. Duan, A. Hollas, Z. Yang, B. Li, Z. Nie, J. Liu, D. Reed, W. Wang, Materials and systems for organic redox flow batteries: status and challenges, ACS Energy Lett 2 (2017) 2187–2204.
[8] Y. Shi, C. Eze, B. Xiong, W. He, H. Zhang, T.M. Lim, A. Ukil, J. Zhao, Recent development of membrane for vanadium redox flow battery applications: a review, Appl. Energy 238 (2019) 202–224.
[9] A. Price, S. Bartley, S. Male, G. Cooley, A novel approach to utility-scale energy storage, Power Eng. J. 13 (1999) 122–129.
[10] J. Ye, Y. Cheng, L. Sun, M. Ding, C. Wu, D. Yuan, X. Zhao, C. Xiang, C. Jia, A green SPEEK/lignin composite membrane with high ion selectivity for vanadium redox flow battery, J. Membr. Sci. 572 (2019) 110–118.
[11] M. Skyllas-Kazacos, F. Grossmith, Efficient vanadium redox flow cell, J. Electrochem. Soc. 134 (1987) 2950–2953.
[12] M. Skyllas-Kazacos, M. Rychcik, R.G. Robins, A. Fane, M. Green, New all-vanadium redox flow cell, J. Electrochem. Soc. 133 (1986) 1057.
[13] M. Skyllas-Kazacos, Novel vanadium chloride/polyhalide redox flow battery, J. Power Sources 124 (2003) 299–302.
[14] M. Skyllas-Kazacos, Y. Limantari, Kinetics of the chemical dissolution of vanadium pentoxide in acidic bromide solutions, J. Appl. Electrochem. 34 (2004) 681–685.
[15] H. Vafiadis, M. Skyllas-Kazacos, Evaluation of membranes for the novel vanadium bromine redox flow cell, J. Membr. Sci. 279 (2006) 394–402.
[16] M.J. Mader, R.E. White, A mathematical model of a Zn/Br_2 cell on charge, J. Electrochem. Soc. 133 (1986) 1297–1307.
[17] K. Cathro, K. Cedzynska, D. Constable, Preparation and performance of plastic-bonded-carbon bromine electrodes, J. Power Sources 19 (1987) 337–356.
[18] J. Jorné, J. Kim, D. Kralik, The zinc-chlorine battery: half-cell overpotential measurements, J. Appl. Electrochem. 9 (1979) 573–579.
[19] L. Zhang, J. Cheng, Y. Yang, Y. Wen, X. Wang, G. Cao, Study of zinc electrodes for single flow zinc/nickel battery application, J. Power Sources 179 (2008) 381–387.
[20] Y. Ito, Nyce, R. Plivelich, M. Klein, S. Banerjee, Gas evolution in a flow-assisted zinc–nickel oxide battery, J. Power Sources 196 (2011) 6583–6587.
[21] J. Zhang, G. Jiang, P. Xu, A.G. Kashkooli, M. Mousavi, A. Yu, Z. Chen, An all-aqueous redox flow battery with unprecedented energy density, Energy Environ. Sci. 11 (2018) 2010–2015.
[22] B. Fang, S. Iwasa, Y. Wei, T. Arai, M. Kumagai, A study of the Ce(III)/Ce(IV) redox couple for redox flow battery application, Electrochim. Acta 47 (2002) 3971–3976.
[23] F. Xue, Y. Wang, W. Wang, X. Wang, Investigation on the electrode process of the Mn(II)/Mn(III) couple in redox flow battery, Electrochim. Acta 53 (2008) 6636–6642.
[24] J.M. Stauber, S. Zhang, N. Gvozdik, Y. Jiang, L. Avena, K.J. Stevenson, C.C. Cummins, Cobalt and vanadium trimetaphosphate polyanions: synthesis, characterization, and electrochemical evaluation for non-aqueous redox-flow battery applications, J. Am. Chem. Soc. 140 (2018) 538–541.
[25] L. Hruska, R. Savinell, Investigation of factors affecting performance of the iron-redox battery, J. Electrochem. Soc. 128 (1981) 18–25.
[26] M.G. Verde, K.J. Carroll, Z. Wang, A. Sathrum, Y.S. Meng, Achieving high efficiency and cyclability in inexpensive soluble lead flow batteries, Energy Environ. Sci. 6 (2013) 1573–1581.
[27] A.D. Modestov, D.V. Konev, O.V. Tripachev, A.E. Antipov, Y.V. Tolmachev, M.A. Vorotyntsev, A hydrogen-bromate flow battery for air-deficient environments, Energy Technol. 6 (2018) 242–245.
[28] L. Su, A.F. Badel, C. Cao, J.J. Hinricher, F.R. Brushett, Toward an inexpensive aqueous polysulfide-polyiodide redox flow battery, Ind. Eng. Chem. Res. 56 (2017) 9783–9792.
[29] E.S. Beh, D. De Porcellinis, R.L. Gracia, K.T. Xia, R.G. Gordon, M.J. Aziz, A neutral pH aqueous organic–organometallic redox flow battery with extremely high capacity retention, ACS Energy Lett 2 (2017) 639–644.
[30] X. Song, L. Ding, L. Wang, M. He, X. Han, Polybenzimidazole membranes embedded with ionic liquids for use in high proton selectivity vanadium redox flow batteries, Electrochim. Acta 295 (2019) 1034–1043.
[31] W. Wang, Q. Luo, B. Li, X. Wei, L. Li, Z. Yang, Recent progress in redox flow battery research and development, Adv. Funct. Mater. 23 (2013) 970–986.
[32] J. Xi, Z. Wu, X. Qiu, L. Chen, Nafion/SiO_2 hybrid membrane for vanadium redox flow battery, J. Power Sources 166 (2007) 531–536.
[33] Q. Luo, H. Zhang, J. Chen, P. Qian, Y. Zhai, Modification of Nafion membrane using interfacial polymerization for vanadium redox flow battery applications, J. Membr. Sci. 311 (2008) 98–103.
[34] B. Jiang, L. Yu, L. Wu, D. Mu, L. Liu, J. Xi, X. Qiu, Insightsinto the impact of the Nafion membrane pretreatment process on vanadium flow battery performance, ACS Appl. Mater. Interfaces 8 (2016) 12228–12238.
[35] J. Zeng, C. Jiang, Y. Wang, J. Chen, S. Zhu, B. Zhao, R. Wang, Studies on polypyrrole modified nafion membrane for vanadium redox flow battery, Electrochem. Commun. 10 (2008) 372–375.
[36] H. Zhang, H. Zhang, X. Li, Z. Mai, J. Zhang, Nanofiltration (NF) membranes: the next generation separators for all vanadium redox flow batteries (VRBs)? Energy Environ. Sci. 4 (2011) 1676–1679.
[37] H. Zhang, H. Zhang, X. Li, Z. Mai, W. Wei, Silica modified nanofiltration membranes with improved selectivity for redox flow battery application, Energy Environ. Sci. 5 (2012) 6299–6303.
[38] X. Wei, L. Li, Q. Luo, Z. Nie, W. Wang, B. Li, G.-G. Xia, E. Miller, J. Chambers, Z. Yang, Microporous separators for Fe/V redox flow batteries, J. Power Sources 218 (2012) 39–45.
[39] X. Wei, Q. Luo, B. Li, Z. Nie, E. Miller, J. Chambers, V.L. Sprenkle, W. Wang, Performance evaluation of microporous separator in Fe/V redox flow battery, ECS Trans 45 (26) (2013) 17–24.
[40] X. Wei, Z. Nie, Q. Luo, B. Li, V. Sprenkle, W. Wang, Polyvinyl chloride/silica nanoporous composite separator for all-vanadium redox flow battery applications, J. Electrochem. Soc. 160 (2013) A1215–A1218.
[41] S. Shin, J. Kim, H. Kim, J. Jeon, B. Min, Preparation and characterization of polyethersulfone microfiltration membranes by a 2-methoxyethanol additive, Desalination 186 (2005) 1–10.
[42] M. Khayet, T. Matsuura, Preparation and characterization of polyvinylidene fluoride membranes for membrane distillation, Eng. Chem. Res. 40 (2001) 5710–5718.
[43] C.Y. Lai, A. Groth, S. Gray, M. Duke, Preparation and characterization of poly (vinylidene fluoride)/nanoclay nanocomposite flat sheet membranes for abrasion resistance, Water Res. 57 (2014) 56–66.
[44] X. Wang, X. Wang, L. Zhang, Q. An, H. Chen, Morphology and formation mechanism of poly (vinylidene fluoride) membranes prepared with immerse precipitation: effect of dissolving temperature, J. Macromol. Sci. B 48 (2009) 696–709.
[45] M.M. Teoh, N. Peng, T.-S. Chung, L.L. Koo, Development of novel multichannel rectangular membranes with grooved outer selective surface for membrane distillation, in: Eng. Chem. Res. vol. 50, 2011, pp. 14046–14054.
[46] A.J. Reuvers, Membrane Formation: Diffusion Induced Demixing Processes in Ternary Polymeric Systems, Twente University, Enschede, The Netherlands, 1987.
[47] W. Xu, X. Li, J. Cao, Z. Yuan, H. Zhang, Morphology and performance of poly (ether sulfone)/sulfonated poly (ether ether ketone) blend porous membranes for vanadium flow battery application, RSC Adv. 4 (2014) 40400–40406.
[48] C. Zhao, Z. Wang, D. Bi, H. Lin, K. Shao, T. Fu, S. Zhong, H. Na, Blend membranes based on disulfonated poly(aryl ether ether ketone)s (SPEEK) and poly (amide imide)(PAI) for direct methanol fuel cell usages, Polymer 48 (2007) 3090–3097.
[49] W.R. Bowen, S.Y. Cheng, T.A. Doneva, D.L. Oatley, Manufacture and characterisation of polyetherimide/sulfonated poly (ether ether ketone) blend membranes, J. Membr. Sci. 250 (2005) 1–10.
[50] X. Ling, C. Jia, J. Liu, C. Yan, Preparation and characterization of sulfonated poly(ether sulfone)/sulfonated poly(ether ether ketone) blend membrane for vanadium redox flow battery, J. Membr. Sci. 415–416 (2012) 306–312.

[51] D. Chen, D. Li, X. Li, Highly symmetric spongy porous poly(ether sulfone) membranes with selective open-cells for vanadium flow battery application, RSC Adv. 6 (2016) 87104–87109.

[52] D. Chen, D. Li, X. Li, Hierarchical porous poly (ether sulfone) membranes with excellent capacity retention for vanadium flow battery application, J. Power Sources 353 (2017) 11–18.

[53] Y. Li, X. Li, J. Cao, W. Xu, H. Zhang, Composite porous membranes with an ultrathin selective layer for vanadium flow batteries, Chem. Commun. 50 (2014) 4596–4599.

[54] H.C. Park, Y.P. Kim, H.Y. Kim, Y.S. Kang, Membrane formation by water vapor induced phase inversion, J. Membr. Sci. 156 (1999) 169–178.

[55] P. Machado, A. Habert, C. Borges, Membrane formation mechanism based on precipitation kinetics and membrane morphology: flat and hollow fiber polysulfone membranes, J. Membr. Sci. 155 (1999) 171–183.

[56] Z. Yuan, Q. Dai, L. Qiao, Y. Zhao, H. Zhang, X. Li, Highly stable aromatic poly (ether sulfone) composite ion exchange membrane for vanadium flow battery, J. Membr. Sci. 541 (2017) 465–473.

[57] Y. Li, H. Zhang, H. Zhang, J. Cao, W. Xu, X. Li, Hydrophilic porous poly(sulfone) membranes modified by UV-initiated polymerization for vanadium flow battery application, J. Membr. Sci. 454 (2014) 478–487.

[58] S.S. Lim, W.R.W. Daud, J.M. Jahim, M. Ghasemi, P.S. Chong, M. Ismail, Sulfonated poly (ether ether ketone)/poly (ether sulfone) composite membranes as an alternative proton exchange membrane in microbial fuel cells, Int. J. Hydrogen Energy 37 (2012) 11409–11424.

[59] Z. Yuan, X. Zhu, M. Li, W. Lu, X. Li, H. Zhang, A highly ion-selective zeolite flake layer on porous membranes for flow battery applications, Angew. Chem. 128 (2016) 3110–3114.

[60] W. Lu, Z. Yuan, Y. Zhao, X. Li, H. Zhang, I.F.J. Vankelecom, High-performance porous uncharged membranes for vanadium flow battery applications created by tuning cohesive and swelling forces, Energy Environ. Sci. 9 (2016) 2319–2325.

[61] W. Wei, H. Zhang, X. Li, H. Zhang, Y. Li, I. Vankelecom, Hydrophobic asymmetric ultrafiltration PVDF membranes: an alternative separator for VFB with excellent stability, Phys. Chem. Chem. Phys. 15 (2013) 1766–1771.

[62] B. Li, B. Wang, Z. Liu, G. Qing, Synthesis of nanoporous PVDF membranes by controllable crystallization for selective proton permeation, J. Membr. Sci. 517 (2016) 111–120.

[63] X. Luo, Z. Lu, J. Xi, Z. Wu, W. Zhu, L. Chen, X. coulombic Qiu, Influences of permeation of vanadium ions through PVDF-g-PSSA membranes on performances of vanadium redox flow batteries, J. Phys. Chem. B 109 (2005) 20310–20314.

[64] X. Lian, X. Yang, H. Liu, H. Liu, J. Zhu, SPES/PVDF/TPA composite membrane as an alternative proton exchange membrane in vanadium redox flow battery application, High Perform. Polym. 30 (2018) 312–317.

[65] L. Zhao, F. Li, Y. Guo, Y. Dong, J. Liu, Y. Wang, J. Kang, G. Zhou, Q. Liu, SPEEK/PVDF binary membrane as an alternative proton-exchange membrane in vanadium redox flow battery application, High Perform. Polym. 29 (2017) 127–132.

[66] H. Jung, M. Cho, T. Sadhasivam, J. Kim, S. Roh, Y. Kwon, High ionic selectivity of low permeable organic composite membrane with amphiphilic polymer for vanadium redox flow batteries, Solid State Ionics 324 (2018) 69–76.

[67] Y. Zhou, P. Qiu, Y. Ma, X. Zhang, D. Xu, J. Lin, Y. Tang, F. Wang, X. He, Z. Zhou, N. Sun, D. Sun, $BaTiO_3$/PVDF-g-PSSA composite proton exchange membranes for vanadium redox flow battery, Ceram. Int. 41 (2015) S758–S762.

[68] J. Cao, Z. Yuan, X. Li, W. Xu, H. Zhang, Hydrophilic poly(vinylidene fluoride) porous membrane with well connected ion transport networks for vanadium flow battery, J. Power Sources 298 (2015) 228–235.

[69] Z. Li, L. Liu, L. Yu, L. Wang, J. Xi, X. Qiu, L. Chen, Characterization of sulfonated poly(ether ether ketone)/poly(vinylidene fluoride-co-hexafluoropropylene) composite membrane for vanadium redox flow battery application, J. Power Sources 272 (2014) 427–435.

[70] L. Ding, X. Song, L. Wang, Z. Zhao, Enhancing proton conductivity of polybenzimidazole membranes by introducing sulfonate for vanadium redox flow batteries applications, J. Membr. Sci. 578 (2019) 126–135.

[71] S. Peng, X. Wu, X. Yan, L. Gao, Y. Zhu, D. Zhang, J. Li, Q. Wang, G. He, Polybenzimidazole membranes with nanophaseseparated structure induced by non-ionic hydrophilic side chains for vanadium flow batteries, J. Mater. Chem. A 6 (2018) 3895–3905.

[72] H. Zhang, H. Zhang, F. Zhang, X. Li, Y. Li, I. Vankelecom, Advanced charged membranes with highly symmetric spongy structures for vanadium flow battery application, Energy Environ. Sci. 6 (2013) 776–781.

[73] H. Zheng, L. Petrik, M. Mathe, Preparation and characterisation of porous poly (2, 5benzimidazole)(ABPBI) membranes using surfactants as templates for polymer electrolyte membrane fuel cells, Int. J. Hydrogen Energy 35 (2010) 3745–3750.

[74] J. Weber, M. Antonietti, A. Thomas, Mesoporous poly (benzimidazole) networks via solvent mediated templating of hard spheres, Macromolecules 40 (2007) 1299–1304.

[75] Y. Wang, S. Wang, M. Xiao, D. Han, Y. Meng, Preparation and characterization of a novel layer-by-layer porous composite membrane for vanadium redox flow battery (VRB) applications, Int. J. Hydrogen Energy 39 (2014) 16088–16095.