Conference paper

Xiongwei Wu, Junping Hu, Jun Liu, Qingming Zhou, Wenxin Zhou, Huiyong Li*
and Yuping Wu*

Ion exchange membranes for vanadium redox flow batteries

Abstract: In recent years, much attention has been paid to vanadium redox flow batteries (VRBs) because of their excellent performance as a new and efficient energy storage system, especially for large-scale energy storage. As one core component of a VRB, ion exchange membrane prevents cross-over of positive and negative electrolytes, while it enables the transportation of charge-balancing ions such as H^+ , SO_4^{2-} , and HSO_4^- to complete the current circuit. To a large extent, its structure and property affect the performance of VRBs. This review focuses on the latest work on the ion exchange membranes for VRBs such as perfluorinated, partially fluorinated, and nonfluorinated membranes. The prospective for future development on membranes for VRBs is also proposed.

Keywords: energy efficiency; ion exchange membrane; NMS-IX; proton; vanadium redox flow batteries (VRBs); vanadium ion permeability.

DOI 10.1515/pac-2014-0101

Introduction

Vanadium redox flow battery

Vanadium redox flow battery (VRB), which employs V(V)/V(IV) couple as positive active electrolyte and V(II)/V(III) couple as negative active electrolyte [1–3] was originally proposed by Maria Skyllas – Kazacos' group from New South Wales, Australia, in 1985, after vanadium compounds were discovered to be used as the electrolyte of redox flow batteries by National Aeronautics and Space Administration (NASA) in 1974 [4–6]. Subsequently, a lot of explorations and investigations have been done around the world. At present, quite some megawatt units for demonstration have been installed in America, Japan and Australia. As a chemical energy storage device, VRB consists of proton exchange membrane, electrolytes, electrodes, frames, current collectors (bipolar plates), end plates, pumps and fluid reservoirs (Fig. 1), and the electrochemical reactions

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Article note: Paper based on a presentation at the 9th International Symposium on Novel Materials and their Synthesis (NMS-IX) and the 23rd International Symposium on Fine Chemistry and Functional Polymers (FCFP-XXIII), Shanghai, China, 17–22 October 2013.

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*Corresponding authors: Huiyong Li, College of Science, Hunan Agricultural University, Changsha 410128, China, e-mail: hy5321@hunau.net; and Yuping Wu, College of Science, Hunan Agricultural University, Changsha 410128, China; New Energy and Materials Laboratory (NEML) and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, China; and Hunan Province Yinfeng New Nenergy Co., Ltd. Changsha 410013, China, e-mail: wuyp@fudan.edu.cn

Xiongwei Wu, Junping Hu, Jun Liu, Qingming Zhou and Wenxin Zhou: College of Science, Hunan Agricultural University, Changsha 410128, China

Fig. 1 Principle of VRB.

are shown in equations (1–3). It is available for energy storage such as wind, solar powers, nuclear powers, emergency uninterruptable system, load levelling for the grids and increasing the stability of power grids [2, 7–9].

Comparing with other battery systems, VRB presents the following advantages:

1. Flexible design. Its capacity is determined by the concentration and volume of electrolytes, and its power is determined by the size of stacks and the number of single cells;
2. No cross-contamination, since both electrolytes use vanadium-based compounds;
3. Long cycling life;
4. Deep-discharge capability;
5. Large discharge current density;
6. Good ability for pulse charge performance;
7. Low cost, since the materials in VRBs are cheap except ion exchange membranes, and the electrolytes can be fully recovered.

Of course, it also has some disadvantages:

1. Low energy density. Current VRBs achieve an energy density of about 25–35 Wh/kg [10].
2. Complex system [11].

The VRB system is suitable for large-scale static energy storage. However, ion exchange membranes (IEMs) have become the main bottleneck for commercialization of VRB because of their high cost and some unsatisfied properties [12, 13]. It is necessary to understand the present status and the future directions for the IEMs.

Ion exchange membranes for VRBs

As shown in Fig. 1, in a VRB system, the positive and negative electrolytes are separated by an IEM which is a core component of flow batteries. Its function is transportation of charge-balancing ions (cation

exchange membrane: H^+ , anion exchange membrane: SO_4^{2-} and HSO_4^-) to prevent cross mixing [12–16]. As charge-balancing ion, H^+ is mostly consumed and produced at the positive electrode, and a proton exchange membrane (PEM) is generally required. As a result, some PEMs for methanol fuel cells and proton exchange membrane fuel cells (PEMFCs) or their modifications can be directly used for VRBs [17–20]. In other words, the cation exchange membranes (CEMs) are the mainstream for VRB applications, especially the Nafion series with high proton conductivity and good chemical stability in the harsh acid and high oxidizing electrolyte surrounding (concentration of vanadium ions: 1–3 M, concentration of sulfuric acid: 1–3 M) [8, 12, 21–24]. However, because of the high vanadium ion permeability and large volume water transference during the charge-discharge processes and high cost, Nafion is not the ideal material for large-scale commercial applications of VRBs [20, 25]. So far, there are fluoride membranes and non-fluoride ones based on the components [26]. They are called anion exchange membranes (AEMs), CEMs, amphoteric ion exchange ones (AIEMs) and non-ionic exchange ones, on the basis of ion selectivity [27–29]. Based on the combination of fixed groups with polymer skeleton of IEMs, there are heterogeneous membranes (physical combination), homogeneous ones (chemical bond), semi-homogeneous ones (both physical and chemical bond).

It is well known that the properties of IEMs have a significant impact on the performances of a VRB. Generally speaking, an ideal membrane for a VRB should have the follow characteristics [30–34]:

1. High ionic conductivity;
2. High ion selection and low vanadium ion permeability;
3. Good chemical stability;
4. Simple process and technology;
5. Low cost.

Evaluation and test methods for performance of ion exchange membranes

With respect to the evaluation methods for the performance of IEMs, some general methods, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), electron dispersive X-ray analysis (EDX), thermogravimetry (TG), differential scanning calorimetry (DSC), Fourier transformation infrared spectroscopy (FT-IR), ultraviolet spectroscopy (UV), and nuclear magnetic resonance (NMR), are used to obtain structure, thickness, mechanical property, water content, electrolyte uptake, swelling ratio, area resistance (AR), ionic conductivity, vanadium ion permeability, ion exchange capacitance (IEC), water migration and stability [22, 35–40]. Some important and special aspects are discussed in this section, and the other characteristics can refer some related references [23, 36–42].

Area resistance

The resistance of membrane is usually evaluated by area resistance (AR) which determines the voltage efficiency (VE) of a VRB. As a part of internal resistance of a VRB, AR is measured with a cell by testing the different values of resistance with and without a membrane in certain concentrations of electrolytes (vanadium sulfate and H_2SO_4 solutions). As previously reported [41], there are two methods to measure the AR: DC and AC impedance method.

Generally, CEMs have much lower AR than AEMs due to the Donnan exclusion effect while homogeneous membranes have higher AR than heterogeneous ones because of the difference in sizes of pores which afford channels for transferring charge-balancing ions [42, 43]. The AR will decrease when the concentration of H^+ increases.

Ionic conductivity and ion exchange capacitance

Ionic conductivity denotes the ability of membranes to transfer ions to complete the current circuit and is characterized by ion exchange capacitance (IEC, usually among 1–5 mEq dg⁻¹) [18]. A high ionic conductivity means a low loss of VE during the charge-discharge processes. The hydrolysis stability of the ion exchange groups has immediate impact on the cycling life of an IEM.

In order to prepare the desired membranes with high proton conductivity for VRBs, it is important and meaningful to understand proton conduction mechanisms – proton transfer. There are two types of mechanisms for the proton conduction [44]. One is “Grotthuss type mechanism” and the other is “Vehicle type mechanism”. The former indicates that proton diffuses through the hydrogen bond network by the formation or cleavage of covalent bonds. While the latter takes for that the high molecular diffusion coefficient also leads to a proton conductivity contribution arising from the simple diffusion of charged complexes such as H₃O⁺, H₅O₂⁺ and H₉O₄⁺ [44].

In a VRB system, the function of the conducting ions especially proton for the IEMs is generally obtained by introducing ion exchange groups, adulterating fillers, sulfonating or quaternizing into/of the polymer skeleton [45–48]. An increase in proton conductivity is usually along with an increase in VE.

Vanadium ion permeability

As the CEMs are most commonly used to separate electrolytes and transport protons to complete the current circuit in VRBs, some cations also can diffuse through them. Permeation of vanadium ions (V²⁺, V³⁺, VO²⁺ and VO₂⁺) causes self-discharge and leads to loss of capacity and CE of the VRBs. The vanadium ion permeability is one of the vital parameters for IEMs, and low vanadium ion permeability is needed. It is usually evaluated by the permeability of VO₂⁺ [49, 50]. Formula for the diffusion of VO₂⁺ is expressed in equation (4) [51, 52]:

$$C = C_0 \times [1 - \exp(-\alpha t)] \quad (4)$$

where C is the concentration of VO₂⁺ at time t , C_0 is equilibrium concentration of VO₂⁺, α is data through curve fitting, and t is time.

Pore size and some characteristics of the ion exchange groups of the IEMs determine the vanadium ion permeability. In general, large pore size means high vanadium ion permeability. Moreover, because of the Donnan exclusion effect, anion exchange groups can decrease the diffusion of vanadium ions. Therefore pore filling, introducing cation, cross-linking and copolymerization of polymers are used to decrease the vanadium ions permeability and accelerate the ion selectivity [29, 53–56].

Chemical stability

Chemical stability is taken into consideration due to the above-mentioned harsh chemical environment for the IEMs in VRBs. In the electrolytes, a high proton concentration leads to low AR and a high vanadium ion concentration indicates high energy density. The strong acidic environment can lead to a serial of hydrolysis-polycondensation reactions and subsequent precipitation of oxoanions [13]. The VO₂⁺ coupled with higher proton concentration possesses higher oxidization ability.

From the above illustration, it can be seen that good chemical stability of the IEMs is the guarantee of good electrochemical performance and excellent cycling life for VRBs. To decrease the burden of strong acid and high oxidation to the IEMs, some aromatic polymers, and those polymers with high stability and inorganic particles are often used to modify the main polymer chains [29, 31, 57–60].

Water transference

It is essential for CEMs to conduct protons, and water can transport across the CEMs, too. The reasons causing water transportation are diverse. Water molecules complexed with ions that are being transported to alleviate concentration gradients between the positive and the negative electrolyte solutions (osmotic pressure), or water molecules can complex to the charge-balancing species such as H^+ , SO_4^{2-} and HSO_4^- [13]. However, the net water transference will lead one electrolyte in one half cell to be diluted and the other to be concentrated, which bring about capacity loss of VRB and heavier burden to the CEMs.

The earlier work on the water transference demonstrates that the net water transport via AEMs and non-ionic membranes in VRBs from the positive half cell to the negative one, while in the case of CEMs the direction is opposite, a significant amount of water is transferred from the negative half cell to the positive one by the hydration shells of V^{2+} and V^{3+} ions under the action of osmotic pressure [23]. Recently, it is found that the direction of preferential water transference across the CEMs is dependent on the state of charge (SOC) of VRB [61]. When the initial SOC is between 100 and 50 %, the direction of water transference is toward the positive half cell. When the SOC is between 50 and 0 %, the direction of water transference moves toward the negative half cell.

To reduce the water transference in VRB, hydrophobic polymers and strongly hydrophobic inorganic particles are used to prepare or modify membranes.

Ion exchange membranes for VRBs

In this review, we expound IEMs according to the above-mentioned classification by the components: fluoride membranes and nonfluoride ones, and part of them are shown in Table 1.

Perfluorinated membranes

Nafion is the most widely used as IEMs in VRBs. It is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer discovered by Walther Grot of DuPont Company in the late 1960s. The synthesis of Nafion include 3 steps [72, 73]: (1) copolymerization of tetrafluoroethylene (TFE) and a derivative of a perfluoro (alkyl vinyl ether) with sulfonyl fluoride ($-\text{SO}_2\text{F}$) groups; (2) conversion of the $-\text{SO}_2\text{F}$ groups into sulfonate ones ($-\text{SO}_3-\text{Na}^+$) with hot NaOH aqueous solution; and (3) conversion of sulfonate groups ($-\text{SO}_3-\text{Na}^+$) to the acid form containing sulfonic acid ($-\text{SO}_3\text{H}$) groups. Finally, Nafion can be cast into thin films by heating in aqueous alcohol at 250 °C in an autoclave [74].

In water, $-\text{SO}_3\text{H}$ groups fixed on the ether branched chain in Nafion membrane are hydrolyzed and this membrane leads to a good cation selectivity and superior proton conduction. Due to high bond energy of C-F (485 kJ mol^{-1}) and electron-rich F atoms which protect the polymer skeleton from oxidation, the main polymer chain has a good chemical stability. However, the high cost, high vanadium ion permeability and unsatisfactory water transference hinder the further application of the Nafion-based membranes in large-scale commercial VRBs.

In order to promote the large-scale commercial application of VRBs, it was found that an IEM based on polytetrafluoroethylene grafted with polystyrene sulfonic acid (PTFE-g-PSSA) could be used [65]. At first, styrene is radiation-induced grafted onto polytetrafluoroethylene (PTFE) membranes by using γ -radiation from a ^{60}Co source at room temperature. Subsequently, sulphonation of the grafted PTFE-g-PS membrane is carried out and a series of IEMs based on PTFE-g-PSSA is prepared. From the observation of SEM, the grafting of styrene occurs not only at surface but also in the micropores of PTFE film. Due to the increase of exchangeable hydrophilic groups from more styrene grafted onto PTFE membrane, the IEC of the PTFE-g-PSSA membranes increases with degree of grafting (DOG), whereas the AR decreases. At the DOG of 25 %, a

Table 1 Structures and properties of some fluoride membranes.

Membranes	Structures	IC	VP	CE	VE	EE	CD
Nafion [62–64]	(generally, $x = 6-10$, $y = 1$, $m = 1$) Different x, y, m determine different Nafion membranes	–	7.95	91.7	92.3	84.7	60(N115)
PTFE- <i>g</i> -PSSA (12 % DOG) [65, 66]		58	0.685	87.9	82.6	72.6	40(N117)
		44	0.00192	94	–	–	80(N212)
		60	–	–	–	–	–
PTFE- <i>g</i> -PSSA- <i>co</i> -PMAc (6 % DOG) [66]		67	–	–	–	–	–
Nafion/PTFE ($N_{0.7}P_{0.3}$) [67]		68.5	0.15	93.3	91.2	85.1	50
ETFE- <i>g</i> -PDMAEMA AEM (40 % DOG) [68]		<N117	0.36	–	–	–	–
ETFE- <i>g</i> -PSSA [63]		24	0.039	–	–	–	–
ETFE- <i>g</i> -PSSA- DMAEMA (AIEM-II) [63]		48	0.0029	95.6	78.6	75.1	40

(Table 1 Continued)

Membranes	Structures	IC	VP	CE	VE	EE	CD
ETFE- <i>g</i> -(VBTA- <i>co</i> -HEMA) (92% DOG) [69]		–	0.49	89.2	78.3	69.8	30
PVDF- <i>g</i> -PSSA [46]		–	64	–	–	–	–
PVDF- <i>g</i> -PSSA-DMAEMA AIEM (26.1 % DOG) [55, 70]		46	1/10 of N117	–	–	>N117	–
PVDF- <i>g</i> -PMAOEDMAC- <i>co</i> -PAMSSA (40 % DOG) [71]		48 54	1.62 0.69	–	–	–	–

IC: ionic conductivity mS cm^{−1}, VP: vanadium permeability/ × 10^{−7} cm² min^{−1}, CE: current efficiency/%, VE: voltage efficiency/%, EE: energy efficiency/%, CD: current density/mA cm^{−2}, >: higher than, <: lower than, N: Nafion membrane.

PTFE-*g*-PSSA membrane excels Nafion membrane in IEC (2.1 meq g^{−1} vs. 0.9 meq g^{−1}) and AR (2.2 Ω vs. 2.5 Ω in the same condition).

PTFE-*g*-PSSA can be further modified by forming a copolymer of PTFE-*g*-PSSA-*co*-PMAc [66]. Comparing with PTFE-*g*-PSSA, PTFE-*g*-PSSA-*co*-PMAc membrane exhibits higher water uptake and IEC, and lower AR on account of the introduced maleic anhydride (MA_n) with good hydrophilicity and can incorporate more exchangeable groups into the membrane at the same DOG. In addition, PTFE-*g*-PSSA-*co*-PMAc with 6 % DOG displays better properties than the Nafion membrane in terms of IEC and AR.

PTFE can be used to modify Nafion by a solution casting method [67]. For the Nafion/PTFE blend membranes, the addition of hydrophobic PTFE reduces their water uptake, IEC and ionic conductivity but increases their crystallinity and thermal stability. Among the blended Nafion (r-Nafion) with PTFE at different

mass ratio ($N_{0.9}P_{0.1}$, $N_{0.7}P_{0.3}$ and $N_{0.5}P_{0.5}$), the $N_{0.7}P_{0.3}$ exhibits a good comprehensive performance which is superior to that of r-Nafion.

Partially fluorinated membranes

Considering the trade-off between cost and electrochemical performance, partial fluorinated IEMs such as poly(ethylene-co-tetrafluoroethylene) (ETFE)-based membranes and poly(vinylidene fluoride) (PVDF)-based ones are another choice. An ETFE-g-PDMAEMA AEM is fabricated by γ -radiation technique [68]. Comparing with the Nafion 117 membrane, at 40 % DOG, the AEM possesses higher IEC, lower AR and significantly lower permeability of vanadium ions (reduced from 1/20 to 1/40). As a result, VRB assembled with this AEM demonstrates better performance (above 1.3 V for more than 50 h) than that with Nafion 117 membrane. Its chemical stability is also better than that of other commercial membranes [75]. Another AEM is prepared by a two-step radiation-induced grafting technique [63]. Firstly, ETFE film is grafted with styrene (ETFE-g-PS), followed by a sulfonation treatment to achieve ETFE-g-PSSA. Later, ETFE-g-PSSA membrane is grafted with dimethylaminoethyl methacrylate (DMAEMA). Then the AEM is used to assemble VRB by using 1.5 M V(II)/V(III) and V(IV)/V(V) in 2.5 M H_2SO_4 solution as the electrolytes. During the charging and discharging cycles at a constant current density of 40 mA cm^{-2} , VRB with this AEM at 16.4 % DOG maintains the open circuit voltage (OCV) of above 1.3 V for more than 300 h, which is much better than that with Nafion 117. Another advantage of this AEM is its dramatically lower vanadium ion permeability (1/130–1/200 of that of Nafion 117) than that of CEMs due to the Donnan exclusion effect.

Considering that AEMs have lower vanadium ions permeability than CEMs, another ETFE-based material, namely ETFE-g-(VBTAC-co-HEMA) AEM, is prepared by radiation-induced graft copolymerization with 2-hydroxyl ethyl methacrylate (HEMA) and vinyl benzyl trimethyl ammonium chloride (VBTAC) onto an ETFE film [69]. The DOG of this membrane increases with the increase of the total irradiation dose and the VBTAC monomer concentration. It is possibly due to steric hindrance within the polymer, the IEC increases with an increase of DOG and the values are similar with that of Nafion 117 when the DOG is 40 % or more. The optimum IEC and water uptake are 0.80 meq g^{-1} and 19.01 %, respectively, at a 61.02 % DOG. Its vanadium ion permeability is lower than that of Nafion 117 (4.9×10^{-8} vs. 8.42×10^{-7} $cm^2 min^{-1}$) and its highest EE of the assembled VRB with 92 % DOG is 73.1 % at the current density of 20 mA cm^{-2} .

With excellent chemical stability, PVDF-based membranes are also widely investigated. In the case of a PVDF-g-PSSA membrane which is prepared via radiation grafting and sulfonating poly(vinylidene fluoride), both its crystallinity and crystallite size decrease after grafting [45]. A further decrease in crystallinity is observed after the sulfonation. Its proton conductivity can be comparable to those of Nafion membranes. PVDF-g-PSSA can be further treated by 0.07–0.11 mol L^{-1} KOH solution for 40–100 minutes. Free radicals can be detected by ESR in the PVDF-g-PSSA films after alkali treatment, and the DOG increases. As a result, the proton conductivity of this membrane increases for an order of magnitude above that of the untreated one to 64.0 mS cm^{-1} [46].

The structure of PVDF-g-PSSA-DMAEMA AIEM is shown in Table 1 [55]. Its properties are strongly dependent on its composition and DOG. Due to the Donnan exclusion effect between $-R_3NH^+$ groups of protonated DMAEMA unit and vanadium ions and the function of ion exchange for $-R_3NH^+$ groups, a higher content of DMAEMA leads to lower vanadium ion permeability and ionic conductivity, while higher DOG means higher sulfonation and protonation leading to higher water uptake, IEC and ionic conductivity. VRB assembled with this AIEM having a DOG of 26.1 % shows much longer time with OCV above 1.2 V than that with Nafion 117. Recently, it was reported that it could be prepared by a combination of radiation grafting technique and solution phase inversion method [70]. The obtained AIEM exhibits higher ionic conductivity than the other AIEMs based on grafted PVDF film. In addition, comparing with Nafion 117, lower vanadium ion permeability (1.62 vs. 7.73 $cm^2 min^{-1}$) and longer time at OCV above 1.3 V (14 vs. 30 h) are obtained when assembled and tested in a VRB system. It has been widely used that grafting of styrene (St) into base films to prepare IEMs. However, the PVDF-g-PSSA-DMAEMA AIEM shows poor chemical stability because the tertiary hydrogen (α -hydrogen)

of St is susceptible to chemical attack by the oxidative radicals. With the purpose of good chemical stability, an AIEM, PVDF-g-PMAOEDMAC-co-PAMSSA, is synthesized by radiation-induced grafting α -methyl styrene (AMS) and DMAEMA into PVDF films, followed by sulfonation and protonation processes. Compared with Nafion 117, at a DOG of about 40 %, the resulting AIEM exhibits similar ionic conductivity (54 vs. 58 mS cm^{-1}), higher IEC (1.2 vs. 0.97 mmol g^{-1}) and lower vanadium ion permeability (0.69×10^{-7} vs. $7.89 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$). Moreover, it exhibits much better chemical stability than the AIEM grafted with St and DMAEMA, and the OCV of VRB with this AIEM shows better performance than that with Nafion 117 (60 h vs. 14 h, OCV $> 1.4 \text{ V}$, 41.1 % DOG) [71].

Non-fluoride membranes

Inspired by PEMFC, non-fluoride materials are another hot direction for VRBs due to their low cost, high ionic selectivity and outstanding mechanical and chemical stability. Some membranes, such as poly(ether ether ketone) (PEEK), poly(phthalazinone ether ketone) (PPEK), poly(phthalazinone ether sulfone ketone) (PPES), poly(arylene ether sulfone) (PAES), poly(aryl ether ketone) (PAEK) and poly(fluorenyl ether ketone) (PFEK), also have a good heat-resistant and chemical resistance, and they can ensure the circulations of VRBs in the rigorous conditions. Some modification methods such as sulfonation and quaternization are commonly used, and some properties of several membranes are summarized in Table 2.

Aromatic ion exchange membranes

The preparation process of poly(aryl ether) ionic polymers is shown in Fig. 2 [79]. Based on this fundamental process, some modification can be carried out and quite some IEMs have been prepared.

SPEEK IEMs with various degree of sulfonation (DS) are prepared by direct aromatic nucleophilic substitution and polymerization, and are used for VRB [62]. The prepared SPEEK membranes show low vanadium ion permeability. For example, the vanadium ion permeability of SPEEK40 is one order of magnitude lower than that of Nafion 115. It is probably attributed to the less connected ionic cluster region in SPEEK membrane, which reduces the permeation rate of vanadium ions [62, 80]. VRB single cells with SPEEK membranes can run continuously more than 80 cycles at a current density of 60 mA cm^{-2} , and their VE ($> 84 \%$) and CE ($> 97 \%$) are much higher than those based on Nafion 115. In the meanwhile, their self-discharge rates are much slower and they show longer duration time above 1.2 V (80 h vs. 160 h). To increase proton conductivity, sulfonated poly(1,4-phenylene ether ether sulfone) (SPPEES) membranes are fabricated with 98 % sulfuric acid at different reaction time [76]. The hydrophilic domains formed by the hydrophilic sulfonic groups are well interconnected, and protons, water and vanadium ions can transport through. Therefore, the water uptake, IEC, proton conductivity and vanadium ion permeability increase with the DS.

Crosslinkable sulfonated poly(diallyl-bisphenol ether ether ketone) (SDPEEK) membranes with different DS can be used for VRB [81]. The SDPEEK membrane with DS of 80 % (SD4-6-100) presents excellent performance. Compared with Nafion 115, SD4-6-100 presents over an order of magnitude lower permeability of VO^{2+} ions (2.4×10^{-8} vs. $1.04 \times 10^{-6} \text{ cm}^2 \text{ min}^{-1}$), higher CE (98 vs. 92 % at 50 mA cm^{-2}) and long self-discharge time (180 h vs. 50 h) above 1.2 V for the assembled VRB.

Poly(phthalazinone ether ketone ketone) anion exchange membranes with pyridinium as anion exchange groups (PyPPEKK) are prepared by reacting chloromethylated poly(phthalazinone ether ketone ketone) membranes with pyridine in solution [42]. The PyPPEKK membranes show IEC values and water uptake in the range of 0.96 – 1.55 mmol g^{-1} and 10.2 – 16.5% , respectively, which are influenced by the concentration of pyridine and degree of chloromethylation. Comparing with Nafion 117, the PyPPEKK membrane shows much lower vanadium ion permeability, higher CE and EE (83.6 vs. 80.7 % at 80 mA cm^{-2}) for the assembled VRB.

Since AEMs present low vanadium ion permeability, a quaternary ammonium functionalized poly(fluorenyl ether) (QA-PFE) AEM is prepared [64]. The 100 % CE can be achieved at all the tested current

Table 2 Structures and properties of some non-fluoride membranes.

Membranes	Structures	IC	VP	CE	VE	EE	CD
SPEEK (73 % DOG) [62]		–	0.36	98.5	88.8	87.5	60
SPPEES [76]		124	24.95	–	–	–	–
SDPEEK (80 % DOG) [81]			0.24	97.8	89.9	87.9	50
PyPPEKK-4 [42]		7	<N117	99.5	–	83.6	80
QAPES1-40 [49]		–	0.09	98.8	89.3	88.3	60

(Table 2 Continued)

Membranes	Structures	IC	VP	CE	VE	EE	CD
QA-PFE [64]		20	0	100	<N212	<N212	80
QA-Radel-2.0 [16]		49	0.00174	>N212	>N212	>N212	80
PSF-TMA+ [78]		3.3 ± 0.1	26 ± 2	96	88	85	30

The meanings of IC, VP, CE, VE, EE and CD are the same as those in Table 1.

Fig. 2 Preparation process of poly(aryl ether) ionic polymer [79].

densities. At current densities lower than 60 mA cm^{-2} , the EE of this AEM-based VRB is higher than that with Nafion 212. With a similar method, quaternary ammonium functionalized Radel (QA-Radel) membranes with excellent properties are also reported [16]. A polysulfone-based AEM functionalized with quaternary benzyl trimethylammonium groups (PSF-TMA⁺) is proposed [78]. Its vanadium ion permeability is reduced for 40-fold when compared with Nafion 212. It remains chemically stable even after exposure to a 1.5 M V(V) solution for 90 days. In addition, it also exhibits excellent EE (85 %, at 30 mA cm^{-2}) after 75 cycles. This kind of work brings us a new direction to membranes for maintenance-free and long life time VRBs.

Other materials

In consideration of the fact that the stokes radius of vanadium ions is much larger than that of H_3O^+ and that the charge density of V(IV), V(II) and V(III) ions is much higher than that of proton, it is possible to separate vanadium ions and protons by using nanofiltration (NF) membranes instead of traditional IEMs [39], which was first proposed and successfully realized for VRBs based on tuning the vanadium/proton selectivity via pore size exclusion by H.M. Zhang's group [24]. A polyacrylonitrile (PAN) NF membrane is fabricated using a phase inversion method. The assembled single VRB cell exhibits comparable performance with that from commercial Nafion membranes. However, its cost is much lower, less than 1/20 of that of Nafion. The CE increases with the increase of current density, while H/V ions selectivity increases with the growth of pore size distribution. To improve the H/V ions selectivity of NF, PAN NF membranes added with silica are prepared [39]. The VRB single cell assemble with the modified NF membrane displays much better CE (89 vs. 98 %) and ion selectivity (almost 4-fold higher than that of the unmodified), while keeping a similar VE and a good ionic conductivity. Recently, NF membranes prepared by PES and PEG also show good properties [82]. The work on NF membranes suggested that NF membranes could be a good candidate as IEMs for VRBs.

Modified membranes

The previous research results show that most commercial membranes (Selemion CMV, CMS, AMV, DMV, ASS, DSV; Dow XUSI 3204.10 and K142) except for Flemion, Nafion 117 and Daramic microporous membranes presents low chemical stability, and most of the above discussed membranes show good ion selectivity except for Dow membranes. The reported membranes has good ionic conductivity, but they cannot prevent from large water transference [14]. In order to improve to the comprehensive properties of the membranes for VRBs, methods such as sulfonation and adulteration are used to increase ionic conductivity, pore filling, introducing positive ions, cross-linking and copolymerization are used to decrease vanadium ion permeability, and introducing benzene ring, cross-linking and copolymerization and adding inorganic fillers are applied to increase chemical stability.

Adding inorganic fillers

Adding inorganic fillers into membranes are widely used to decrease the vanadium ion permeability since the pores or polar clusters are filled by the fillers such as SiO_2 , TiO_2 , WO_3 and ZrP which are stable in the electrolytes. The chemical stability of these membranes is also improved.

An Nafion/ SiO_2 composite membrane is fabricated by a sol-gel method (Fig. 3a) [53]. The incorporated SiO_2 particles (9.2 wt %) are distributed in the hydrophilic channel network leading to smaller ion transport channel. Comparing with unmodified Nafion 117, the composite membrane possess a slightly decrease water uptake (26.0 vs. 21.5 wt %), similar IEC (0.97 vs. 0.96 mmol g^{-1}) and proton conductivity (58.7 vs. 56.2 mS cm^{-1}) and significantly decrease of all vanadium ions permeability (Fig. 3b). The time of open circuit voltage (OCV) stable above 1.2 V is doubled with Nafion/ SiO_2 composite membrane, indicating a slower self-discharge of the assembled VRB. The VRB single cell with the modified membrane owns higher CE and EE, especially at low current density ($<30 \text{ mA cm}^{-2}$). At the current density of 20 mA cm^{-2} the EE improves from 73.8 % (Nafion 117) to 79.9 % (Nafion/ SiO_2). The lower vanadium ions permeability of modified membrane is due to the added SiO_2 , which irreversibly binds to $-\text{HSO}_3^-$ groups along the side walls of channels in the Nafion membranes, hindering the interaction and movement of V^{4+} ions [56].

TiO_2 can be added into Nafion by a hydrothermal method to get a Nafion/ TiO_2 hybrid membrane [21]. Compared with Nafion, the AR and IEC are similar, and the water uptake of Nafion/ TiO_2 hybrid membrane decreases from 21.15 to 19.13 %. Since the polar clusters of Nafion membrane are partially filled by TiO_2 particles, the vanadium ion permeability decreases from 2.26×10^{-5} to $6.72 \times 10^{-6} \text{ cm}^2 \text{ min}^{-1}$, which leads to a lower self-discharge rate. Its VRB single cell presents a higher EE and CE (88.8 vs. 86.3 % and 71.5 vs. 69.7 % at 60 mA cm^{-2}).

WO_3 can be added into sulfonated SPPEK by a hydrothermal method to get a SPPEK/ WO_3 hybrid membrane for VRBs [83]. The hybrid membrane presents a higher AR than Nafion ($0.91 \Omega \text{ cm}^2$ vs. $0.87 \Omega \text{ cm}^2$), and higher ion selectivity ($5.81 \times 10^4 \text{ min S cm}^{-3}$ vs. $0.25 \times 10^4 \text{ min S cm}^{-3}$). The vanadium ion permeability of SPPEK/ WO_3 and SPPEK membranes are 3.97×10^{-7} and $2.77 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$, respectively. At the current density of 50 mA cm^{-2} , VRB with the hybrid membrane possesses higher CE and EE than that with Nafion (98.07 vs. 92.81 %, 78.60 vs. 76.19 %, respectively) and presents a lower self-discharge rate (218 h, $>0.8 \text{ V}$) together with a little higher discharge capacity.

Fig. 3 (a) Schematic depiction of the preparation of Nafion/ SiO_2 hybrid membrane, and (b) comparison of the vanadium ion permeability of the Nafion and Nafion/ SiO_2 membranes [53].

Sulfonation and quaternization

Sulfonation and quaternization can be used to obtain or enhance the IEC for the membranes. Since HSO_3^- are anions, the outcome of sulfonation for polymer membranes is the increase of anion-exchange capacitance. Sulfonation is the most frequently-used method for nonionic polymers, as mentioned above, such as PVDF-g-PSSA, ETFE-g-PSSA, SPEEK, SPEEK and SPFEK.

As mention in section 3.2, quaternized polymers such as QAPES, QA-PFE and QA-Radel achieve excellent performance in VRBs. The introduction of quaternary ammonium ion into the polymer skeleton makes cation-exchange capacitance. A quaternized poly(phthalazinone ether sulfone ketone) (QAPPESK) is prepared as follows. At first, a mixture of sulfone/ketone (S/K) in the molar ratio of 8:2 is dissolved into 98 % concentrated sulfuric acid. Subsequently, chloromethyl octyl ethers (CMOE) is used as a chloromethylated reagent to prepare chloromethylated PPESK (CMPPEK). Finally, trimethylamine solution is used to quaternize CMPPEK to get QAPPESK with quaternary ammonium groups. Compared with Nafion 117, VRB cell from QAPPESK presents better electrochemical performance (CE: 96.4 %, VE: 91.6%, EE:88.3 %) [84].

Cross-linking and copolymerization

Cross-linking and copolymerization are mostly used to enhance the IEC, ion selectivity and chemical stability of membranes. Together with cross-linker, organic agents are added to films or membranes to reduce the size of pores or functionalize them. Functional copolymers obtained by modification of existing polymers using radiation induced or chemical graft copolymerization are attractive materials for the membranes [85, 86].

In order to reduce the vanadium ions permeability of membrane while keeping its chemical stability, a sulfonated poly(ether ether ketone) (SPEEK)/polypropylene (PP)/perfluorosulfonic acid (PFSA) sandwich-type composite membrane (S/P/P membrane) is proposed for VRBs [54]. The PFSA layer serves as a shield preventing the composite membrane from oxidation degradation by VO^{2+} ions in the positive electrolyte. Comparing with Nafion 112, S/P/P membrane shows much lower vanadium ions permeability (Fig. 4a) but slightly higher AR, accompanying with higher CE and EE but lower VE for the assembled VRB (Fig. 4b).

A hydrocarbon blend membrane consisting of SPEEK and polysulfone-2-amide-benzimidazole (PSf-ABIm) (SPEEK/PSf-ABIm) can block the crossover of VO^{2+} ions due to the introduction of 2-amidebenzimidazole groups into the ionic domains of SPEEK. Consequently, the vanadium ion (VO^{2+}) permeability of the SPEEK/PSf-ABIm membrane is about 50 times lower than that of Nafion 117, and 4 times lower than that of

Fig. 4 (a) Vanadium ion concentration in the right reservoir of a VRB single cell with a Nafion 212 membrane and an S/P/P membrane, respectively, and (b) comparison of EE for the VRBs assembled with Nafion 212 and S/P/P membranes [54].

the plain SPEEK [87]. In addition, its other properties such as IEC, water uptake and mechanical performance are also good. A similar blend membrane, sulfonated poly(ether sulfone) (SPES) with SPEEK (SPES/SPEEK membrane), is also reported [88]. This blend membrane is prepared through dissolving PEEK and SPES in 98 % H_2SO_4 with a followed drying process. As the water uptake and the swelling behavior of membrane is dependent on the phase morphology and number of sulfonic acid groups in the membrane while the IEC is dependent on the density of sulfonic acid groups in the membrane matrix, the water uptake (21.6 %) and swelling behavior (in plane direction, $\Delta l = 8.3$ %; in thickness direction, $\Delta d = 18.2$ %) of SPES/SPEEK membrane indicate significantly strong mechanical strength, and low permeability of VO^{2+} ion [88]. The time of OCV above 0.85 V of VRB with SPES/SPEEK membrane is 24 h longer than that with Nafion 212 (60 vs. 36 h), which is tested at 75 % SOC. Higher CE (98 %) and EE (84 %) are achieved at 50 mA cm^{-2} , and there is no significant decline up to 100 cycles. With good properties and low cost, SPES/SPEEK membrane shows promising prospects for application in VRBs [88].

In order to improve the chemical and mechanical stability of SPEEK, a PTFE reinforced SPEEK (SPEEK/PTFE) composite membrane is prepared [77]. Results show that SPEEK/PTFE composite membrane has lower water uptake and swelling ratio, higher elongation ratio and better mechanical stability (stable cycles: 700 vs. 27) than SPEEK membrane since the porous PTFE has strong hydrophilicity and chemical stability. Lower water uptake and swelling ratio lead to an improved ion selectivity of membranes. Compared with the pristine SPEEK, VRB assembled with the composite membrane presents longer retention time (27 vs. 14 h) at OCV above 1.3 V. It indicates that SPEEK/PTFE composite membrane has lower vanadium ion permeability than the SPEEK one. In addition, VRB from PEEK/PTFE composite membrane shows higher VE (89.6 ± 1 % vs. 86.7 ± 1 %) and EE (86.7 ± 1 % vs. 82 ± 1 %) compared with that from Nafion 115 [76].

Summary and outlook

As the renewable energy has become such popular subject, VRBs become more and more important as large-scale energy storage system which is going to get further development. As a core component for VRBs, though a lot of efforts have been made, IEM is still the main factor which limits its commercial applications in large-scale. Nafion membranes are still the most widely used IEMs. Though some IEMs with better properties than Nafion have been synthesized, they still present some shortcomings and are still far from large-scale commercial applications. Considering the cost and comprehensive properties, there are several future directions to be done:

1. Partially fluorinated and nonfluoride IEMs with good chemical stability should replace perfluorinated membranes;
2. Nanofiltration membranes deserve attraction to the medication of their chemical stability;
3. Easy and green preparation methods of good IEMs should be explored since in most cases sulfonation is needed.

Acknowledgment: Financial support from NSFC (21374021) and STCSM (12JC1401200) is greatly appreciated.

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