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Recent Development of Membrane for Vanadium Redox Flow Battery Applications: a Review

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Abstract

Responding to rapid growth of the renewable energy applications, it is crucial to develop low cost and high efficient large-scale energy storage systems in order to smooth out the intermittency of the renewable energy resources. As one of the most promising large-scale energy storage systems, vanadium redox flow battery (VRFB) has attracted great attention in recent times. Membrane is one of the key components of VRFB which not only affects the whole cyclability performance but also determines the economic viability of the system. The membrane separates the positive and negative half-cells and prevents the cross-mixing of vanadium ions while providing required ionic

conductivity. The ideal membrane should have good ionic exchange capacity; high ionic conductivity, low water uptake, swelling ratio, area electrical resistance and vanadium and other poly-halide ions permeability; and good chemical stability, as well as low cost. Numerous efforts have been spent on the development of different types of membranes, including different functional groups ion exchange membrane and non-ionic porous membrane. This paper reviews the research on membranes in VRFB system, including the properties, development of traditional commercial membranes as well as recently developed membranes. It explores various methods of fabrication of the membrane products which have received relatively little attention. A detailed summary table of the new membranes with their properties, fabrication and costs is provided to serve as a reference guide for researchers and industrialists interested in VRFB system building and dynamic modelling set. Subsequently, the challenges and future directions of membrane research are examined.

Keywords: vanadium redox flow batteries, membrane, properties.

Nomenclature

1. Introduction

1.1 Introduction of vanadium redox flow battery

With the development of technology and increasing of population, the global energy consumption will increase to 53 billion kWh in 2020 [1]. To meet the substantial daily needs of electrical power usage without environmental degradation caused by depletable fossil fuels, renewable energy and smart grids have become topics of current research interests [2]. A key point of this is to develop a large scale energy storage system which can smooth out intermittent renewable energy sources induced by the environmental uncertainty [3], to deal with the problems of peak-shaving, emergency back-up and so on [4], and incorporate an effective demand-side management (DSM).

Among the traditional large-scale storage systems, electro-chemical energy storage system,

especially the secondary redox flow battery has attracted the most attention nowadays [5]. The lithium-ions battery, which is a commonly used commercial battery product, has long life cycles and high energy density. But the cost of the battery material-lithium is much higher than the vanadium since the later one is abundant in nature [1]. The lead-acid battery is another commercial batteries with low cost and it is a good candidate to large-scale storage system [6]. But the lifecycles and energy density of traditional lead-acid batteries are much lower than lithium battery system, and the environmental damage it causes especially to water resources is also a big problem.

The Ragone plot in Fig. 1 [7] shows the power vs energy density profiles of different energy storage systems, including the different batteries and the VRFB, which supports the viability of the VRFB batteries.

Thus, vanadium redox flow battery (VRFB) with large availability, high energy efficiency, low capital cost, long life cycle [8, 9] and low-toxicity is currently one of the most competitive electro-chemical secondary battery storage systems. Till date, VRFB already has been tested in Germany (0.3 MW/1.3 MW h), Italy (0.45 MW/1.44 MW h) and the USA (2 MW/8 MW h) [10]. It is widely believed that the VRFB has the potential to cooperate with other systems such as renewables integration including photovoltaic (PV) systems [11] and wind power [12] in ramping up electric supply capacity [5] in the future.

Though research into VRFB started in the mid-1980s [13] at the University of New South Wales by Skyllas-Kazacos research group, however, this Generation 1(G1) VRFB was only significantly promoted throughout the early 2000s [14]. The chemical reactions of the G1 VRFB are based on the following equations:

At the positive electrode:

At the negative electrode:

88

89 Although G1 VRFB reduces the problem of electrolyte cross-contamination, its application is
 90 limited by its low specific energy (15-25 Wh·kg⁻¹) and narrow working temperature range
 91 (10°C-40°C) [15, 16]. Further research on exploring the alternative solution to improve the
 92 solubility of the vanadium ions were carried out and led to the second generation 2 (G2 V/Br). G2
 93 uses a mixture of vanadium chloride and vanadium bromide as the electrolyte [17]. The reactions
 94 of the G2 V/Br are based on the following formulation:

95

96 The positive electrode:

98 The negative electrode:

100 Where open-circuit voltage at 50% state of charge = 1.1-1.2 V [18]

101

102 The specific energy of G2 is higher than G1 at 25-50 Wh·kg⁻¹ due to the higher solubility of
 103 vanadium bromide [14] than vanadium sulphate, as well as wider temperature range(0-50°C) [19,
 104 20]. However, the G2 V/Br still faces high-cost issue because of the need to use expensive
 105 bromine complexing agents to prevent potential release of bromine gas.

106

107 Recently, researchers from Pacific Northwest National Laboratory (PNNL) in the US offered an
 108 improved VRFB system (G3) with mixed H₂SO₄/HCl electrolyte solutions in both half-cells to
 109 improve the stability and the solubility over a wider range of temperature. Comparing with the G1,
 110 G3 has higher stack efficiency, wider range of operating temperature which means simple system
 111 design and operation with low capital cost caused by temperature control [21]. Also, the high
 112 energy efficiency could be achieved without thermal precipitation. Comparing with the G1, G3
 113 has faster reaction kinetics, there is no chlorine gas evolution during charging, up to 1.5V in G3.

114

115 1.2 The introduction of membranes used in the VRFB

Typically, a redox flow battery has two soluble redox couples in solutions to achieve the oxidation and reduction reactions. VRFB stores energy in two vanadium solutions contained in two different electrolyte tanks, and exchanges ions through the membranes in the reaction cell by pumping the solutions from the tanks [22]. This structure shown in Fig.2 implies that the VRFB can increase the battery capacity by adding more solutions in a larger tank and it can increase the power output by adding more reaction cells. The all-vanadium redox flow battery developed at the University of New South Wales shows a high energy efficiency (over 80%) [13] because it uses the same vanadium element in both half-cells, and thus avoids the problem of cross-contamination which occurs in other battery types having different electrolyte elements in both half-cells.

The membranes used in VRFB can be classified into ion exchange membranes and the non-ionic porous membranes. The ion exchange membranes include the cation membrane, anion membrane, and amphoteric ion exchange membrane, depending on the type of ionic functional groups attached to the membrane. The ideal membrane should have good ionic exchange capacity, high ionic conductivity, low water uptake, low swelling ratio, low area electrical resistance and low vanadium and other polyhalide ions permeability, good chemical and thermal stability, as well as low cost. In order to find suitable membranes, different technologies and materials are developed in recent years. In this paper, recent research works focussing on the development of other low cost and high-performance membranes are summarized.

1.3 Contribution of this study

- 1, It conducts a complete and critical review of the membrane used in the VRFB system, especially with respect to the fabrication of the membrane which is still almost unexplored.
- 2, It summarizes recent research results of the membrane developed in VRFB systems. A summary table is provided of new membranes with the vanadium ions permeability, conductivity, the energy efficiency and the working current density, the technologies, the stability and the cost, to serve as a reference guide for researchers and industrialists interested in VRFB system building and dynamic modelling set.

3, The feature of four different types of membrane as well as future research trend are concluded.

1.4 Organization of the paper

The key point of this paper is divided into three parts, including how to measure the properties of membrane, how to fabricate them and the detailed comparison of four different types of membrane which include CEM, AEM, AIEM and porous membrane. In the first part, section 2, 12 different experimental measurement methods of membranes' main properties are summarized. Then, in section 3, the manufacturing methods of different types of membrane are studied, as well as four typical membrane preparation methods introduced step by step. Finally, in section 4, these four different types of membrane are studied. They are analyzed in general at the beginning, including the advantages and disadvantages. After that, different membranes, especially the recently published ones are introduced with respect to their shortages and the penalties that accompany their improvements. The working condition and performance with their reasons are stated. Some membranes used in the same material, but different structure or manufacturing methods are compared. At the end of each main types studied, the main method to mitigate the problems of this kind of membrane are summarized, as well as the main shortage after development when compared with the commercial membrane Nafion. Moreover, at the end of section 4, it is concluded with a summary table of recent development and future research trends.

2. Measurements of membrane performance

Experiments are usually conducted to assess the membrane performance and properties. These experiments are described in the following sections.

2.1 Cell performance

The performance of membrane is usually assessed through charge discharge test in a VRFB cell.

Based on the measured single cell's charge-discharge behaviour, the coulombic efficiency (*CE*), the energy efficiency (*EE*) and the voltage efficiency (*VE*) which are the main parameters of the

VRFB systems can be determined according to the following equations, respectively [23]:

$$CE = \frac{\int I_d dt}{\int I_c dt} \times 100\% = \frac{\sum_{j=0}^{m-1} \frac{1}{2} (I_j + I_{j+1}) (t_{j+1} - t_j)}{\sum_{k=0}^{n-1} \frac{1}{2} (I_k + I_{k+1}) (t_{k+1} - t_k)} \times 100\%, \quad (5)$$

$$VE = \frac{\sum_{j=0}^{m-1} \frac{1}{2} (V_j + V_{j+1}) (t_{j+1} - t_j)}{\sum_{k=0}^{n-1} \frac{1}{2} (V_k + V_{k+1}) (t_{k+1} - t_k)} \times 100\% \quad (6)$$

$$EE = CE \times VE = \frac{\int V_d I_d dt}{\int V_c I_c dt} \times 100\% \quad (7)$$

where I_c, V_c, I_k, V_k, t_k denote the current, the voltage and the reaction time during the charge, while I_d, V_d, I_j, V_j, t_j denote the current, the voltage and the reaction time during the discharge respectively.

2.2 Membrane properties

2.2.1 Ion exchange capacity (IEC)

Ion exchange capacity can be calculated by a back-titration method [24, 25]. Firstly, the membrane is immersed in 30 ml HCl (0.01M) for 18 hours, and then the resulting solution is titrated with NaOH (0.01 M). After that, the membrane is rinsed with 18.2 MΩ cm water, dried in a vacuum desiccator for 24 hours, and weighed. The amount of H⁺ and OH⁻ can be calculated from titration, and the ion exchange capacity is calculated by the following Eq. (8):

$$IEC = \frac{C_{HCl} V_{HCl} - C_{NaOH} V_{NaOH}}{m_{dry}} \quad (8)$$

Where C is concentration, V is volume, and m is the mass of the dried membrane following titration.

2.2.2 Water uptake (WU), swelling ratio (SR) and water transport.

Water uptake refers to the ratio of absorbed water weight to the dry membrane weight, while the swelling ratio means the ratio of length change from dry to wet membrane [26]. The membranes are soaked in de-ionised (DI) water for 24 hours at the room temperature firstly, then the membranes are dried under vacuum at 80°C for 24 hours. After that, the WU and SR can be calculated using Eq. (9) and Eq. (10):

$$WU = \frac{W_w - W_d}{W_d} \times 100\%, \quad (9)$$

$$SR = \frac{L_w - L_d}{L_d} \times 100\% \quad (10)$$

Where W_w , W_d are the weight of membranes after and before absorption respectively, while L_w , L_d are the length of the wet and dry membrane respectively [27].

The diffusion coefficient and release time of water in the membrane can be measured by the water transport parameters [28]. To test the static water transfer across the membrane, a typical experiment was designed by the Mohammadi *et al.* [29]. In the experiment, each half cell was simulated at the 50% state of charge (SOC), the solutions of half cells are used as followed:

A tube is connected to each cell as shown in Fig. 3, and the electrolytes are delivered through the tubes. As the initial solutions in each half cell are at the same level; therefore, the volume change reflects the water transport of the membranes after certain duration.

2.2.3 Area resistance (R) and proton conductivity (σ)

The area resistance and proton conductivity are tested by the method designed by H. Vafiadis *et al.* [17]. The resistances of the cell with or without the membrane are recorded to estimate the resistance of membrane according to Eq. (13) [30]:

$$R = (r_1 - r_2) \times A \quad (13)$$

Where R denotes the area resistance of the membrane tested, r_1 and r_2 denote the resistance of the cell with and without the membrane, and A denotes the area of the membrane. The membrane thickness is neglected in this calculation.

The proton conductivity experiment was carried out by Chen *et al.* [31]. Because the membranes are tested in DI water, the proton conductivity $\sigma_{//}$ of the membrane can be neglected. The overall proton conductivity can be calculated by Eq. (14):

$$\sigma = \sigma_{\perp} = \frac{l}{Ar} \quad (14)$$

Where l denotes the thickness of the membrane, A denotes the area of the electrode area, and r is the resistance value measured. The conductivity of the membrane increases roughly linearly with increasing water content [28].

2.2.4 VO²⁺ permeability (P_0) and ion selectivity (S)

The concentration of ions can be calculated through the absorbance of the solution by the UV-Visible spectroscopy [32] according to Beer's Law. Skyllas-Kazacos and co-workers set a standard permeability test [33]. In this experiment, two cells (A and B) are set and divided by a membrane. Initially, cell A contains 1 M VOSO₄ and 2 M H₂SO₄ solution, while the cell B contains 1 M MgSO₄ and 2 M H₂SO₄. MgSO₄ in the cell B are used to balance the osmotic pressure between the two solutions and to decrease the effect of water transport across the membrane. The diffusive permeability P_0 can then be calculated by Eq. (15):

$$P_0 = -\frac{V_B l}{2At} \ln \frac{A_0 - 0}{(A_0 - B) - B} = -\frac{V_B l}{2At} \ln \frac{A_0}{A_0 - 2B} = -\frac{V_B l}{2At} \ln \frac{1}{1 - 2x_B} \quad (15)$$

Where V_B is the volume of each cell, l is the thickness of the membrane, t is the time of reaction, A_0 is the initial absorbance of solution A, B is the absorbance of solution B, and x_B is the

concentration of crossover species in B side normalized by the initial concentration in cell A.

Ao Tang reported that the unbalanced diffusion of different values of vanadium would cause an accumulation of the vanadium ions, which then led to a slow loss of capacity. However, this problem can be restored by remixing the solutions in two tanks periodically[34]. The capacity loss was also studied by Skyllas-Kazacos [35].

Ion selectivity S can be calculated once the proton conduction value is known by Eq. (16) [36]:

$$S = \frac{\sigma}{P_0} \quad (16)$$

Where σ denotes the conductivity.

2.3 Chemical stability

Because the membrane used in VRFB system is immersed in the highly oxidising electrolyte, chemical stability is a major limiting factor of membrane lifetime. Long-term chemical stability can be evaluated using three different approaches [37].

In the first approach, a pre-weighted sample (0.30 g) is soaked in a 25.0 ml solution containing 0.1 M V(V) ions. The oxidation of membrane by yellow V(V) ions leads to the formation of blue V(IV) ions. The concentration of the vanadium ions can be measured using the ultraviolet absorption spectrometry and calculated based on Beer's Law. In this case, the concentration of V(IV) ions is estimated at wavelength of 765.5nm which is the maximum absorbance of V(IV) ions [38]. The concentration of the solution is monitored periodically to determine the rate of oxidation. To standardize the method for comparison study, the experiment is repeated at a constant area (10.5 cm × 5.0 cm), and different ratios of solutions are prepared with mixtures of 0.1 M V (IV) and 0.1 M V (V) solutions.

In the second approach, the membranes are exposed to 2.0 M V(V) solution of the VRFB, and then the cell performances, area resistance, vanadium permeability and IEC values are measured

periodically.

The last technique is to test the membranes under continuous charge-discharge cycling, and the cell performances are evaluated to indicate any changes of the membrane caused by fouling (by monitoring area resistance) or degradation.

3. Fabrication methods of different membranes used in VRFB system

Although there are several existing review papers which summarized the membranes in the battery system, very few of these focused on the details of membrane manufacturing methods, which is an inevitable process in the research of membrane study. In other words, fabrication of the membrane products has received relatively little attention. The fabrication methods not only impact the microstructure of the membrane as well as the structure of loading additions but also influence the cost of the membrane products. In this section, first, the classification of membranes including their operating principles are introduced. Then, the general preparation of these different types of membranes are studied. After that, the typical membrane preparation methods are introduced. Finally, the environmental impacts of the membrane preparations are summarized.

3.1 Approach to classify membrane

According to the bulk structures [39], materials [40] and applications, VRFB membranes used can be classified into ion exchange membrane and non-ionic porous membrane. For the ion exchange membrane, the H^+ or OH^- are exchanged by the functional ion groups, while the non-ionic porous membrane prevents big ions to migrate across the membrane by physical barrier. And the information on membrane classification is shown as *Table 1*.

Ion exchange membranes are made of cross-linked linear polymer chains in a three-dimensional network where the functional groups are attached to enable the exchange of ions. The ions which are attached to the membrane can move inside and out of the membrane [41]. Hence, the rate of ions transport depends on the strength of the bond, as well as the density of electrolytes. Based on

ionic functional groups attached to the membrane, ion exchange membrane can be classified into five types of membranes: cation exchange membrane (CEM), anion exchange membrane (AEM), amphoteric ion exchange membrane (AIEM), bipolar ion exchange membrane and mosaic ion exchange membrane [42].

Cation exchange membrane (CEM) contains negatively charged groups, like sulfonyl (-SO₃H), carboxyl (-COOH), phenol group and other acidic functional groups which can ionize H⁺ to exchange the positive ions in the solution. In contrast, anion exchange membrane (AEM) contains positively charged groups, like quaternary amine (-NRH₃) and other basic groups which can ionize OH⁻ to exchange the negative ions.

Amphoteric ion exchange membrane (AIEM) has both anion and cation exchange groups randomly throughout the membrane. Fig.4 shows the ion exchange process of an anion particle. Bipolar ion exchange membrane has both cation exchange membrane layer and anion exchange membrane layer (bi-layer membrane) while mosaic ion exchange membrane has both two exchange groups over the cross-sections of the membrane [43]. These three membranes all contain two different ion groups, but the existing forms are different. For the applications in the VRFB, the AIEM with less cost is the best option in three.

The reaction of anion exchange membrane is shown in Eq. (17) [44]:

The ion exchange process of CEM is depicted in Fig. 5.

For the porous membrane, without functional ion exchange groups, microporous separator selects electrolyte through physical barriers. The size difference between vanadium ions and protons makes it possible to use pore size exclusion to separate the electrolyte. Generally, the microporous membrane is made from a variety of inorganic, organic or natural materials, and contains pores or holes with diameters greater than 50-100Å [45]. Comparing with ion exchange membrane, the porous membrane can achieve high chemical stability due to the physical exchange method and

material selection [46]. Besides, the porous membranes are highly conductive in strong acid electrolyte environment of VRFB systems because it can absorb sulfuric acid which comes from the electrolyte and becomes conductive for protons [47]. In addition to the low cost, it is a promising membrane used in the battery, as well as additional layer to enhance the properties of other membranes [48].

3.2 General preparation of the membranes

Besides the chemical nature of the polymer matrix and the functionality bound of the material, the production method is another factor that determines the properties of the membrane. It is important to note that preparation method can affect the morphology of the membrane, which then will impact the ions transport properties and swelling behaviour of the membrane.

Basically, three essential criteria are required for an ion exchange membrane preparation [42], namely:

- 1) It has to be a membrane to select ions;
- 2) It is insoluble in solvents;
- 3) It has constant charges in the membrane.

Ion exchange membranes can be divided into heterogeneous membranes and homogeneous membranes based on their microstructures. For heterogeneous ion exchange membranes preparation, generally, powdered exchange resins are blended and heated with a thermoplastic polymer homogeneously at the beginning, and then the polymer blend is formed into the membrane by pressing and/or heating [49].

For homogeneous ion exchange membranes preparation, the approaches can be categorised into three types according to their starting materials [50, 51]. The starting materials include:

- Monomer which contains ion exchange groups. This monomer can be copolymerized with

the non-functionalized monomer to form an ion exchange membrane.

- The polymer films. The film can be modified by introducing ionic characters either directly by grafting a functional monomer or indirectly by grafting non-functional monomer followed by functionalization reaction.
- Polymer particles. The particles can be modified by introducing anionic or cationic moieties, and then embedded in a polymer binder and processed to make a foil (membrane).

For type 1 preparation, styrene and divinylbenzene are the commonly used neutral starting materials [41]. Basic strong AEM [52] are prepared by two steps, chloromethylation and quaternary ammonium attachment; while the CEM [53] are prepared by sulfonation. These methods to prepare the homogeneous ion exchange membrane have been reported by many research groups. [54, 55].

For type 2 and type 3 preparation, generally, the polymers are insoluble to any solvent. In such route, cation character is defined by carboxylic acid (weakly acidic) and sulfonic acid (strongly acidic). The former can be prepared by grafting acrylic monomer or epoxy acrylate monomers. For AEM preparation, the membranes can be made from analogous polymer films, which can be prepared by grafting or copolymerization of vinyl monomers [56, 57]. There are three main methods to produce the homogeneous ion exchange membrane (beside condensation) if the membrane is prepared by vinyl monomers polymerization. And the detail processes are described by Sata *et al.* in ‘Ion Exchange Membranes’ [42].

For soluble solvents such as PEK-C, PEK, PS, PES or their copolymers, the preparation process of the membrane which can be transposed is as follows [58-60]:

- Introduce the moieties, including anionic or cationic ones;
- Dissolve polymer and cast it into a film.

However, since the polymers are soluble, the chemical stability often needs post-treatment, which includes crosslinking with diamine for AEM preparation [61].

For the non-ionic porous membrane, the main material is semi-crystalline polyolefin materials, include polybenzimidazole (PBI) [62] and polypropylene (PP). There are two types of fabrication of microporous membranes, including dry process and wet process. The detailed processes are described by Zhang *et al.* [63]. Also, the pore diameter of the film can be controlled through phase-separation method [64].

3.3 Typical preparation method

3.3.1 Radiation grafting method

Radiation grafting method is a traditional technique which is well-known for polymer surface modification since 1962 [65]. This method offers a good way to change the physical and chemical properties of the polymers. [66]

By using an ionizing radiation source such as Co, γ -rays, and electron-beams [67] to induce ionic chemical groups or free radicals on the polymers, a polymer main chain can be initiated from another monomer's polymerization [41]. That means it can combine two highly incompatible polymers into one material with both characteristics. Here, composition and properties of the membrane can be controlled by proper selection of the degree of grafting. Besides, grafting started with a film in membrane form that can overcome the sharpening problem [49]. Therefore, this method has been proposed as a valid option to prepare a variety of ion-conducting polymeric membranes [68]. However, the radiation grafting like UV-induced grafting and plasma grafting methods need reactors for irradiation, thus incurring high energy cost [69].

3.3.2 Casting method (solvent cast process)

Continuous solution casting process is a well-established plastic film manufacturing process which has been developed more than hundred years ago.

The production process is shown in *Fig. 6*. Once the first layer solidifies, the secondary film can [70-72] be added to the product through the same process with different mixture solution. It implies several layers can be encapsulated after multiple casting steps.

The advantages of this method include uniform thickness distribution, excellent flatness and dimensional stability [73]. Also, it can offer the ability to alter the membranes' properties, such as lubricity and strength based on individual layers [74, 75]. It can even transform a membrane from a symmetrical structure to an asymmetrical structure, so that it can increase selectivity without increasing hydrodynamic resistance [76]. Moreover, it allows other components to be incorporated into the structures. For examples, after forming a bare membrane, polymers such as PPEK, PPES or PPESK can be chloromethylated with a catalytic agent to produce the sites for quaternary ammonium groups. Another notable advantage is that it has lower manufacturing cost than conventional technologies due to the use of inexpensive materials and adaptability of the manufacturing line, such as injection mold components and extruded tubes made of high-performance polymers like PTFE, PEBAX, and polyimide [77, 78].

However, the shortcoming is that it might lead the coated surface layer to be swept away due to weak interaction between the membrane and coated layer [79].

3.3.3 Sol-gel method

The interest in sol-gel processing can be traced back to the mid-1800s and to date, over 35,000 papers have been published worldwide based on this method [80, 81].

As shown in *Fig.7*, various structures can be built because the sol-gel method is not a single process. Generally, the sol gel process can be described in the following steps [82-85]:

- **Mixing:** After hydrolysis and polymerisation, the desired metal alkoxides ($M(OR)_n$, where M is the metal and R is an alkyl radical), disperse in a liquid to form a sol.

- **Gelation/Crosslinking:** The deposition of solution products will generate different forms due to various processes as shown in the *Fig. 7* including coatings on the substrates to be xerogel film or the polycondensation which produces colloidal particles linked together to become a 3-D network;
- **Aging/drying:** The particles in solution are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network.
- **Heating:** The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating.

One of the distinct advantages of using this methodology is that it could form a high-temperature ceramic from a liquid at room temperature. This methodology can be used to deal with no heat application like the metal organic precursor. Also, it can precisely control over purity, as well as yield the highest specific surface area, including very thin film metal oxides [86]. But this method lacks universality since unique polymers are needed [69].

3.3.4 Layer-by-layer self-assembly method

As the name implies, layer-by-layer self-assembly method means a disordered system which forms an organized structure or pattern layer by layer spontaneously instead of external direction, as shown in *Fig. 8*. It is an eye-catching procedure for the formation of multilayer thin film by controlling architecture and composition [87].

Fig. 8 shows that the procedure includes alternating consecutive immersion (dipping) of a solid or flexible substrate in oppositely charged solutions. It is necessary to induce intervening rinsing step between each layer forming to remove the weakly attached molecules [79].

Many types of the assembly method have been developed, such as dip-coating, spin-coating, spraying, electromagnetic assembly and fluidic assembly [88, 89]. The detailed information is shown in *Fig. 9*.

The merits of the layer-by-layer self-assembly technique include:

- Better nanoscale organization and a higher degree of structure control. It accurately organizes the film thickness at the nanometer scale [90];
- Highly tuneable with parameters such as pH and ionic strength [91];
- Film properties improvement by changing the electrolyte types [79].

This method can alleviate the decrease of water flux and the increase of the hydraulic resistance [92], while some reports show that other grafting method might also reduce the water flux [69].

3.4 Environmental impacts

As widely accepted, the applications of the membrane are sustainable. However, for large-scale membrane fabrication, there are still potential environmental impacts since most of the membrane's preparations requires toxic solvent [93]. For example, the pristine Nafion membrane is generally prepared by the casting method containing DMF and DMAc mixtures [94], which are common solvents for membrane production. These two solvents are health hazards. The fabrication also contains processes that involve cleanings with corrosive inorganic solutions, such as H₂SO₄. Besides, almost all additional polymers already mentioned are petroleum derivatives, including PEEK, PTFE, and PPEK. Thus, to decrease the environmental impact, biopolymers and eco-friendly solvents are required for inclusion in future research.

4. Characteristics of membranes

4.1 Cation exchange membrane (CEM)

4.1.1 Nafion

The chemical structure of Nafion is shown in *Fig. 10*. It combines a hydrophobic Teflon-like backbone with hydrophilic ionic side groups [95].

Among the perfluorinated sulfonic acid cation exchange membranes (CEM), Nafion is still among the best available and commonly used membrane in VRFB due to its remarkable properties including:

- High water swelling ratio and proton conductivity [96]. Because of the sulfonic acid group ($\text{-SO}_3\text{H}$) added into the polymer backbone, when materials are exposed to water, the hydrolyzed form ($\text{-SO}_3^-\text{H}_3\text{O}^+$) appears and makes proton transport across the materials [97].
- Excellent electro-chemical properties [98].
- High mechanical strength and chemical stability [98]. It shows low release rate of degradation and high resistance to chemical attacks [97].
- High thermal stability and operation temperature range (up to 190°C) [97, 99].

However, it still has shortcomings, which limit its practical application in VRFB system, including:

- High cost [100]. At present, the price of Nafion ranges from $\$500$ to $\$1000\cdot\text{m}^{-2}$, though this cost is forecasted to be lower at $\$200\cdot\text{m}^{-2}$ in the future according to detailed economy analysis by Minke *et al.* [101].
- Fast crossover of vanadium ions and low ion selectivity [32]. It will lead to the decrease of *EE* and capacity loss in VRFB system quickly [95, 97, 99]. Also, with the increasing current density on the polarization curves, it will drop the cell voltage [102].
- High Ohmic loss at high current density, and proton conductance deterioration at low humidity or high temperature [74].

Although other membranes with lower cost and better cell performances have been developed, it is still difficult for these membranes to be used widely due to their poor chemical stability. As a result, Nafion membranes are still currently applied in most large-scale VRFB system [103].

4.1.1.1 Typical commercial Nafion

Nafion is a commercial product of DuPont [104]. The typical commercial extruded Nafion series include N115, N117, and N112 as well as N1135 and N1100, while the dispersion-cast ones are coded as NR211 and NR 212. The thickness of commercial Nafion ranges from 25 μ m (NR211) to 183 μ m (N117). The minimum membrane thickness value of 25 μ m is set because if the thickness of the membrane is below 25 μ m, the mixing of the hydrogen and air (or oxygen) reactant gases would result in an efficiency loss [105]. Some fundamental parameters of Nafion are listed in Table 2 [103, 106]:

Many literatures have compared the performance of these traditional Nafion membranes in VRFB application. Jiang *et al.* and Slade *et al.* compared N112, N1135, N115 and N117 [103, 105], Peron *et al.* compared N1110, N117, N115, NR212 and NR211, Reed *et al.* compared N115, NR212 and NR211 [107], Kraytsberg *et al.* compared N112, N115, N117 and N1110 [97], Teng *et al.* and Jeong *et al.* compared NR212 and N117 [100, 108]. Because of the similar chemical structure, the properties of Nafion membranes can be determined by the thickness and other operational factors such as current density, operating temperature, and state of charge. Based on these papers, the performance of the Nafion membranes are summarized in the following sections.

1) Cell performances

Current efficiency (*CE*) is determined by electrode corrosion, side reaction and vanadium ions permeability, while the first one can be controlled by the charge voltage or material [109], the second one can be reduced by the N₂. The last one can be reduced by increasing of the thickness so that the order of *CE* is N117 > N115 > N1135 > N112, while NR 212 and NR 211 are higher than N115 which might be attributed to their different micro-structure due to different preparation methods. Besides, *CE* will be higher at higher current density [103, 110].

Voltage efficiency (*VE*) decreases with the increase of area resistance or current density. This is due to the internal loss, including ohmic loss, activation loss and, mass transfer loss caused by membrane thickness. Hence, thinner membrane will have higher *VE*. The order of *VE* is N112 > N1135 > N115 > N117 [103]. It is also important to note that higher current density results in

higher ohmic losses which eventually leads to lower *VE* [111].

Energy efficiency (*EE*) is used to evaluate the energy loss during the charge-discharge process, which is affected by *CE* and *VE*. The order of *EE* is N117 > N115 > N1135 > N112 [103], while NR 212 and NR 211 have similar *EE* values which are still higher than N115 [107]. High current density will lead to lower *EE* [111] for the same membrane.

2) Membrane properties

The ion exchange capacity (*IEC*) of these Nafion membranes are similar and close to their theoretical value of $0.91 \text{ mmol} \cdot \text{g}^{-1}$ due to their similar ionomer chemical structure [103].

With respect to water uptake(*WU*) and swelling ratio(*SR*), a small difference is observed which is due to the slight difference in their inside micro-structure [112] under similar membrane thickness. Thinner membranes such as N112 will lead to higher *WU*. which is likely due to easier to absorb water [103]. Other pre-treatment factors such as temperature can also affect the water uptake [105]. High *IEC* can also lead to high *WU* [113].

Proton conductivities of Nafion membranes show similar values ($100 \text{ mS} \cdot \text{cm}^{-1}$) [103]. This is mainly due to the fact that proton conductivity is determined by *IEC*. High *IEC* means high concentration of protonic charge carriers and high activation enthalpy [113], thus, their similar *IECs* result in similar conductivity values. Higher water contents can also improve conductivity [44, 113]. For the same membrane, the conductivity can be increased with increasing temperature and hydration number [106].

The area resistance of Nafion membrane increases with increasing thickness, which can be explained through the Ohm's law. However, this relationship is not linear. The area resistance is also affected by uneven water distribution and current density [105]. The order of area resistance is N117 > N115 > N1135 > N112 [103].

Vanadium permeability of Nafion decreases with increasing membrane thickness. As thicker membrane leads to longer and more complicated water channels, water and ions diffuse through the membrane will decrease at the same time [95] under similar micro-structure.

3) The cycling performances

After charge-discharge cycling, the capacity fades due to vanadium ions crossing. The crossover results in self-discharge, side reaction which then leads to the imbalance of volume and concentration of vanadium between the two half-cells [14, 48]. Thus, thicker Nafion membranes, having lower vanadium permeability, will have better cycling performance. However, the capacity fading and electrolyte imbalance can be partially addressed by remixing the electrolytes periodically.

Furthermore, the charge-discharge time is also a factor that can affect the cycling performance. For membrane working at high current density, their capacity fading rate will be lower. [103]

4) Membrane cost

Minke *et al.* [101] reported that the price of N117 would not fall below \$62 .m⁻² since the costs of input material and production were estimated to be \$35 .m⁻² and \$27 .m⁻², respectively. . Hence, consideration other operational costs and profits, the price of the N117 was estimated to be in the range of \$500-1000 .m⁻² with the possibility of reduction to \$200.m⁻² in the future.

5) Summary of Nafion

The relationships between different properties of Nafion membranes are summarized here. Membrane thickness is the main factor in determining the performance of the Nafion membranes because they all have similar chemical structures. Thicker membrane will have lower permeability but higher area resistance, which will then affect the properties of the membrane and cell performances. In order to find the optimized thickness to keep a balance between these two factors,

comparative research was carried out where N212 was found to give a better performance [107, 111].

However, membrane thickness is not the only factor that influences the cell performance. Xi *et al.* [114] evaluated the cell performance using different kinds of CEM and AEM within a working temperature range of -20–50 °C, including Nafion 115 and Nafion 212, the Selemion CMV, and the promising candidate SPEEK and anion exchange membranes (i.e. the Selemion AMV and APS). The study indicated N115 membrane was the best choice for VRFB application at all climate due to that lower crossover rate and better chemical stability at all temperatures. Besides, current densities, state of charge or other cycling conditions as well as production, also affect the membrane performance. Thinner membrane is more suitable at high current density while thicker one is better for low current density in VRFB system [103]. The membrane conductivity can also be enhanced by sulfuric acid in the electrolyte resulting in increasing proton concentration in the membrane [110, 115]. Hence, to optimize the battery system, it is necessary to find suitable membrane to balance between performance, operation environment, and electrolyte composition.

4.1.1.2 Nafion composite membrane

To address the high vanadium crossover rate in Nafion membrane, different kinds of composite membranes based on Nafion have been proposed including addition of additives such as SiO₂ [99], TiO₂ [116, 117] and other inorganic materials or metal thin film. Nafion could also be incorporated with other layers such as SPEEK [118], PTFE [100], GO [119, 120], PP [121] membrane or fluorocarbon surfactant [98]. The research on nanocomposite membranes and multilayer structure are currently on-going to achieve better properties.

Kim *et al.* [122] developed a silicate D-AMH-3 layer on Nafion by solution casting and hot pressing method, and this layer acts as a selective layer to reduce the crossover rate of vanadium ions. The low crossover rate improves the capacity and *CE* when compared with N117. However, this Nafion-based composite membrane (ND) has higher cell resistance, which leads to slightly lower *EE* at higher current density but higher *EE* at lower current density. Stable cycling ability is also observed for over 100 cycles. Its sandwich structure also improves the membrane lifetime.

Interestingly, the increased cell resistance can be reduced by optimizing content and modifying the surface. The cycling test results under $40 \text{ mA}\cdot\text{cm}^{-2}$ current density are tabulated in Table 2.

Yang *et al.* [123] prepared a colloidal silicalite-Nafion composite membrane by suspension casting method. This membrane has a top layer of colloidal silicalite on the Nafion layer. The 5wt% composite membrane (ZNM-5) shows much lower resistance, higher energy efficiency, and better cell performances i.e. higher *CE*, *VE*, and *EE* in VRFB than N117. The composite membrane also has a good working stability and low permeability than N117, due to smaller zeolitic pores, which makes them accessible to water but does not allow the vanadium ions to diffuse. The detailed data are shown in Table 3.

Teng *et al.* [100, 124] developed a thin polytetrafluoroethene (PTFE)/Nafion (P/N) composite membrane by solution casting method or a sol-gel method. Comparing with NR 212 membrane, P/N membrane has lower *IEC*, conductivity, water transfer rate, vanadium ions crossover rate, water uptake and swelling ratio due to its thinner membrane and the hydrophobic nature of porous PTFE. Thus, the *CE*, *VE* and *EE* of the VRFB system with P/N membrane are higher at all tested current densities. The cycling stability performance of P/N is also better than NR 212, including better capacity retention ability and lower self-discharge. Besides, the cost of PTFE is lower than that of Nafion, and the lighter weight also makes P/N membrane cheaper. The experimental data of both NR 212 and P/N are shown in Table 4. In this table, the *SOC* starts from 50% while the current density is $40 \text{ mA}\cdot\text{cm}^{-2}$.

Teng *et al.* [32] tried to add silica into the P/N membrane to improve the water content later. This ultra-thin polytetrafluoroethene/Nafion/silica membrane (P/N/S) is prepared through solution casting method or sol-gel method at various nano-SiO₂ composition (including 1%, 3%, 5%, 7% and 9%). The introduction of nano-SiO₂ leads to reduction in the water uptake of P/N/S, which leads to lower conductivity and permeability. The P/N/S with 3% composition membrane (P/N/S–cast-3) shows better cell performances among all these composite membranes, as it has higher *CE* and *EE*, but lower *VE* due to lower proton conductivity. As a result of its lower permeability, the cycling stability of P/N/S is also better than P/N, including lower self-discharge

rate and good oxidation stability. Also, since the Si distribution of the membrane prepared by the sol-gel method is more homogeneous than solution casting method, the former has better membrane performance, indicating that homogeneous distribution of the nano-SiO₂ will improve the membrane properties. The result of this study is shown in Table 5. In this table, the SOC is 50% while the current density is 50 mA·cm⁻²:

As a new kind of carbon material, the graphene oxide (GO) can offer a new possible additive to decrease the permeability and improve the cell performances of the pristine Nafion by adding particle. GO related materials have high surface area and a unique two-dimensional layered structure, therefore the Nafion combined membrane can achieve higher water uptake and improved proton transport channels [125]. Thus, researchers use the GO to increase water uptake of Nafion to decline the permeability of vanadium ions. Through casting methods, Lee *et al.* [126] prepared a GO/Nafion117 composite membrane while Lue *et al.* [102] prepared a Nafion 212 /graphene oxide membrane (N212/GO). After comparing the composite membranes with a different weight fraction of GO additive and the Nafion type's membrane, the composite membrane's properties are much better due to lower value of the inter-planar space dimension. With the increase in GO content, the conductivity and permeability of the GO/Nafion decline. The SC-0.067 (spin-coated 0.067 wt% membrane) which has a 1-2 µm thin top well-aligned GO layer but low GO content (4.73×10^{-6} g·cm⁻²) shows the lowest permeability and highest cell performances.

After that, fibre which can create proton transport channels are analysed. The fibre materials can make the swelling ration decrease, and then leads to a higher ion selectivity. The fibre structure offers higher physical strength, which increases the stability of the membrane in the acid electrolyte. Abdul Aziz *et al.* [127] used porous ZrNT to fabricate a Nafion-ZrNT membrane. The resultant tubular structure of ZrNT gives lower permeability and higher physical strength, and thus displays higher water uptake, proton conductivity, and oxidation stability as well as lower swelling ratio, IEC, and activation energy than N117. Thus, it offers a higher performance of efficiency (CE 97.5%, VE 80.5%, EE 78.5%) at a current density of 40 mA cm⁻².

Similarly, Bang *et al.* [128] prepared a Nafion/PVA electrospun fibre-modified membrane. Because it is based on a porous Celgard PP membrane, the hydrophobic nature results in lower swelling ratio than NR 212. The electrospun fibre matrix has lower vanadium ions permeability due to reduction in permeability channels which leads to a better cell performance in the VRFB system i.e. higher *CE*, *VE*, and *EE* than NR 212 at all of the tested current densities. The porous supports also offer high mechanical stability. The detailed data are shown in Table 6. Thus, the electrospun fibre-modified Celgard membrane has lower crossover rate and better performance than the current commercial membrane Nafion.

Besides adding composites or other fibre-modified membranes, another important technique that affects the properties of the membrane is its structure, especially for the multilayer membranes. The loading layer might decrease the permeability of vanadium ions as well as the conductivity. To achieve a balance between these two factors, experiment for comparisons need to be conducted. Recently, Sun *et al.* [129] prepared (Nafion/(WO₃)_x) hybrid membranes. Different loading levels of WO₃ nano-filler (0.024 and 0.329) were added to the surface of a thin Nafion film by solvent-casting method. The combined material showed less hydrophilicity than Nafion, resulting in decreasing vanadium ions permeability (almost half of Nafion) but a slight decrease in conductivity. The hybrid membrane is stable under long term operation indicating long term dimensional stability of WO₃ nano-filler.

Similarly, S. Shi *et al.* [130] developed Nafion XL membrane with a sandwich structure where Nafions were added on both sides of the micro-porous PTFE-rich support layer. Because of the PTFE, the swelling behaviour can be reduced by increasing the thickness or decreasing the plane. Moreover, it will also reduce the conductivity by increasing in area or decreasing in thickness direction which is due to its resistances arising from PTFE or its interactions with the Nafion. Also, PTFE size could control the membrane stability and conductivity since the mechanical properties and stability will be affected by increasing transport resistance.

Moreover, a multilayer structure containing Nafion as middle layer has also been studied, including Nafion-(PDDA/ZrP)_n [131], Nafion-(PDDA-PSS)_n [96] and Nafion-(CS-PWA)_n [132](n

means the number of the multilayer added). The barrier layers are added to the surface of Nafion by a layer-by-layer self-assembly method. Because the ion-transfer pathway on the surface of Nafion is covered by the PDDA/ZrP, PDDA-PSS or CS-PWA, they all show lower permeability, higher *CE* and *EE*, lower self-discharge rate and similar stability than Nafion membrane. The number of layers can also influence the membrane properties, and among those multilayer structures studied, Nafion-(PDDA/ZrP)₃, Nafion-(PDDA-PSS)₅ and Nafion-(CS-PWA)₃ show better performance as shown in Table. 8-10, while the current density of Nafion-(PDDA-PSS)₅ tested is 20 mA·cm⁻², the Nafion-(PDDA/ZrP)₃ and Nafion-(CS-PWA)₃ tested is 30 mA·cm⁻².

4.1.1.3 Technology to enhance the performance

There are several methods that could be used to enhance the properties during preparation of the same membrane.

Zhao *et al.* [74] developed a low-polarity nonsolvent tetrachloroethylene(TCE) casting solution method and found it enhanced proton conductivity, water content and water permeability of the membrane due to the larger clusters of sulfonate groups in Nafion after casting. This solution makes the ionomer self-organized and also makes the original transparent Nafion made in DMF solution to be opaque.

Dai *et al.* [133] evaluated the effect of casting solvents (DMF, DMSO, NMP, EtOH) and annealing temperature (100, 140, 180) on the microstructure, proton conductivity, vanadium permeability and the cell performances of recast Nafion membranes. Though both of them can affect the membrane properties, the solvent effect was found to have more dominant effect on the properties of the recast membranes at lower temperature while the effect is insignificant at higher temperature. The crystallinity of membranes decreased with increasing annealing temperature, which means lower vanadium permeability. Higher temperature also offers better mechanical properties. Membrane prepared from EtOH has the worst properties. Single cell performance of membrane is also better when it is prepared at 180°C than at 140°C and 100°C when the same solvent is used.

Xie *et al.* [134] also indicated that pre-treatment can affect proton conductivity and vanadium ions permeability of Nafion. All membranes have similar or lower permeability after heat-treatment. Besides, they have similar and higher permeability after immersion in boiling sulfuric acid and water. Further, extruded membranes have higher permeability than casting ones, and this difference is largest for the membranes prior to electrolyte soaking. The difference becomes smaller after soaking in electrolyte and much smaller after soaking in water. All membranes display similar membrane selectivity after heat treatment. The selectivity could be similar or reduced after immersion in boiling sulfuric acid. Extruded membranes have lower selectivity than casting ones, and the selectivity worsen after being exposed to water at room temperature. The soaking time also affects the permeability of the membrane where vanadium ions permeability increases sharply during the first several hours in water and first several days in the electrolyte, however the increase eventually evens out thereafter.

4.1.2 Other cation exchange membranes

Although Nafion based membranes have high stability and excellent electrochemical properties, they still have high permeability and cost. Thus, efforts have been also spent to develop more cost effective and better permeability ion exchange membranes to Nafion such as poly (ether ketone) [135], poly (arylene ether) [136], poly (fluorenyl ether ketone sulfone) [137], poly (phthalazinone ether ketone) [138] and other polymers. The development of these membranes is described in the following sections.

4.1.2.1 SPEEK based membranes

Sulfonated poly (ether ketone) membrane(SPEEK) under all three generations of VRFB were evaluated by many groups, including Winardi *et al.* [135]. This low-cost membrane is prepared by casting method. The SPEEK membrane has lower resistance, slower self-discharge rate than N117, while it shows similar conductivity. Thus, it shows better cell performances, including slightly

higher *VE*, *CE*, and *EE*. Further, although Nafion membrane used in this paper is thicker than SPEEK membrane, the former one still had higher permeability due to the different microstructures. The cell performances tested at $40\text{mA}\cdot\text{cm}^{-2}$ current density are shown in Table II.

The swelling ratio of SPEEK is much higher than that of Nafion. This is caused by the high water uptake, leading to the decline in mechanical properties and lower mechanical stability. Also, although better than Nafion, its permeability is still high. Like composite Nafion membranes, the performance of the SPEEK can be improved by introducing inorganic materials into the polymer matrix, utilize the interaction of interfacial functional groups or tune the size of transport channels to selectively transport protons [139]. The additions can be particles like TiO_2 [140] and lignin [141], or nanotube like dopamine-modified halloysite nanotubes (DHNTs) [139], or nano layer like such as graphene oxide nanosheet [142], mesoporous silica hybrid membrane [143], or polymer layers like zirconium phosphate sulfophenylphosphonates (ZrPSPP) [144], graphitic carbon nitride nanosheets (SPEEK/g-C₃N₄), [145] poly (vinylidene fluoride-co-hexafluoropropylene) (P(VDF-co-HFP)) [25, 146], polymer (polysulfone-2-amide-benzimidazole, PSf-ABIm) [147], or porous polymer membranes like PVDF [148]. The performance of SPEEK membrane can also be improved by changing the microstructure of the SPEEK to integrally thin skinned asymmetric, like ITSA-SPEEK [149]. All these methods offer lower swelling ratio and hence good stability, and lower permeability than pristine SPEEK and N115 or N117. By keeping a good balance between the vanadium ions permeability and conductivity, their cell performances can also be improved i.e. higher *CE* and *EE*.

As the permeability and conductivity are antagonistic, their conductivity also decreases. To increase conductivity, other particles or functional groups are added onto the membrane, including carboxylic acid groups (C-SPEEK) [150], or higher moiety of sulfonic group which means a higher degree of sulfonation (DS) [151] have also been studied. C-SPEEK-50 showed better performance while S67-DMF showed good mechanical properties and high ion selectivity due to suitable DS and water uptake. With respect to S67-DMF, the performance of different casting

solution is also compared, and the DMF shows the best cell performances and life-cycles.

Recently, a mussel-inspired polydopamine coated carbon nanotube embedded SPEEK mixed matrix membrane (S/CNT@PDA MMM) has been studied by Yu *et al.* [152]. This group uses CNT@PDA filler mixed with SPEEK matrix to create more effective proton transfer pathway which contributes to higher conductivity. The acid-based interface and improved physicochemical property also lead to high stability of the membrane. The performance of this membrane was evaluated and compared with seven different SPEEK based membranes. The study indicates that, this membrane shows high *EE* (75.4%) and long-term stability at high current density ($200\text{mA}\cdot\text{cm}^{-2}$), with extremely low capacity fading rate (0.04% per cycle) over 1000 cycles. Although the comparison is made under different tested current density which means further experiments are needed to reach conclusion, this membrane offers a new potential low cost and high-quality matrix membrane for VRFB.

Chen *et al.* [153] developed SPEEK-PBI blend membranes for VRFB. The cross-link networks are created by transference of H^+ -SPEEK to Na^+ -SPEEK, which leads to more transfer tunnels and hence increase in conductivity. The 1.5% PBI in SPEEK has higher *CE* (from 0.724 to 0.985) and *EE* (from 0.669 to 0.898) than SPEEK membrane at $80\text{mA}\cdot\text{cm}^{-2}$ [153]. Furthermore, the performance of this membrane was tested for 350 cycles at $180\text{mA}\cdot\text{cm}^{-2}$ with no significant capacity fading observed. Moreover, its permeability is much lower than SPEEK.

4.1.2.2 Other polymeric CEM

Yin *et al.* [137] compared various degrees of branched(DB) for sulfonated poly (fluorenyl ether ketone sulfone)s (HSPAEEK) membranes prepared by solution casting method. Increasing DB results in membrane having higher conductivity, water uptake, and stability with lower swelling ratio but lower breaking strength. Thus, high DB will not improve all the properties of the membrane at the same time. Among various degrees of DB tested, the 8% degree of branching (DB) shows better performance so further experiment on VRFB system was set. HSPAEEK shows lower swelling ratio and proton conductivity than N117. It still has higher ion selectivity, *IEC*,

breaking strength, cell performances (*CE* and *EE*) at $80 \text{ mA}\cdot\text{cm}^{-2}$, and longer self-discharge time. The detailed data are shown in Table 11. HSPAEEK, being cheaper, is a promising substitute to Nafion Membrane for VRFB system.

Sulfonated poly (phthalazinone ether ketone) (SPPEK) backbone contains the special rigid unsymmetrical phthalazinone moiety, which makes it much more stable. However, the higher sulfonation degree leads to higher swelling ratio and vanadium crossover. To improve the proton conductivity of the low-cost SPPEK while maintaining low vanadium ions permeability, Wang *et al.* fabricated composite membrane based on SPPEK with tungstophosphoric acid (TPA) [138] by casting method or using WO_3 by a hydrothermal method [154]. Both composite membranes are more stable and have better permeability, lower area resistance but higher water uptake and better cell performances than N117 and SPEEK. Chen *et al.* [155] loaded pendant phenyl moieties on the SPPEK. Due to the aggregation of sulfonic acid functional groups on the side chains of the aromatic polymers, the membrane had hydrophilic/hydrophobic separation leading to improved proton conduction of the membrane. This structure makes the composite membrane much lower vanadium permeability where no permeation of VO^{2+} ions through the membranes was detected, even after 8 weeks.

Sulfonated polyimide (SPI) is another low-cost polymer which offers much low vanadium ions crossover rate as well as excellent stability. However, it has a lower conductivity than Nafion N117. Because of that, Li *et al.* has modified this polymer by combining with other materials to improve its conductivity including boehmite(AlOOH) [156], chitosan(CS) [157], ZrO_2 [158], TiO_2 [159], hydrophobic trifluoromethyl groups ($-\text{CF}_3$) [160], functionalized graphene oxide(ZGO) [27], molybdenum disulfide nanosheets($\text{MoS}_2\text{-ns}$) [161], sulfonated molybdenum disulfide (s-MoS_2) [162] and branched side-chain-type sulfonated polyimide membrane(6F-s-bSPI) [160]. All of them are much more stable than Nafion 117 due to their low self-discharge rate. Besides, they all have much lower vanadium ions permeability, which is nearly an eighth of N117, while SPI/ AlOOH and SPI/CS are one-tenth. Moreover, they all have higher *CE* and *EE* at tested current densities of $20\text{-}80 \text{ mA}\cdot\text{cm}^{-2}$ except SPI/CS which is only tested on $40 \text{ mA}\cdot\text{cm}^{-2}$. The weight percent of the additive can also affect the performance of the membrane. To keep the balance of

the ability like permeability and conductivity, 15% ZrO₂ or 10% ALOOH shows the best performance

Pu *et al.* [163] also studied branched sulfonated polyimide (bSPI). Their research compared the performance of SPI with different non-sulfonated diamine monomers including APABI, MDA, and BAPP. The bSPI (APABI) had the lowest permeability of vanadium ions ($1.7 \times 10^{-7} \text{ cm}^2 \cdot \text{min}^{-1}$) while bSPI (MDA) had the highest *IEC* (1.37 mmol/g). The bSPI (BAPP) had the best conductivity which overcame the shortage of SPI membrane. High conductivity leads to high efficiency in VRFB cycling. In addition to the good stability, the VRFB with bSPI (BAPP) has been tested for 500 cycles where the *CE* and *EE* was maintained at over 97.1% and 61.6% at 120 mA·cm⁻². The capacity decay is also comparable to N117. This group also studied the stability of SPI in VRFB [164].

Chromik *et al.* [165] compared the partially fluorinated membrane (S1B1) and the non-fluorinated membrane S2B2 with N117 and SPEEK, and found that the S1B1 shows better chemical stability with highest *CE* and stable *VE* and *EE* to those of N117 and S2B2. Besides, both of S1B1 and S2B2 have comparable power density to N117. This indicates the durability of membranes can be improved by adding blend components such as sulfonated ionomers and covalent cross-links.

Recently, the cross-linked structures which can enhance mechanical properties and long-term cycling stability of SPI are studied by Xi *et al.* [166, 167]. They compared SPI acid-based membrane synthesized under different proportions of imidazole rings and sulfonic groups. The intermolecular ionic cross-linking between sulfate radical and protonated imidazole groups create proton transport channels which can increase the conductivity of the SPI. SPI50 shows nearly 10 times lower vanadium permeability than N115 and shows the best performance in VRFB running compared to other SPIX. The reported higher *CE* and *EE* in VRFB by SPI50 than N115 under 40-160 mA·cm⁻² current density is likely due to the high conductivity and low permeability. The *EE* was maintained at over 75% for 400 cycles at 160 mA·cm⁻². This research group also compared SPI with the aforementioned SPI combined membrane and noted that the SPI50 offered better long-term performance at high current density. However, this comparison is made under different experimental conditions, thus further study needs to be done.

Yan *et al.* [168] introduced a controllable acylation with 4-fluorobenzoyl chloride long side chains onto the PPO backbone and subsequently congealed it with sodium 4-hydroxybenzenesulfonate to form S-L-PPO-51% membrane. Due to hydrophilic/hydrophobic micro-phase separation structure, this membrane keeps a good balance between the conductivity ($44 \text{ mS}\cdot\text{cm}^{-1}$) and permeability ($4.3\times 10^{-9} \text{ cm}^2\cdot\text{s}^{-1}$) which leads to good performance in VRFB system, including higher *EE* than N212 at various current densities. The *EE* was found to be 89.8% at $120 \text{ mA}\cdot\text{cm}^{-2}$, and *CE*, *VE*, and *EE* remained unchanged for 100 cycles at $80 \text{ mA}\cdot\text{cm}^{-2}$.

4.2 Anion exchange membranes (AEM)

Although many methods are applied to decrease the high vanadium ions permeability of CEM, this main shortcoming of the CEM still exists. This shortcoming can be addressed by using AEM.

According to Donnan exclusion effect, the quaternary ammonium groups in anion exchange membranes(AEM) can prevent cation ions including vanadium ions from going through the membrane [113]. In addition to their narrower hydrophilic channel in aromatic-hydrocarbon-based AEM [169], AEM has extremely low vanadium ion permeability and high *CE* in the VRFB system. But comparing to CEM, since the membranes are soaked in the strongly oxidizing electrolyte, AEM have typically lower redox-stability, especially in the positive half-cell. Besides, it may not assist in the conduction of protons, which decreases the *VE*. Thus, relatively, limited number of publications about AEMs for VRFB is found in literature, even other aqueous acid-based redox flow batteries [170]. Thus, researchers are trying to improve the stability and conductivity of AEM by increasing *IEC* and water uptake through microstructure changes.

The performance of Commercial AEMs are compared by Choi *et al.* [171], including ammonium-type AEM AHA and antifouling AEM AFN from the ASTOM of Japan, aminated polysulphone AEM APS from Asahi Glass Co.. Comparing with the larger membrane resistance and instability of AHA, AFN offers constant cell resistance under different *SOCs* and *SODs* (state of discharges). Besides, AFN also offers similar *EE* as N117, which means it can be a suitable

separator for VRFB.

Similar to CEM, AEM also uses the polymer backbones, including poly(arylether), like QADMPEK [159] poly(fluorenyl ether), like QA-PFE [172]; poly(phenylene)s, like QDAPP [173]; cardo-poly(ether ketone) (PEK-C) [174]; poly(phenyl sulfone), like PyPPSU [175]; poly(phthalazinone ether ketone ketone) which also belong to the poly(arylether), such as PyPPEKK [176], QBPPEK [177], QAPPEK [178]. These membranes have lower vanadium permeability, nearly 100% *CE*, similar or lower *VE* and higher *EE* than Nafion membranes due to similar or larger area resistance.

Based on these AEMs, factors affecting the properties of the membrane can be summarized in the following paragraphs.

The density of the functional groups and the monomer units permits are one of the keys to improve the membrane performance. Most of AEMs are using quaternary ammonium group as the functional groups, however, some researchers used other amine-functionalized groups like dimethylamine (DMA) [179], (3-glycidyloxypropyl) trimethoxysilane (GPTMS) [180], trimethylamine (TMA) [181], and further N-(trimethoxysilylpropyl)-N,N,N-trimethylammonium (TMSP-TMA) [169]. It was noted that additive groups can improve *IEC* and water uptake, leading to higher conductivity. Controlling the degree of the functional groups can also lower permeability and enhance the stability of the membrane, resulting in better *CE* and *EE*.

Attaching inorganic additives like nano silica [182], ZrO_2 [183] or BrPPO/Py-56 [184] with different density on the pure AEM can enhance the AEM microstructure. These particles are uniformly formed throughout channel networks which lead to a reduction of free volume for water uptake. Higher *IEC* and conductivity, as well as lower permeability than pristine AEM and Nafion can be achieved. Thus, the composite membranes have higher discharge capacity and *CE*. However, the long-term chemical stability and aging properties still need to be studied in the future.

Cha *et al.* [185] reported a polysulfone-based AEM (CAPSU-x) that could change the microstructure to enhance the membrane durability by crosslinking of the membrane with a primary diamine-based crosslinker at various degrees. Chloromethylated polysulfone is used as a precursor polymer for the crosslink. CAPSU-2.5 shows better performance. the crosslinked membrane offered much lower permeability ($0.272 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$). The conductivity was also improved especially at high temperature. The VRFB using this membrane showed high efficiency ($EE=0.86$) at $50 \text{ mA} \cdot \text{cm}^{-2}$ and excellent CE (almost 100%) up to the 100 cycles.

Moreover, the preparation process of the membrane, including the time, temperature and concentration of the amination process, can affect the membrane properties [70]. With the increase of these three factors, the IEC and water content of the membrane increase while the area resistance decreases. The stability of the membrane depends on the dimension change, which can be affected by high temperature.

Besides, the performance of AEM can be enhanced by their preparation method which can change their microstructure. For example, simultaneous polymerization and quaternization can result in low vanadium permeability due to the high degree of crosslinking, while the dimensional and chemical stability are still retained [186]. And Ma *et al.* [187] used side chain hydrolysis method load anion groups in the porous membrane. They built cross-links to enhance the microstructure by using TMHDA and give quaternary ammonium on a porous membrane and combined the beneficial features of AEM and porous membranes which means high ion selectivity and stability.

Sol-gel method can also change the microstructure of AEM by grafting other polymers, for example, ETFE-g-(VBTAC-co-HEMA) [67]. The degree of grafting (DG) can affect the properties of this composite AEM. With the increase of DG, the concentration of the functional groups and the degree of hydrophilicity are enhanced, respectively. The IEC and water uptake can also be improved. Similarly, the permeability of this composite membrane is also lower than N117 while it keeps stable after long time.

As operating condition can affect the cell performance, Yun *et. al* [168] found that increasing

current density resulted in better ion conductivity of anion exchange membrane.

4.3 Amphoteric ion exchange membranes (AIEM)

CEM has high ionic conductivity and good chemical stability, but the high vanadium permeability led to low *CE* and poor cyclability. For AEM, the vanadium crossover rate is much lower which offers them higher *CE*. But AEM also suffers low ionic conductivity which results in low *VE* and high rate of capacity loss.

The amphoteric ion exchange membrane (AIEM), which combines both properties of AEM and CEM, was proposed by Sollner firstly in 1932 [188]. Since AIEM has both two types of functional groups, it has both two membranes' advantages, including low permeability and high ionic conductivity [189]. However, since the permeability and the conductivity are antagonistic, the improvement will depend on percentages of these two functional groups. Besides, as the preparation of the membrane is complicated and expensive, the main direction of research is to find an easy method to produce low cost and stable AIEM with balanced density functional groups [190].

To introduce the anion functional groups on the CEM, many methods are used. Grafting methods were studied by Qiu *et al.* When combined with other preparation methods like sol-gel and solution phase inversion method, many membranes have been developed including grafting DMAEMA [191], DMAEMA and SSS [192], DMAEMA and AMS [193]. These membranes are prepared simultaneously through irradiation grafting technique on PVDF; or grafting St on ETFE-g-PS to be the ETFE-g-PSSA which can then be grafted by DMAEMA [194], or pre-irradiation induced graft copolymerization on ETFE [195]. Since higher grafting yield brings higher water uptake, *IEC* and conductivity, and higher content of DMAEMA which will lead to lower permeability and conductivity, the properties of the membrane can be controlled by choosing proper grafting conditions. All these membranes have significantly lower permeability and better cell performance than that of N117. They also have superior conductivity compared with PVDF. The long-time performance in which the *OCV* of the system can be maintained over

1.3V also indicates these three AIEMs can be good candidates for VRFB system.

Other methods can also be used to develop the AIEM.

Wang *et al.* [196] developed a solution casting method to control the density of the quaternary ammonium groups on SPEFK in order to decrease the permeability of the vanadium ions. Due to the Donnan exclusion effect, the AIEM-20% has 4.4% vanadium ion permeability of N115 while its stability and proton conductivity are comparable to SPFEK. Similarly, Yan *et al.* [197] also combined SPEEK with imidazolium-functionalized polysulfone (ImPSf) to reduce the permeability. Due to the Donnan repelling effect of the imidazolium cations on the vanadium ions and the low swelling ratio of the amphoteric membranes, the introduction of ImPSf can decrease the migration of vanadium ions efficiently. The amphoteric membrane with an ImPSf mass ratio of 17% shows much lower vanadium permeability and area resistance than NR212. This membrane shows higher *CE* and *EE* than NR212 at high current density. It can also keep *OCV* > 0.8V for twice the duration of NR212, indicating lower capacity decay on the VRFB system.

Lin *et al.* [110] developed a Nafion/amino-SiO₂ hybrid membrane which is filled with amino-SiO₂ nanoparticles (the amino group density is 9.85 nmol·cm⁻²) by electrostatic attraction through the sol-gel process. The membrane has lower vanadium ion permeability and higher *IEC* than Nafion N117 while almost retaining the same conductivity. Because of the additional amino groups on the exposed surface, the contact angle decreased, leading to lower permeability, resulting in higher *CE* (by 3.5%), *VE* (by 1.9%) and *EE* (by 4.2%) than N117's at current density of 80 mA·cm⁻². In the cycling test, the Nafion/amino-SiO₂ hybrid membrane also showed better chemical stability in both vanadium and acid solutions. The detailed data collected from this research group (*SOC* started from 75%, the capacity is 1920 mAh while the current density is 80 mA·cm⁻²) are listed in Table. 13:

Another kind of combined Nafion based AIEM was studied by Kondratenko *et al.* [198]. They combined Nafion membranes with amino groups of AATMS by sol-gel. With a balance between two kinds of functional groups, this combined membrane has improved proton conductivity and

ion selectivity.

Recently, Dai *et al.* [199] grafted zwitterionic SBMA (sulfobetaine methacrylate) onto N115 via SI-ATRP technique to build a novel AIEM named N115-g-PSBMA membrane. The RN_4^+ and SO_3^- enables the membrane to have both kinds of negative and positive exchange groups, leading to lower vanadium ions permeability than the pristine N115 membrane. Although the conductivity is lower than pristine N115, the low permeability contributes to better battery performance, including 2.6% higher *EE* than N115 at current density of $40\text{--}80\text{ mA}\cdot\text{cm}^{-2}$. Further, the polymers used cheaper poly sulfone and poly ether ketone which also led to low cost of the membrane manufacturing.

AIEM with extreme low vanadium permeability known as cross-linked 60SPAEEK-6F-co-15%BI membrane was studied by Liao *et al.* [200]. The permeability of this cross-linked membrane was 1117 times lower than N117 due to narrow ion transporting channels, resulting in longer battery self-discharge time (3 times) and good proton conductivity. The cell performance was also improved or comparable to N117.

To reduce the cost of AIEM, Liu *et al.* developed AIEM by using low-cost backbone SPEEK with QAPEI through the blending method [201]. This membrane also offers a high degree of micro-phase separated structure which is beneficial towards ion transmission. The membrane had lower vanadium permeability and higher selectivity than N115. It was also very stable. The blended N-based functionalized graphene oxide (GO-NH_2) on SPEEK was also studied by this research group [202]. The blending layer which had $-\text{SO}_3$ groups and N-base groups was found to change the ion transport pathway structure of SPEEK, leading to higher conductivity and lower permeability than pristine SPEEK membranes. The combined membrane was tested on VRFB cell for 100 cycles where its capacity remained over 92%. This research group also developed a UiO-66 loaded SPEEK membrane [203] where they found that the ion selectivity and stability were improved due to the presence of micropore sizes of UiO-66 within the radius of protons and the additional material through hydrogen bonding.

Li *et al.* [204] developed a solvent-free strategy to cast poly(VBC-co-DVB)-PEKC-TEPA (ZPPT) onto PETEX between 2 PVC. The combined membrane showed low vanadium permeability, high chemical stability, and ionic conductivity. It also offered higher *CE* than N117 and better cycling ability.

4.4 Non-ionic porous membranes

Beside ion exchange membrane, non-ionic porous membrane with their excellent mechanical, chemical stability and lower cost has also attracted much attention for VRFB application. Without functional groups, they exchange the proton through the pores while the vanadium and other polyhalide ions are rejected because of pore size exclusion effect [205]. However, since its ion selectivity is not as effective as the IEM, these membranes have higher permeability. The high crossover rate will lead to imbalanced transport of vanadium ions between the positive and negative side, in addition to the self-reaction, and finally result in unbalanced concentration, volume change and capacity decay [206, 207] which ultimately leads to bad cell performances.

To address this problem, Zhou *et al.* carried out more research and set a model on how the porous membranes influence ion transport through the porous separator [208]. The factors include the pore size, electrolyte flow rate and membrane thickness and operation mode based on nanoporous polyvinyl chloride (PVC)/silica separator. The transport mechanisms can be divided into three types, namely diffusion, convection, and migration. When the pore size decreases to 15nm, convection, the dominant crossover mechanism is minimized while the other two can only be decreased dramatically after the pore size is close to the size of vanadium ions (2nm). Thus, with the pore size declining, the *CE* increases due to the reduction in the permeability of the vanadium ions, while the *VE* decreases due to the increase in ohmic resistance. Because of the trade-off between the permeability and resistance, the highest *EE* can be achieved at pore size of 5nm. For the same reason, the optimal membrane with pore size of 30nm is 400 μ m. Another important factor is the operation modes, such as flow rate, as it can affect the pressure on the surface of the separator.

Hence, to decrease the permeability of the porous membrane, decreasing the pore size is a good method. This can be done by adding additives like polymer on the surface of and inside the porous membrane. Functional groups can also be added onto the membrane to improve the ion selectivity.

PVDF with its simple production process has been applied in many fields owing to its good stability and low cost. However, because of the super hydrophobic characteristic which leads to the drastic decrease in the porous conduction, and high permeability caused by micro-porous membrane selectivity, the cell performances of PVDF is also not good [209] and thus needs to be improved.

Many research groups have focussed on improving the performance of non-ionic porous membranes. Cao *et al.* [209] found an effective way to graft PVP on the PVDF while Zhou *et al.* [210] has grafted PSSA and BaTiO₃ on PVDF and Qiu *et al.* [211] grafted styrene and maleic anhydride. Besides grafting, Ren *et al.* [212] used quaternized polysulfone (QAPSF) while Tian *et al.* [213] used functional groups to make the PVDF to be an AEM. All of these modified membranes decrease the permeability by narrowing the transport channels and thus improving *CE*, however, they also increase the area resistance. To find the balance point between these two factors, the grafting density is controlled, and then found to give the higher *EE* than both PVDF and Nafion membranes

Cao *et al.* [214] also analyzed the importance of the experimental parameters such as temperature, the composition of the polymer solution, evaporation time, ambient humidity and the types of supporting material on the structure of the PVDF. However, the group finally concluded that the pore size is still the one that defines the performance of the membrane.

Except PVDF, other combined porous membranes including micro-porous and nano-porous membranes are also studied for VRFB system recently. Like PVDF, researchers combined different materials using various methods to enhance the properties or to reduce the cost of the nano-porous membrane.

Xi *et al.* [215] introduced silica on PES to control the pore size by sol-gel method as well as change the affinity of the membrane while Luo *et al.* [216] combined nanoporous PBI matrix and porous PBI membrane to achieve the properties of a typical nanoporous membrane with low cost. Wu *et al.* [217] combined PSF/PVP-50 PSF as skeleton, PVP as functional exchange addition, and based on this porous membrane, GO nanosheet framework [218] was added to decrease the crossover of vanadium ions. Maurya *et al.* [219] combined an AIEM and nanoporous membrane to improve the membrane properties. Chen *et al.* [220] used different percentages of phenolphthalein (FT) in PES/SPEEK to build PES hierarchical porous membranes. The structure of the membrane with phenolphthalein-templating pathway became sponge-like pores, which means high conductivity and stability in strong acid. Z. Yuan *et al.* [221] produced PES-IEC membrane which combined PES with TPA/PVP at low cost. Due to the stable characteristic of porous membranes and high electrochemical performance of IEM particles, the PES-IEC membrane can offer higher *CE* and *EE* than N115 with stable performance over 1200 cycles at the current density of 140 mAcm⁻².

Recently, Kim *et al.* [222] combined SPEEK and Engelhard titanosilicate-10 (ETS-10) on PTFE by solution casting method, and found 3 wt% ETS-10 (SE3/P) show the best battery performance. SPEEK-ETS-10 composite dispersing on PTFE, proton exchange groups were added, which led to lower vanadium permeability. Owing to the stable structure of the PTFE, VRFB cell performance test was conducted 40 mA cm⁻² over 200 cycles with no significant decline in efficiency. Since the swelling ratio of this membrane was lower than SPEEK, the total conductivity (43.6mS·cm⁻¹) was higher than SPEEK, however it was still lower than N115, which led to lower *CE*. But the overall *EE* is higher than Nafion N115, and the cost of material is also lower than Nafion. Besides, this group combined SPEEK and microporous AMH-3 (G-AMH-3) to enhance the performance of membrane [223]. Due to interaction between SPEEK and G-AMH-3, the swelling ratio and mechanical properties are improved, and the membrane can be cycled work for 100 times in VRFB. However, the longer pathways for protons result in lower conductivity and permeability.

Different fabrication methods to decrease the pore size are developed. Sizov *et al.* [224] used

supercritical CO₂ assisted phase-inversion method to create highly selective porous ABPBI membrane for VRFB applications, while Luo *et al.* [225] used phase separation process induced by water vapor by different viscosity solution to manufacture the ABPBI. Low viscosity or supercritical CO₂ assisted phase-inversion method resulted in much more porosity leading to slightly higher vanadium ion permeability but also higher conductivity than PBI resulting in better cell performance.

Beside organic material, flat porous glass membranes with pore sizes in the range from 2 to 50 nm have been applied to VRFB by Mögeli *et al.* [226]. This membrane is prepared by mixing analytical grade SiO₂, B₂O₃, and Na₂CO₃. These materials are which cheaper than Nafion. The chemical, thermal and mechanical stability of these materials are tested and found to be suitable for VRFB operating environment. However, the inner resistance of the membrane is higher than N117, leading to lower efficiency at high current density although the *EE* can achieve up to 76.3% at current density of 20 - 60 mA cm⁻². This study shows the potential of glass membrane application in VRFB. However, further study needs to be done like loading IEM particles or layers to improve the proton conductivity.

All of these membranes improve ion selectivity by narrowing the transport channel or adding IEM particles, and hence achieving higher *CE* at low self-discharge rate which means good stability. But the area resistance is still a problem, which leads to a similar or lower *VE* to Nafion. Comparing with pristine porous membrane and Nafion, they all have better stability and higher *EE* at low current density. Besides, due to the high stability and low cost, the porous material become a basic layer to loading ionic groups [181, 227] or an addition [139] to enhance the microstructure of IEM in the recent membrane development. By combining these two different membranes, the beneficial features can be combined.

4.5 The membrane used on air/Vanadium battery

As a new type of vanadium redox battery, air/V battery also needs a membrane to exchange proton. Till date, it still uses CEM which is also used in VRFB, such as Nafion and Nafion combined

membrane [228, 229], SPEEK and the combined membrane [230, 231]. However, since the air/V battery is not as stable as the VRFB, their efficiency and cell performances are also not so good. Thus, as the key factor, future studies on suitable membranes are still required.

4.6 The diffusion/crossover modelling of VRFB with different membranes

The dynamic model for predicting battery capacity by simulating self-discharge and side reactions would be invaluable in the development of sophisticated control systems for the VRFB. As one of the most important components in the VRFB, membranes are key factor to the diffusion/crossover modelling of the VRFB [232]. The early mathematical modelling of VRFB began around 1970s-80s at NASA, while the first model was published in 1988 at UNSW. [233]. This model explained the VRFB capacity decay caused by the diffusion and self-reactions, which are caused by the vanadium permeability of the membrane as well as the vanadium concentration imbalance between the two electrodes due to different crossover rate for the membrane.

To improve the accuracy of model, more complicated operation and controlled conditions were considered in the model analysis, and Zheng *et al.* [234] summarised different types of methods to VRFB modelling. Tang *et al.* incorporated the heat transfer into Skyllas-Kazacos and Goh's model to analyse the capacity of the battery by comparing the VRFB with three different membranes (Nafion 115, Selemion AMV and Selemion CMV) [235]. Ling *et al.* [236] took into account the impact of pulsating flow on the efficiency by using Nafion. Rajagopalan *et al.* [237] combined the effect of temperature change and bulk electrolyte transfer to analyse the working performance of battery with three different membranes. Won *et al.* [238] considered the reacting times and heat transfer in 3-D model to study fresh and degraded membrane in VRFB.

From these models which analysed battery working performance by combining membranes with other operating factors, it can be observed that the membranes which define the crossover rates of four vanadium ions have a fundamental impact to battery including self-reaction [239], permeability and state of health [36]. Besides, Doan *et al.* and Leung *et al.* have estimated that membrane contributes to 20% cost of the whole VRFB system (>USD\$ 200/kWh) [240, 241].

This high cost component has led to research into developing lower cost membrane for all three generations of VRFB systems.

4.7 The summary of membranes

A summary table comparing 84 main types of the membrane in this review is tabulated in Table.14 where half of these are published within the last two years (2017-2018). The table listed the properties including vanadium ions permeability, conductivity, and energy efficiency and working current density, preparation technologies, stability and cost of these membranes. As the VRFB energy efficiency with respect to membranes reported in these research papers is tested under different experimental conditions (temperature, current density, etc.), thus this table only offers qualitative data when the results are compared with the commonly used Nafion membrane. Furthermore, the membrane cost reported in these research papers are based on comparison with Nafion as a reference. However, they minimize the cost is due to reduction in the dosage of Nafion and using much cheaper materials during the preparation of the membrane product. Thus, fewer papers mention about the production cost such as machine used and the manual work undertaken, especially for the high-performance membrane (such as SPEEK-ETS-10 [222]) which uses over three kinds of material. Also, the method of production might take a large amount of the cost in quantity production. Thus, the cost of membranes summarized in this table is qualitative on material cost. except for Nafion and SPEEK membranes.

Among the membranes used, CEM is still the most commonly used and studied membrane in VRFB. CEM suffers from high permeability which prompts numerous efforts spent to overcome this shortcoming including adding anion groups or porous materials. And these developments lead to much more AIEM percentage in all membranes studied in recent times. The development of porous membrane is also very fast, including development of new materials like glass and PBI. Many research groups have focused on decreasing the pore size or increasing the number of pores channel to improve the conductivity and to decrease the permeability at the same time. In summary, the membrane which can combine the advantages of different ions group with cheap materials in a long life is the main trend of the membrane development. And with the cost

decrease and lifetime improvement of the membrane, the total VRFB systems will become an economical power store system to cooperate with other system like renewables integration in ramping up electric supply capacity in the future.

5. Conclusions

Different types of membranes used in the VRFB system, including their working principles, performance measurement, fabrication, and characteristics are summarized in this paper. The membranes used in VRFB can be classified into ion exchange membrane (IEM) and non-ionic porous membrane based on the ion selection principle. The IEM can be further divided into cation exchange membrane (CEM), anion exchange membrane (AEM) and Amphoteric ion exchange membranes (AIEM).

As a widely used commercial CEM, Nafion membranes have shown high chemical stability and excellent electro-chemical properties, however it suffers from high permeability and cost. Because Nafion membranes are using same material, the performance of them in VRFB is affected by thickness and the preparation methods which define their microstructure. Thicker membranes have lower permeability but higher area resistance, which affects the cell performance and membrane properties. To reduce the crossover rate of membrane, introducing hydrophobic additive and/or polymers have been applied on the Nafion. This leads to even higher Nafion membrane cost. Thus, other low costs CEM such as SPEEK or SPI based CEM have been developed and studied. Although these low-cost membranes show low permeability, they also have low conductivity and stability. Thus, like Nafion membranes, these low-cost CEM have also been modified to improve its desirable properties for VRFB by adding lower swelling ratio matrix. Recently, numerous porous membranes or materials have been used to enhance the stability of CEM and to date, CEM is still the most commonly used membrane in VRFB.

The main shortcoming of these CEM is the high permeability. AEM with the opposite exchanging ions shows much lower permeability. However, the low redox stability and conductivity limit the application of AEM. Researchers have spent efforts to overcome these shortcomings by changing

the microstructure or improving the *IEC* and water uptake through the introduction of additives.

AIEM have both types of functional groups which lead to reasonably better performances. But the complex preparations, which require controlling the balance between the densities of two functional groups, result in high cost. Consequently, most of AIEM researches are focusing on finding an easier method to produce better-balanced AIEM.

With different ion exchange principle, the non-ionic porous membrane offers an excellent mechanical and chemical stability at low cost. However, the ineffectiveness of the ion exchange worsens the performances of the membrane. To overcome this shortcoming, the pore size reduction or even adding functional groups are widely investigated.

Fabrication methods can affect the membrane performance. According to the summary table, most of the particles combined membranes are fabricated by solution casting method, while the multilayer membranes are made by a layer-by-layer self-assembly method. As the fabrication method can change the microstructure and hence its membrane performance and cost.

Hence, to improve the membrane properties, the composite membrane that can combine the advantages of different materials has been the main focus of research in recent years. Since permeability and conductivity are antagonistic, therefore most of the current membrane research is focussing on controlling the density of the additive in order to achieve better performance in the membrane. And to reduce the cost, the cheap materials are used as one of the combined matrices.

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- 1 • Review of membrane used in the vanadium redox flow batteries (VRFB) is
- 2 conducted.
- 3 • Working principle, working performance and cost of VRFB are discussed.
- 4 • Various methods of fabrication of the membrane products are explored.
- 5 • Methods to enhance CEM, AEM, AIEM and porous membrane are discussed.
- 6 • The challenges and future directions of membrane research are examined.

Recent Development of Membrane for Vanadium Redox Flow Battery Applications: a
Review

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Abstract

Responding to rapid growth of the renewable energy applications, it is crucial to develop low cost and high efficient large-scale energy storage systems in order to smooth out the intermittency of the renewable energy resources. As one of the most promising large-scale energy storage systems, vanadium redox flow battery (VRFB) has attracted great attention in recent times. Membrane is one of the key components of VRFB which not only affects the whole cyclability performance but also determines the economic viability of the system. The membrane separates the positive and negative half-cells and prevents the cross-mixing of vanadium ions while providing required ionic

conductivity. The ideal membrane should have good ionic exchange capacity; high ionic conductivity, low water uptake, swelling ratio, area electrical resistance and vanadium and other poly-halide ions permeability; and good chemical stability, as well as low cost. Numerous efforts have been spent on the development of different types of membranes, including different functional groups ion exchange membrane and non-ionic porous membrane. This paper reviews the research on membranes in VRFB system, including the properties, development of traditional commercial membranes as well as recently developed membranes. It explores various methods of fabrication of the membrane products which have received relatively little attention. A detailed summary table of the new membranes with their properties, fabrication and costs is provided to serve as a reference guide for researchers and industrialists interested in VRFB system building and dynamic modelling set. Subsequently, the challenges and future directions of membrane research are examined.

Keywords: vanadium redox flow batteries, membrane, properties.

Nomenclature

1. Introduction

1.1 Introduction of vanadium redox flow battery

With the development of technology and increasing of population, the global energy consumption will increase to 53 billion kWh in 2020 [1]. To meet the substantial daily needs of electrical power usage without environmental degradation caused by depletable fossil fuels, renewable energy and smart grids have become topics of current research interests [2]. A key point of this is to develop a large scale energy storage system which can smooth out intermittent renewable energy sources induced by the environmental uncertainty [3], to deal with the problems of peak-shaving, emergency back-up and so on [4], and incorporate an effective demand-side management (DSM).

Among the traditional large-scale storage systems, electro-chemical energy storage system,

especially the secondary redox flow battery has attracted the most attention nowadays [5]. The lithium-ions battery, which is a commonly used commercial battery product, has long life cycles and high energy density. But the cost of the battery material-lithium is much higher than the vanadium since the later one is abundant in nature [1]. The lead-acid battery is another commercial batteries with low cost and it is a good candidate to large-scale storage system [6]. But the lifecycles and energy density of traditional lead-acid batteries are much lower than lithium battery system, and the environmental damage it causes especially to water resources is also a big problem.

The Ragone plot in *Fig. 1* [7] shows the power vs energy density profiles of different energy storage systems, including the different batteries and the VRFB, which supports the viability of the VRFB batteries.

Thus, vanadium redox flow battery (VRFB) with large availability, high energy efficiency, low capital cost, long life cycle [8, 9] and low-toxicity is currently one of the most competitive electro-chemical secondary battery storage systems. Till date, VRFB already has been tested in Germany (0.3 MW/1.3 MW h), Italy (0.45 MW/1.44 MW h) and the USA (2 MW/8 MW h) [10]. It is widely believed that the VRFB has the potential to cooperate with other systems such as renewables integration including photovoltaic (PV) systems [11] and wind power [12] in ramping up electric supply capacity [5] in the future.

Though research into VRFB started in the mid-1980s [13] at the University of New South Wales by Skyllas-Kazacos research group, however, this Generation 1(G1) VRFB was only significantly promoted throughout the early 2000s [14]. The chemical reactions of the G1 VRFB are based on the following equations:

At the positive electrode:

At the negative electrode:

88

89 Although G1 VRFB reduces the problem of electrolyte cross-contamination, its application is
 90 limited by its low specific energy (15-25 Wh·kg⁻¹) and narrow working temperature range
 91 (10°C-40°C) [15, 16]. Further research on exploring the alternative solution to improve the
 92 solubility of the vanadium ions were carried out and led to the second generation 2 (G2 V/Br). G2
 93 uses a mixture of vanadium chloride and vanadium bromide as the electrolyte [17]. The reactions
 94 of the G2 V/Br are based on the following formulation:

95

96 The positive electrode:

98 The negative electrode:

100 Where open-circuit voltage at 50% state of charge = 1.1-1.2 V [18]

101

102 The specific energy of G2 is higher than G1 at 25-50 Wh·kg⁻¹ due to the higher solubility of
 103 vanadium bromide [14] than vanadium sulphate, as well as wider temperature range(0-50°C) [19,
 104 20]. However, the G2 V/Br still faces high-cost issue because of the need to use expensive
 105 bromine complexing agents to prevent potential release of bromine gas.

106

107 Recently, researchers from Pacific Northwest National Laboratory (PNNL) in the US offered an
 108 improved VRFB system (G3) with mixed H₂SO₄/HCl electrolyte solutions in both half-cells to
 109 improve the stability and the solubility over a wider range of temperature. Comparing with the G1,
 110 G3 has higher stack efficiency, wider range of operating temperature which means simple system
 111 design and operation with low capital cost caused by temperature control [21]. Also, the high
 112 energy efficiency could be achieved without thermal precipitation. Comparing with the G1, G3
 113 has faster reaction kinetics, there is no chlorine gas evolution during charging, up to 1.5V in G3.

114

115 1.2 The introduction of membranes used in the VRFB

Typically, a redox flow battery has two soluble redox couples in solutions to achieve the oxidation and reduction reactions. VRFB stores energy in two vanadium solutions contained in two different electrolyte tanks, and exchanges ions through the membranes in the reaction cell by pumping the solutions from the tanks [22]. This structure shown in *Fig.2* implies that the VRFB can increase the battery capacity by adding more solutions in a larger tank and it can increase the power output by adding more reaction cells. The all-vanadium redox flow battery developed at the University of New South Wales shows a high energy efficiency (over 80%) [13] because it uses the same vanadium element in both half-cells, and thus avoids the problem of cross-contamination which occurs in other battery types having different electrolyte elements in both half-cells.

The membranes used in VRFB can be classified into ion exchange membranes and the non-ionic porous membranes. The ion exchange membranes include the cation membrane, anion membrane, and amphoteric ion exchange membrane, depending on the type of ionic functional groups attached to the membrane. The ideal membrane should have good ionic exchange capacity, high ionic conductivity, low water uptake, low swelling ratio, low area electrical resistance and low vanadium and other polyhalide ions permeability, good chemical and thermal stability, as well as low cost. In order to find suitable membranes, different technologies and materials are developed in recent years. In this paper, recent research works focussing on the development of other low cost and high-performance membranes are summarized.

1.3 Contribution of this study

- 1, It conducts a complete and critical review of the membrane used in the VRFB system, especially with respect to the fabrication of the membrane which is still almost unexplored.
- 2, It summarizes recent research results of the membrane developed in VRFB systems. A summary table is provided of new membranes with the vanadium ions permeability, conductivity, the energy efficiency and the working current density, the technologies, the stability and the cost, to serve as a reference guide for researchers and industrialists interested in VRFB system building and dynamic modelling set.

3, The feature of four different types of membrane as well as future research trend are concluded.

1.4 Organization of the paper

The key point of this paper is divided into three parts, including how to measure the properties of membrane, how to fabricate them and the detailed comparison of four different types of membrane which include CEM, AEM, AIEM and porous membrane. In the first part, section 2, 12 different experimental measurement methods of membranes' main properties are summarized. Then, in section 3, the manufacturing methods of different types of membrane are studied, as well as four typical membrane preparation methods introduced step by step. Finally, in section 4, these four different types of membrane are studied. They are analyzed in general at the beginning, including the advantages and disadvantages. After that, different membranes, especially the recently published ones are introduced with respect to their shortages and the penalties that accompany their improvements. The working condition and performance with their reasons are stated. Some membranes used in the same material, but different structure or manufacturing methods are compared. At the end of each main types studied, the main method to mitigate the problems of this kind of membrane are summarized, as well as the main shortage after development when compared with the commercial membrane Nafion. Moreover, at the end of section 4, it is concluded with a summary table of recent development and future research trends.

2. Measurements of membrane performance

Experiments are usually conducted to assess the membrane performance and properties. These experiments are described in the following sections.

2.1 Cell performance

The performance of membrane is usually assessed through charge discharge test in a VRFB cell. Based on the measured single cell's charge-discharge behaviour, the coulombic efficiency (*CE*), the energy efficiency (*EE*) and the voltage efficiency (*VE*) which are the main parameters of the

VRFB systems can be determined according to the following equations, respectively [23]:

$$CE = \frac{\int I_d dt}{\int I_c dt} \times 100\% = \frac{\sum_{j=0}^{m-1} \frac{1}{2} (I_j + I_{j+1}) (t_{j+1} - t_j)}{\sum_{k=0}^{n-1} \frac{1}{2} (I_k + I_{k+1}) (t_{k+1} - t_k)} \times 100\%, \quad (5)$$

$$VE = \frac{\sum_{j=0}^{m-1} \frac{1}{2} (V_j + V_{j+1}) (t_{j+1} - t_j)}{\sum_{k=0}^{n-1} \frac{1}{2} (V_k + V_{k+1}) (t_{k+1} - t_k)} \times 100\% \quad (6)$$

$$EE = CE \times VE = \frac{\int V_d I_d dt}{\int V_c I_c dt} \times 100\% \quad (7)$$

180

181 where I_c , V_c , I_k , V_k , t_k denote the current, the voltage and the reaction time during the charge, while
 182 I_d , V_d , I_j , V_j , t_j denote the current, the voltage and the reaction time during the discharge
 183 respectively.

184

185 2.2 Membrane properties

186

187 2.2.1 Ion exchange capacity (IEC)

188

189 Ion exchange capacity can be calculated by a back-titration method [24, 25]. Firstly, the
 190 membrane is immersed in 30 ml HCl (0.01M) for 18 hours, and then the resulting solution is
 191 titrated with NaOH (0.01 M). After that, the membrane is rinsed with 18.2 MΩ cm water, dried in
 192 a vacuum desiccator for 24 hours, and weighed. The amount of H^+ and OH^- can be calculated from
 193 titration, and the ion exchange capacity is calculated by the following Eq. (8):

$$IEC = \frac{C_{HCl} V_{HCl} - C_{NaOH} V_{NaOH}}{m_{dry}} \quad (8)$$

195 Where C is concentration, V is volume, and m is the mass of the dried membrane following
 196 titration.

197

198 2.2.2 Water uptake (WU), swelling ratio (SR) and water transport.

Water uptake refers to the ratio of absorbed water weight to the dry membrane weight, while the swelling ratio means the ratio of length change from dry to wet membrane [26]. The membranes are soaked in de-ionised (DI) water for 24 hours at the room temperature firstly, then the membranes are dried under vacuum at 80°C for 24 hours. After that, the WU and SR can be calculated using *Eq. (9)* and *Eq. (10)*:

$$WU = \frac{W_w - W_d}{W_d} \times 100\% , \quad (9)$$

$$SR = \frac{L_w - L_d}{L_d} \times 100\% \quad (10)$$

Where W_w , W_d are the weight of membranes after and before absorption respectively, while L_w , L_d are the length of the wet and dry membrane respectively [27].

The diffusion coefficient and release time of water in the membrane can be measured by the water transport parameters [28]. To test the static water transfer across the membrane, a typical experiment was designed by the Mohammadi *et al.* [29]. In the experiment, each half cell was simulated at the 50% state of charge (*SOC*), the solutions of half cells are used as followed:

A tube is connected to each cell as shown in *Fig. 3*, and the electrolytes are delivered through the tubes. As the initial solutions in each half cell are at the same level; therefore, the volume change reflects the water transport of the membranes after certain duration.

2.2.3 Area resistance (R) and proton conductivity (σ)

The area resistance and proton conductivity are tested by the method designed by H. Vafiadis *et al.* [17]. The resistances of the cell with or without the membrane are recorded to estimate the resistance of membrane according to *Eq. (13)* [30]:

$$R = (r_1 - r_2) \times A \quad (13)$$

Where R denotes the area resistance of the membrane tested, r_1 and r_2 denote the resistance of the cell with and without the membrane, and A denotes the area of the membrane. The membrane thickness is neglected in this calculation.

The proton conductivity experiment was carried out by Chen *et al.* [31]. Because the membranes are tested in DI water, the proton conductivity $\sigma_{//}$ of the membrane can be neglected. The overall proton conductivity can be calculated by Eq. (14):

$$\sigma = \sigma_{\perp} = \frac{l}{Ar} \quad (14)$$

Where l denotes the thickness of the membrane, A denotes the area of the electrode area, and r is the resistance value measured. The conductivity of the membrane increases roughly linearly with increasing water content [28].

2.2.4 VO^{2+} permeability (P_0) and ion selectivity (S)

The concentration of ions can be calculated through the absorbance of the solution by the UV-Visible spectroscopy [32] according to Beer's Law. Skyllas-Kazacos and co-workers set a standard permeability test [33]. In this experiment, two cells (A and B) are set and divided by a membrane. Initially, cell A contains 1 M VOSO_4 and 2 M H_2SO_4 solution, while the cell B contains 1 M MgSO_4 and 2 M H_2SO_4 . MgSO_4 in the cell B are used to balance the osmotic pressure between the two solutions and to decrease the effect of water transport across the membrane. The diffusive permeability P_0 can then be calculated by Eq. (15):

$$P_0 = -\frac{V_B l}{2At} \ln \frac{A_0 - 0}{(A_0 - B) - B} = -\frac{V_B l}{2At} \ln \frac{A_0}{A_0 - 2B} = -\frac{V_B l}{2At} \ln \frac{1}{1 - 2x_B} \quad (15)$$

Where V_B is the volume of each cell, l is the thickness of the membrane, t is the time of reaction, A_0 is the initial absorbance of solution A, B is the absorbance of solution B, and x_B is the

concentration of crossover species in B side normalized by the initial concentration in cell A.

Ao Tang reported that the unbalanced diffusion of different values of vanadium would cause an accumulation of the vanadium ions, which then led to a slow loss of capacity. However, this problem can be restored by remixing the solutions in two tanks periodically[34]. The capacity loss was also studied by Skyllas-Kazacos [35].

Ion selectivity S can be calculated once the proton conduction value is known by *Eq. (16)* [36]:

$$S = \frac{\sigma}{P_0} \quad (16)$$

Where σ denotes the conductivity.

2.3 Chemical stability

Because the membrane used in VRFB system is immersed in the highly oxidising electrolyte, chemical stability is a major limiting factor of membrane lifetime. Long-term chemical stability can be evaluated using three different approaches [37].

In the first approach, a pre-weighted sample (0.30 g) is soaked in a 25.0 ml solution containing 0.1 M V(V) ions. The oxidation of membrane by yellow V(V) ions leads to the formation of blue V(IV) ions. The concentration of the vanadium ions can be measured using the ultraviolet absorption spectrometry and calculated based on Beer's Law. In this case, the concentration of V(IV) ions is estimated at wavelength of 765.5nm which is the maximum absorbance of V(IV) ions [38]. The concentration of the solution is monitored periodically to determine the rate of oxidation. To standardize the method for comparison study, the experiment is repeated at a constant area (10.5 cm × 5.0 cm), and different ratios of solutions are prepared with mixtures of 0.1 M V (IV) and 0.1 M V (V) solutions.

In the second approach, the membranes are exposed to 2.0 M V(V) solution of the VRFB, and then the cell performances, area resistance, vanadium permeability and *IEC* values are measured

periodically.

The last technique is to test the membranes under continuous charge-discharge cycling, and the cell performances are evaluated to indicate any changes of the membrane caused by fouling (by monitoring area resistance) or degradation.

3. Fabrication methods of different membranes used in VRFB system

Although there are several existing review papers which summarized the membranes in the battery system, very few of these focused on the details of membrane manufacturing methods, which is an inevitable process in the research of membrane study. In other words, fabrication of the membrane products has received relatively little attention. The fabrication methods not only impact the microstructure of the membrane as well as the structure of loading additions but also influence the cost of the membrane products. In this section, first, the classification of membranes including their operating principles are introduced. Then, the general preparation of these different types of membranes are studied. After that, the typical membrane preparation methods are introduced. Finally, the environmental impacts of the membrane preparations are summarized.

3.1 Approach to classify membrane

According to the bulk structures [39], materials [40] and applications, VRFB membranes used can be classified into ion exchange membrane and non-ionic porous membrane. For the ion exchange membrane, the H^+ or OH^- are exchanged by the functional ion groups, while the non-ionic porous membrane prevents big ions to migrate across the membrane by physical barrier. And the information on membrane classification is shown as *Table 1*.

Ion exchange membranes are made of cross-linked linear polymer chains in a three-dimensional network where the functional groups are attached to enable the exchange of ions. The ions which are attached to the membrane can move inside and out of the membrane [41]. Hence, the rate of ions transport depends on the strength of the bond, as well as the density of electrolytes. Based on

ionic functional groups attached to the membrane, ion exchange membrane can be classified into five types of membranes: cation exchange membrane (CEM), anion exchange membrane (AEM), amphoteric ion exchange membrane (AIEM), bipolar ion exchange membrane and mosaic ion exchange membrane [42].

Cation exchange membrane (CEM) contains negatively charged groups, like sulfonyl (-SO₃H), carboxyl (-COOH), phenol group and other acidic functional groups which can ionize H⁺ to exchange the positive ions in the solution. In contrast, anion exchange membrane (AEM) contains positively charged groups, like quaternary amine (-NRH₃) and other basic groups which can ionize OH⁻ to exchange the negative ions.

Amphoteric ion exchange membrane (AIEM) has both anion and cation exchange groups randomly throughout the membrane. *Fig.4* shows the ion exchange process of an anion particle. Bipolar ion exchange membrane has both cation exchange membrane layer and anion exchange membrane layer (bi-layer membrane) while mosaic ion exchange membrane has both two exchange groups over the cross-sections of the membrane [43]. These three membranes all contain two different ion groups, but the existing forms are different. For the applications in the VRFB, the AIEM with less cost is the best option in three.

The reaction of anion exchange membrane is shown in *Eq. (17)* [44]:

The ion exchange process of CEM is depicted in *Fig. 5*.

For the porous membrane, without functional ion exchange groups, microporous separator selects electrolyte through physical barriers. The size difference between vanadium ions and protons makes it possible to use pore size exclusion to separate the electrolyte. Generally, the microporous membrane is made from a variety of inorganic, organic or natural materials, and contains pores or holes with diameters greater than 50-100Å [45]. Comparing with ion exchange membrane, the porous membrane can achieve high chemical stability due to the physical exchange method and

material selection [46]. Besides, the porous membranes are highly conductive in strong acid electrolyte environment of VRFB systems because it can absorb sulfuric acid which comes from the electrolyte and becomes conductive for protons [47]. In addition to the low cost, it is a promising membrane used in the battery, as well as additional layer to enhance the properties of other membranes [48].

3.2 General preparation of the membranes

Besides the chemical nature of the polymer matrix and the functionality bound of the material, the production method is another factor that determines the properties of the membrane. It is important to note that preparation method can affect the morphology of the membrane, which then will impact the ions transport properties and swelling behaviour of the membrane.

Basically, three essential criteria are required for an ion exchange membrane preparation [42], namely:

- 1) It has to be a membrane to select ions;
- 2) It is insoluble in solvents;
- 3) It has constant charges in the membrane.

Ion exchange membranes can be divided into heterogeneous membranes and homogeneous membranes based on their microstructures. For heterogeneous ion exchange membranes preparation, generally, powdered exchange resins are blended and heated with a thermoplastic polymer homogeneously at the beginning, and then the polymer blend is formed into the membrane by pressing and/or heating [49].

For homogeneous ion exchange membranes preparation, the approaches can be categorised into three types according to their starting materials [50, 51]. The starting materials include:

- Monomer which contains ion exchange groups. This monomer can be copolymerized with

the non-functionalized monomer to form an ion exchange membrane.

- The polymer films. The film can be modified by introducing ionic characters either directly by grafting a functional monomer or indirectly by grafting non-functional monomer followed by functionalization reaction.
- Polymer particles. The particles can be modified by introducing anionic or cationic moieties, and then embedded in a polymer binder and processed to make a foil (membrane).

For type 1 preparation, styrene and divinylbenzene are the commonly used neutral starting materials [41]. Basic strong AEM [52] are prepared by two steps, chloromethylation and quaternary ammonium attachment; while the CEM [53] are prepared by sulfonation. These methods to prepare the homogeneous ion exchange membrane have been reported by many research groups. [54, 55].

For type 2 and type 3 preparation, generally, the polymers are insoluble to any solvent. In such route, cation character is defined by carboxylic acid (weakly acidic) and sulfonic acid (strongly acidic). The former can be prepared by grafting acrylic monomer or epoxy acrylate monomers. For AEM preparation, the membranes can be made from analogous polymer films, which can be prepared by grafting or copolymerization of vinyl monomers [56, 57]. There are three main methods to produce the homogeneous ion exchange membrane (beside condensation) if the membrane is prepared by vinyl monomers polymerization. And the detail processes are described by Sata *et al.* in '*Ion Exchange Membranes*' [42].

For soluble solvents such as PEK-C, PEK, PS, PES or their copolymers, the preparation process of the membrane which can be transposed is as follows [58-60]:

- Introduce the moieties, including anionic or cationic ones;
- Dissolve polymer and cast it into a film.

However, since the polymers are soluble, the chemical stability often needs post-treatment, which includes crosslinking with diamine for AEM preparation [61].

For the non-ionic porous membrane, the main material is semi-crystalline polyolefin materials, include polybenzimidazole (PBI) [62] and polypropylene (PP). There are two types of fabrication of microporous membranes, including dry process and wet process. The detailed processes are described by Zhang *et al.* [63]. Also, the pore diameter of the film can be controlled through phase-separation method [64].

3.3 Typical preparation method

3.3.1 Radiation grafting method

Radiation grafting method is a traditional technique which is well-known for polymer surface modification since 1962 [65]. This method offers a good way to change the physical and chemical properties of the polymers. [66]

By using an ionizing radiation source such as Co, γ -rays, and electron-beams [67] to induce ionic chemical groups or free radicals on the polymers, a polymer main chain can be initiated from another monomer's polymerization [41]. That means it can combine two highly incompatible polymers into one material with both characteristics. Here, composition and properties of the membrane can be controlled by proper selection of the degree of grafting. Besides, grafting started with a film in membrane form that can overcome the sharpening problem [49]. Therefore, this method has been proposed as a valid option to prepare a variety of ion-conducting polymeric membranes [68]. However, the radiation grafting like UV-induced grafting and plasma grafting methods need reactors for irradiation, thus incurring high energy cost [69].

3.3.2 Casting method (solvent cast process)

Continuous solution casting process is a well-established plastic film manufacturing process which has been developed more than hundred years ago.

The production process is shown in *Fig. 6*. Once the first layer solidifies, the secondary film can [70-72] be added to the product through the same process with different mixture solution. It implies several layers can be encapsulated after multiple casting steps.

The advantages of this method include uniform thickness distribution, excellent flatness and dimensional stability [73]. Also, it can offer the ability to alter the membranes' properties, such as lubricity and strength based on individual layers [74, 75]. It can even transform a membrane from a symmetrical structure to an asymmetrical structure, so that it can increase selectivity without increasing hydrodynamic resistance [76]. Moreover, it allows other components to be incorporated into the structures. For examples, after forming a bare membrane, polymers such as PPEK, PPES or PPESK can be chloromethylated with a catalytic agent to produce the sites for quaternary ammonium groups. Another notable advantage is that it has lower manufacturing cost than conventional technologies due to the use of inexpensive materials and adaptability of the manufacturing line, such as injection mold components and extruded tubes made of high-performance polymers like PTFE, PEBAX, and polyimide [77, 78].

However, the shortcoming is that it might lead the coated surface layer to be swept away due to weak interaction between the membrane and coated layer [79].

3.3.3 Sol-gel method

The interest in sol-gel processing can be traced back to the mid-1800s and to date, over 35,000 papers have been published worldwide based on this method [80, 81].

As shown in *Fig.7*, various structures can be built because the sol-gel method is not a single process. Generally, the sol gel process can be described in the following steps [82-85]:

- **Mixing:** After hydrolysis and polymerisation, the desired metal alkoxides ($M(OR)_n$, where M is the metal and R is an alkyl radical), disperse in a liquid to form a sol.

- Gelation/Crosslinking: The deposition of solution products will generate different forms due to various processes as shown in the *Fig. 7* including coatings on the substrates to be xerogel film or the polycondensation which produces colloidal particles linked together to become a 3-D network;
- Aging/drying: The particles in solution are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network.
- Heating: The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating.

One of the distinct advantages of using this methodology is that it could form a high-temperature ceramic from a liquid at room temperature. This methodology can be used to deal with no heat application like the metal organic precursor. Also, it can precisely control over purity, as well as yield the highest specific surface area, including very thin film metal oxides [86]. But this method lacks universality since unique polymers are needed [69].

3.3.4 Layer-by-layer self-assembly method

As the name implies, layer-by-layer self-assembly method means a disordered system which forms an organized structure or pattern layer by layer spontaneously instead of external direction, as shown in *Fig. 8*. It is an eye-catching procedure for the formation of multilayer thin film by controlling architecture and composition [87].

Fig. 8 shows that the procedure includes alternating consecutive immersion (dipping) of a solid or flexible substrate in oppositely charged solutions. It is necessary to induce intervening rinsing step between each layer forming to remove the weakly attached molecules [79].

Many types of the assembly method have been developed, such as dip-coating, spin-coating, spraying, electromagnetic assembly and fluidic assembly [88, 89]. The detailed information is shown in *Fig. 9*.

The merits of the layer-by-layer self-assembly technique include:

- Better nanoscale organization and a higher degree of structure control. It accurately organizes the film thickness at the nanometer scale [90];
- Highly tuneable with parameters such as pH and ionic strength [91];
- Film properties improvement by changing the electrolyte types [79].

This method can alleviate the decrease of water flux and the increase of the hydraulic resistance [92], while some reports show that other grafting method might also reduce the water flux [69].

3.4 Environmental impacts

As widely accepted, the applications of the membrane are sustainable. However, for large-scale membrane fabrication, there are still potential environmental impacts since most of the membrane's preparations requires toxic solvent [93]. For example, the pristine Nafion membrane is generally prepared by the casting method containing DMF and DMAc mixtures [94], which are common solvents for membrane production. These two solvents are health hazards. The fabrication also contains processes that involve cleanings with corrosive inorganic solutions, such as H_2SO_4 . Besides, almost all additional polymers already mentioned are petroleum derivatives, including PEEK, PTFE, and PPEK. Thus, to decrease the environmental impact, biopolymers and eco-friendly solvents are required for inclusion in future research.

4. Characteristics of membranes

4.1 Cation exchange membrane (CEM)

4.1.1 Nafion

The chemical structure of Nafion is shown in *Fig. 10*. It combines a hydrophobic Teflon-like backbone with hydrophilic ionic side groups [95].

Among the perfluorinated sulfonic acid cation exchange membranes (CEM), Nafion is still among the best available and commonly used membrane in VRFB due to its remarkable properties including:

- High water swelling ratio and proton conductivity [96]. Because of the sulfonic acid group ($\text{-SO}_3\text{H}$) added into the polymer backbone, when materials are exposed to water, the hydrolyzed form ($\text{-SO}_3^-, \text{H}_3\text{O}^+$) appears and makes proton transport across the materials [97].
- Excellent electro-chemical properties [98].
- High mechanical strength and chemical stability [98]. It shows low release rate of degradation and high resistance to chemical attacks [97].
- High thermal stability and operation temperature range (up to 190°C) [97, 99].

However, it still has shortcomings, which limit its practical application in VRFB system, including:

- High cost [100]. At present, the price of Nafion ranges from $\$500$ to $\$1000 \cdot \text{m}^{-2}$, though this cost is forecasted to be lower at $\$200 \cdot \text{m}^{-2}$ in the future according to detailed economy analysis by Minke *et al.* [101].
- Fast crossover of vanadium ions and low ion selectivity[32]. It will lead to the decrease of *EE* and capacity loss in VRFB system quickly [95, 97, 99]. Also, with the increasing current density on the polarization curves, it will drop the cell voltage [102] .
- High Ohmic loss at high current density, and proton conductance deterioration at low humidity or high temperature [74].

Although other membranes with lower cost and better cell performances have been developed, it is still difficult for these membranes to be used widely due to their poor chemical stability. As a result, Nafion membranes are still currently applied in most large-scale VRFB system [103].

4.1.1.1 Typical commercial Nafion

Nafion is a commercial product of DuPont [104]. The typical commercial extruded Nafion series include N115, N117, and N112 as well as N1135 and N1100, while the dispersion-cast ones are coded as NR211 and NR 212. The thickness of commercial Nafion ranges from 25 μ m (NR211) to 183 μ m (N117). The minimum membrane thickness value of 25 μ m is set because if the thickness of the membrane is below 25 μ m, the mixing of the hydrogen and air (or oxygen) reactant gasses would result in an efficiency loss [105]. Some fundamental parameters of Nafion are listed in Table 2 [103, 106]:

Many literatures have compared the performance of these traditional Nafion membranes in VRFB application. Jiang *et al.* and Slade *et al.* compared N112, N1135, N115 and N117 [103, 105], Peron *et al.* compared N1110, N117, N115, NR212 and NR211, Reed *et al.* compared N115, NR212 and NR211 [107], Kraytsberg *et al.* compared N112, N115, N117 and N1110 [97], Teng *et al.* and Jeong *et al.* compared NR212 and N117 [100, 108]. Because of the similar chemical structure, the properties of Nafion membranes can be determined by the thickness and other operational factors such as current density, operating temperature, and state of charge. Based on these papers, the performance of the Nafion membranes are summarized in the following sections.

1) Cell performances

Current efficiency (*CE*) is determined by electrode corrosion, side reaction and vanadium ions permeability, while the first one can be controlled by the charge voltage or material [109], the second one can be reduced by the N₂. The last one can be reduced by increasing of the thickness so that the order of *CE* is N117 > N115 > N1135 > N112, while NR 212 and NR 211 are higher than N115 which might be attributed to their different micro-structure due to different preparation methods. Besides, *CE* will be higher at higher current density [103, 110].

Voltage efficiency (*VE*) decreases with the increase of area resistance or current density. This is due to the internal loss, including ohmic loss, activation loss and, mass transfer loss caused by membrane thickness. Hence, thinner membrane will have higher *VE*. The order of *VE* is N112 > N1135 > N115 > N117 [103]. It is also important to note that higher current density results in

higher ohmic losses which eventually leads to lower *VE* [111].

Energy efficiency (*EE*) is used to evaluate the energy loss during the charge-discharge process, which is affected by *CE* and *VE*. The order of *EE* is $N117 > N115 > N1135 > N112$ [103], while NR 212 and NR 211 have similar *EE* values which are still higher than N115 [107]. High current density will lead to lower *EE* [111] for the same membrane.

2) Membrane properties

The ion exchange capacity (*IEC*) of these Nafion membranes are similar and close to their theoretical value of $0.91 \text{ mmol} \cdot \text{g}^{-1}$ due to their similar ionomer chemical structure [103].

With respect to water uptake(*WU*) and swelling ratio(*SR*), a small difference is observed which is due to the slight difference in their inside micro-structure [112] under similar membrane thickness. Thinner membranes such as N112 will lead to higher *WU*. which is likely due to easier to absorb water [103]. Other pre-treatment factors such as temperature can also affect the water uptake [105]. High *IEC* can also lead to high *WU* [113].

Proton conductivities of Nafion membranes show similar values ($100 \text{ mS} \cdot \text{cm}^{-1}$) [103]. This is mainly due to the fact that proton conductivity is determined by *IEC*. High *IEC* means high concentration of protonic charge carriers and high activation enthalpy [113], thus, their similar *IECs* result in similar conductivity values. Higher water contents can also improve conductivity [44, 113]. For the same membrane, the conductivity can be increased with increasing temperature and hydration number [106].

The area resistance of Nafion membrane increases with increasing thickness, which can be explained through the Ohm's law. However, this relationship is not linear. The area resistance is also affected by uneven water distribution and current density [105]. The order of area resistance is $N117 > N115 > N1135 > N112$ [103].

Vanadium permeability of Nafion decreases with increasing membrane thickness. As thicker membrane leads to longer and more complicated water channels, water and ions diffuse through the membrane will decrease at the same time [95] under similar micro-structure.

3) The cycling performances

After charge-discharge cycling, the capacity fades due to vanadium ions crossing. The crossover results in self-discharge, side reaction which then leads to the imbalance of volume and concentration of vanadium between the two half-cells [14, 48]. Thus, thicker Nafion membranes, having lower vanadium permeability, will have better cycling performance. However, the capacity fading and electrolyte imbalance can be partially addressed by remixing the electrolytes periodically.

Furthermore, the charge-discharge time is also a factor that can affect the cycling performance. For membrane working at high current density, their capacity fading rate will be lower. [103]

4) Membrane cost

Minke *et al.* [101] reported that the price of N117 would not fall below $\$62 \cdot \text{m}^{-2}$ since the costs of input material and production were estimated to be $\$35 \cdot \text{m}^{-2}$ and $\$27 \cdot \text{m}^{-2}$, respectively. . Hence, consideration other operational costs and profits, the price of the N117 was estimated to be in the range of $\$500\text{-}1000 \cdot \text{m}^{-2}$ with the possibility of reduction to $\$200 \cdot \text{m}^{-2}$ in the future.

5) Summary of Nafion

The relationships between different properties of Nafion membranes are summarized here. Membrane thickness is the main factor in determining the performance of the Nafion membranes because they all have similar chemical structures. Thicker membrane will have lower permeability but higher area resistance, which will then affect the properties of the membrane and cell performances. In order to find the optimized thickness to keep a balance between these two factors,

comparative research was carried out where N212 was found to give a better performance [107, 111].

However, membrane thickness is not the only factor that influences the cell performance. Xi *et al.* [114] evaluated the cell performance using different kinds of CEM and AEM within a working temperature range of -20–50 °C, including Nafion 115 and Nafion 212, the Selemion CMV, and the promising candidate SPEEK and anion exchange membranes (i.e. the Selemion AMV and APS). The study indicated N115 membrane was the best choice for VRFB application at all climate due to that lower crossover rate and better chemical stability at all temperatures. Besides, current densities, state of charge or other cycling conditions as well as production. also affect the membrane performance. Thinner membrane is more suitable at high current density while thicker one is better for low current density in VRFB system [103]. The membrane conductivity can also be enhanced by sulfuric acid in the electrolyte resulting in increasing proton concentration in the membrane [110, 115]. Hence, to optimize the battery system, it is necessary to find suitable membrane to balance between performance, operation environment, and electrolyte composition.

4.1.1.2 Nafion composite membrane

To address the high vanadium crossover rate in Nafion membrane, different kinds of composite membranes based on Nafion have been proposed including addition of additives such as SiO₂ [99], TiO₂ [116, 117] and other inorganic materials or metal thin film. Nafion could also be incorporated with other layers such as SPEEK [118], PTFE [100], GO [119, 120], PP [121] membrane or fluorocarbon surfactant [98]. The research on nanocomposite membranes and multilayer structure are currently on-going to achieve better properties.

Kim *et al.* [122] developed a silicate D-AMH-3 layer on Nafion by solution casting and hot pressing method, and this layer acts as a selective layer to reduce the crossover rate of vanadium ions. The low crossover rate improves the capacity and *CE* when compared with N117. However, this Nafion-based composite membrane (ND) has higher cell resistance, which leads to slightly lower *EE* at higher current density but higher *EE* at lower current density. Stable cycling ability is also observed for over 100 cycles. Its sandwich structure also improves the membrane lifetime.

Interestingly, the increased cell resistance can be reduced by optimizing content and modifying the surface. The cycling test results under $40 \text{ mA}\cdot\text{cm}^{-2}$ current density are tabulated in *Table 2*.

Yang *et al.* [123] prepared a colloidal silicalite-Nafion composite membrane by suspension casting method. This membrane has a top layer of colloidal silicalite on the Nafion layer. The 5wt% composite membrane (ZNM-5) shows much lower resistance, higher energy efficiency, and better cell performances i.e. higher *CE*, *VE*, and *EE* in VRFB than N117. The composite membrane also has a good working stability and low permeability than N117, due to smaller zeolitic pores, which makes them accessible to water but does not allow the vanadium ions to diffuse. The detailed data are shown in *Table 3*.

Teng *et al.* [100, 124] developed a thin polytetrafluoroethene (PTFE)/Nafion (P/N) composite membrane by solution casting method or a sol-gel method. Comparing with NR 212 membrane, P/N membrane has lower *IEC*, conductivity, water transfer rate, vanadium ions crossover rate, water uptake and swelling ratio due to its thinner membrane and the hydrophobic nature of porous PTFE. Thus, the *CE*, *VE* and *EE* of the VRFB system with P/N membrane are higher at all tested current densities. The cycling stability performance of P/N is also better than NR 212, including better capacity retention ability and lower self-discharge. Besides, the cost of PTFE is lower than that of Nafion, and the lighter weight also makes P/N membrane cheaper. The experimental data of both NR 212 and P/N are shown in *Table 4*. In this table, the *SOC* starts from 50% while the current density is $40 \text{ mA}\cdot\text{cm}^{-2}$.

Teng *et al.* [32] tried to add silica into the P/N membrane to improve the water content later. This ultra-thin polytetrafluoroethene/Nafion/silica membrane (P/N/S) is prepared through solution casting method or sol-gel method at various nano-SiO₂ composition (including 1%, 3%, 5%, 7% and 9%). The introduction of nano-SiO₂ leads to reduction in the water uptake of P/N/S, which leads to lower conductivity and permeability. The P/N/S with 3% composition membrane (P/N/S–cast-3) shows better cell performances among all these composite membranes, as it has higher *CE* and *EE*, but lower *VE* due to lower proton conductivity. As a result of its lower permeability, the cycling stability of P/N/S is also better than P/N, including lower self-discharge

rate and good oxidation stability. Also, since the Si distribution of the membrane prepared by the sol-gel method is more homogeneous than solution casting method, the former has better membrane performance, indicating that homogeneous distribution of the nano-SiO₂ will improve the membrane properties. The result of this study is shown in *Table 5*. In this table, the *SOC* is 50% while the current density is 50 mA·cm⁻²:

As a new kind of carbon material, the graphene oxide (GO) can offer a new possible additive to decrease the permeability and improve the cell performances of the pristine Nafion by adding particle. GO related materials have high surface area and a unique two-dimensional layered structure, therefore the Nafion combined membrane can achieve higher water uptake and improved proton transport channels [125]. Thus, researchers use the GO to increase water uptake of Nafion to decline the permeability of vanadium ions. Through casting methods, Lee *et al.* [126] prepared a GO/Nafion117 composite membrane while Lue *et al.* [102] prepared a Nafion 212 /graphene oxide membrane (N212/GO). After comparing the composite membranes with a different weight fraction of GO additive and the Nafion type's membrane, the composite membrane's properties are much better due to lower value of the inter-planar space dimension. With the increase in GO content, the conductivity and permeability of the GO/Nafion decline. The SC-0.067 (spin-coated 0.067 wt% membrane) which has a 1-2 µm thin top well-aligned GO layer but low GO content (4.73×10^{-6} g·cm⁻²) shows the lowest permeability and highest cell performances.

After that, fibre which can create proton transport channels are analysed. The fibre materials can make the swelling ration decrease, and then leads to a higher ion selectivity. The fibre structure offers higher physical strength, which increases the stability of the membrane in the acid electrolyte. Abdul Aziz *et al.* [127] used porous ZrNT to fabricate a Nafion-ZrNT membrane. The resultant tubular structure of ZrNT gives lower permeability and higher physical strength, and thus displays higher water uptake, proton conductivity, and oxidation stability as well as lower swelling ratio, *IEC*, and activation energy than N117. Thus, it offers a higher performance of efficiency (*CE* 97.5%, *VE* 80.5%, *EE* 78.5%) at a current density of 40 mA cm⁻².

Similarly, Bang *et al.* [128] prepared a Nafion/PVA electrospun fibre-modified membrane. Because it is based on a porous Celgard PP membrane, the hydrophobic nature results in lower swelling ratio than NR 212. The electrospun fibre matrix has lower vanadium ions permeability due to reduction in permeability channels which leads to a better cell performance in the VRFB system i.e. higher *CE*, *VE*, and *EE* than NR 212 at all of the tested current densities. The porous supports also offer high mechanical stability. The detailed data are shown in *Table 6*. Thus, the electrospun fibre-modified Celgard membrane has lower crossover rate and better performance than the current commercial membrane Nafion.

Besides adding composites or other fibre-modified membranes, another important technique that affects the properties of the membrane is its structure, especially for the multilayer membranes. The loading layer might decrease the permeability of vanadium ions as well as the conductivity. To achieve a balance between these two factors, experiment for comparisons need to be conducted. Recently, Sun *et al.* [129] prepared (Nafion/(WO₃)_x) hybrid membranes. Different loading levels of WO₃ nano-filler (0.024 and 0.329) were added to the surface of a thin Nafion film by solvent-casting method. The combined material showed less hydrophilicity than Nafion, resulting in decreasing vanadium ions permeability (almost half of Nafion) but a slight decrease in conductivity. The hybrid membrane is stable under long term operation indicating long term dimensional stability of WO₃ nano-filler.

Similarly, S. Shi *et al.* [130] developed Nafion XL membrane with a sandwich structure where Nafions were added on both sides of the micro-porous PTFE-rich support layer. Because of the PTFE, the swelling behaviour can be reduced by increasing the thickness or decreasing the plane. Moreover, it will also reduce the conductivity by increasing in area or decreasing in thickness direction which is due to its resistances arising from PTFE or its interactions with the Nafion. Also, PTFE size could control the membrane stability and conductivity since the mechanical properties and stability will be affected by increasing transport resistance.

Moreover, a multilayer structure containing Nafion as middle layer has also been studied, including Nafion-(PDDA/ZrP)_n [131], Nafion-(PDDA-PSS)_n [96] and Nafion-(CS-PWA)_n [132](n

means the number of the multilayer added). The barrier layers are added to the surface of Nafion by a layer-by-layer self-assembly method. Because the ion-transfer pathway on the surface of Nafion is covered by the PDDA/ZrP, PDDA-PSS or CS-PWA, they all show lower permeability, higher *CE* and *EE*, lower self-discharge rate and similar stability than Nafion membrane. The number of layers can also influence the membrane properties, and among those multilayer structures studied, Nafion-(PDDA/ZrP)₃, Nafion-(PDDA-PSS)₅ and Nafion-(CS-PWA)₃ show better performance as shown in *Table. 8-10*, while the current density of Nafion-(PDDA-PSS)₅ tested is 20 mA·cm⁻², the Nafion-(PDDA/ZrP)₃ and Nafion-(CS-PWA)₃ tested is 30 mA·cm⁻².

4.1.1.3 Technology to enhance the performance

There are several methods that could be used to enhance the properties during preparation of the same membrane.

Zhao *et al.* [74] developed a low-polarity nonsolvent tetrachloroethylene(TCE) casting solution method and found it enhanced proton conductivity, water content and water permeability of the membrane due to the larger clusters of sulfonate groups in Nafion after casting. This solution makes the ionomer self-organized and also makes the original transparent Nafion made in DMF solution to be opaque.

Dai *et al.* [133] evaluated the effect of casting solvents (DMF, DMSO, NMP, EtOH) and annealing temperature (100, 140, 180) on the microstructure, proton conductivity, vanadium permeability and the cell performances of recast Nafion membranes. Though both of them can affect the membrane properties, the solvent effect was found to have more dominant effect on the properties of the recast membranes at lower temperature while the effect is insignificant at higher temperature. The crystallinity of membranes decreased with increasing annealing temperature, which means lower vanadium permeability. Higher temperature also offers better mechanical properties. Membrane prepared from EtOH has the worst properties. Single cell performance of membrane is also better when it is prepared at 180°C than at 140°C and 100°C when the same solvent is used.

Xie *et al.* [134] also indicated that pre-treatment can affect proton conductivity and vanadium ions permeability of Nafion. All membranes have similar or lower permeability after heat-treatment. Besides, they have similar and higher permeability after immersion in boiling sulfuric acid and water. Further, extruded membranes have higher permeability than casting ones, and this difference is largest for the membranes prior to electrolyte soaking. The difference becomes smaller after soaking in electrolyte and much smaller after soaking in water. All membranes display similar membrane selectivity after heat treatment. The selectivity could be similar or reduced after immersion in boiling sulfuric acid. Extruded membranes have lower selectivity than casting ones, and the selectivity worsen after being exposed to water at room temperature. The soaking time also affects the permeability of the membrane where vanadium ions permeability increases sharply during the first several hours in water and first several days in the electrolyte, however the increase eventually evens out thereafter.

4.1.2 Other cation exchange membranes

Although Nafion based membranes have high stability and excellent electrochemical properties, they still have high permeability and cost. Thus, efforts have been also spent to develop more cost effective and better permeability ion exchange membranes to Nafion such as poly (ether ketone) [135], poly (arylene ether) [136], poly (fluorenyl ether ketone sulfone) [137], poly (phthalazinone ether ketone) [138] and other polymers. The development of these membranes is described in the following sections.

4.1.2.1 SPEEK based membranes

Sulfonated poly (ether ketone) membrane(SPEEK) under all three generations of VRFB were evaluated by many groups, including Winardi *et al.* [135]. This low-cost membrane is prepared by casting method. The SPEEK membrane has lower resistance, slower self-discharge rate than N117, while it shows similar conductivity. Thus, it shows better cell performances, including slightly

higher *VE*, *CE*, and *EE*. Further, although Nafion membrane used in this paper is thicker than SPEEK membrane, the former one still had higher permeability due to the different microstructures. The cell performances tested at $40\text{mA}\cdot\text{cm}^{-2}$ current density are shown in *Table II*.

The swelling ratio of SPEEK is much higher than that of Nafion. This is caused by the high water uptake, leading to the decline in mechanical properties and lower mechanical stability. Also, although better than Nafion, its permeability is still high. Like composite Nafion membranes, the performance of the SPEEK can be improved by introducing inorganic materials into the polymer matrix, utilize the interaction of interfacial functional groups or tune the size of transport channels to selectively transport protons [139]. The additions can be particles like TiO_2 [140] and lignin [141], or nanotube like dopamine-modified halloysite nanotubes (DHNTs) [139], or nano layer like such as graphene oxide nanosheet [142], mesoporous silica hybrid membrane [143], or polymer layers like zirconium phosphate sulfophenylphosphonates (ZrPSPP) [144], graphitic carbon nitride nanosheets (SPEEK/g-C₃N₄), [145] poly (vinylidene fluoride-co-hexafluoropropylene) (P(VDF-co-HFP)) [25, 146], polymer (polysulfone-2-amide-benzimidazole, PSf-ABIm) [147], or porous polymer membranes like PVDF [148]. The performance of SPEEK membrane can also be improved by changing the microstructure of the SPEEK to integrally thin skinned asymmetric, like ITSA-SPEEK [149]. All these methods offer lower swelling ratio and hence good stability, and lower permeability than pristine SPEEK and N115 or N117. By keeping a good balance between the vanadium ions permeability and conductivity, their cell performances can also be improved i.e. higher *CE* and *EE*.

As the permeability and conductivity are antagonistic, their conductivity also decreases. To increase conductivity, other particles or functional groups are added onto the membrane, including carboxylic acid groups (C-SPEEK) [150], or higher moiety of sulfonic group which means a higher degree of sulfonation (DS) [151] have also been studied. C-SPEEK-50 showed better performance while S67-DMF showed good mechanical properties and high ion selectivity due to suitable DS and water uptake. With respect to S67-DMF, the performance of different casting

solution is also compared, and the DMF shows the best cell performances and life-cycles.

Recently, a mussel-inspired polydopamine coated carbon nanotube embedded SPEEK mixed matrix membrane (S/CNT@PDA MMM) has been studied by Yu *et al.* [152]. This group uses CNT@PDA filler mixed with SPEEK matrix to create more effective proton transfer pathway which contributes to higher conductivity. The acid-based interface and improved physicochemical property also lead to high stability of the membrane. The performance of this membrane was evaluated and compared with seven different SPEEK based membranes. The study indicates that, this membrane shows high *EE* (75.4%) and long-term stability at high current density ($200\text{mA}\cdot\text{cm}^{-2}$), with extremely low capacity fading rate (0.04% per cycle) over 1000 cycles. Although the comparison is made under different tested current density which means further experiments are needed to reach conclusion, this membrane offers a new potential low cost and high-quality matrix membrane for VRFB.

Chen *et al.* [153] developed SPEEK-PBI blend membranes for VRFB. The cross-link networks are created by transference of H^+ -SPEEK to Na^+ -SPEEK, which leads to more transfer tunnels and hence increase in conductivity. The 1.5% PBI in SPEEK has higher *CE* (from 0.724 to 0.985) and *EE* (from 0.669 to 0.898) than SPEEK membrane at $80\text{mA}\cdot\text{cm}^{-2}$ [153]. Furthermore, the performance of this membrane was tested for 350 cycles at 180mA cm^{-2} with no significant capacity fading observed. Moreover, its permeability is much lower than SPEEK.

4.1.2.2 Other polymeric CEM

Yin *et al.* [137] compared various degrees of branched(DB) for sulfonated poly (fluorenyl ether ketone sulfone)s (HSPAEEK) membranes prepared by solution casting method. Increasing DB results in membrane having higher conductivity, water uptake, and stability with lower swelling ratio but lower breaking strength. Thus, high DB will not improve all the properties of the membrane at the same time. Among various degrees of DB tested, the 8% degree of branching (DB) shows better performance so further experiment on VRFB system was set. HSPAEEK shows lower swelling ratio and proton conductivity than N117. It still has higher ion selectivity, *IEC*,

breaking strength, cell performances (*CE* and *EE*) at $80 \text{ mA}\cdot\text{cm}^{-2}$, and longer self-discharge time. The detailed data are shown in Table 11. HSPAEEK, being cheaper, is a promising substitute to Nafion Membrane for VRFB system.

Sulfonated poly (phthalazinone ether ketone) (SPPEK) backbone contains the special rigid unsymmetrical phthalazinone moiety, which makes it much more stable. However, the higher sulfonation degree leads to higher swelling ratio and vanadium crossover. To improve the proton conductivity of the low-cost SPPEK while maintaining low vanadium ions permeability, Wang *et al.* fabricated composite membrane based on SPPEK with tungstophosphoric acid (TPA) [138] by casting method or using WO_3 by a hydrothermal method [154]. Both composite membranes are more stable and have better permeability, lower area resistance but higher water uptake and better cell performances than N117 and SPEEK. Chen *et al.* [155] loaded pendant phenyl moieties on the SPPEK. Due to the aggregation of sulfonic acid functional groups on the side chains of the aromatic polymers, the membrane had hydrophilic/hydrophobic separation leading to improved proton conduction of the membrane. This structure makes the composite membrane much lower vanadium permeability where no permeation of VO^{2+} ions through the membranes was detected, even after 8 weeks.

Sulfonated polyimide (SPI) is another low-cost polymer which offers much low vanadium ions crossover rate as well as excellent stability. However, it has a lower conductivity than Nafion N117. Because of that, Li *et al.* has modified this polymer by combining with other materials to improve its conductivity including boehmite(AlOOH) [156], chitosan(CS) [157], ZrO_2 [158], TiO_2 [159], hydrophobic trifluoromethyl groups ($-\text{CF}_3$) [160], functionalized graphene oxide(ZGO) [27], molybdenum disulfide nanosheets($\text{MoS}_2\text{-ns}$) [161], sulfonated molybdenum disulfide (s-MoS_2) [162] and branched side-chain-type sulfonated polyimide membrane(6F-s-bSPI) [160]. All of them are much more stable than Nafion 117 due to their low self-discharge rate. Besides, they all have much lower vanadium ions permeability, which is nearly an eighth of N117, while SPI/ AlOOH and SPI/CS are one-tenth. Moreover, they all have higher *CE* and *EE* at tested current densities of $20\text{-}80 \text{ mA}\cdot\text{cm}^{-2}$ except SPI/CS which is only tested on $40 \text{ mA}\cdot\text{cm}^{-2}$. The weight percent of the additive can also affect the performance of the membrane. To keep the balance of

the ability like permeability and conductivity, 15% ZrO₂ or 10% ALOOH shows the best performance

Pu *et al.* [163] also studied branched sulfonated polyimide (bSPI). Their research compared the performance of SPI with different non-sulfonated diamine monomers including APABI, MDA, and BAPP. The bSPI (APABI) had the lowest permeability of vanadium ions ($1.7 \times 10^{-7} \text{ cm}^2 \cdot \text{min}^{-1}$) while bSPI (MDA) had the highest *IEC* (1.37 mmol/g). The bSPI (BAPP) had the best conductivity which overcame the shortage of SPI membrane. High conductivity leads to high efficiency in VRFB cycling. In addition to the good stability, the VRFB with bSPI (BAPP) has been tested for 500 cycles where the *CE* and *EE* was maintained at over 97.1% and 61.6% at 120 mA·cm⁻². The capacity decay is also comparable to N117. This group also studied the stability of SPI in VRFB [164].

Chromik *et al.* [165] compared the partially fluorinated membrane (S1B1) and the non-fluorinated membrane S2B2 with N117 and SPEEK, and found that the S1B1 shows better chemical stability with highest *CE* and stable *VE* and *EE* to those of N117 and S2B2. Besides, both of S1B1 and S2B2 have comparable power density to N117. This indicates the durability of membranes can be improved by adding blend components such as sulfonated ionomers and covalent cross-links.

Recently, the cross-linked structures which can enhance mechanical properties and long-term cycling stability of SPI are studied by Xi *et al.* [166, 167]. They compared SPI acid-based membrane synthesized under different proportions of imidazole rings and sulfonic groups. The intermolecular ionic cross-linking between sulfate radical and protonated imidazole groups create proton transport channels which can increase the conductivity of the SPI. SPI50 shows nearly 10 times lower vanadium permeability than N115 and shows the best performance in VRFB running compared to other SPIX. The reported higher *CE* and *EE* in VRFB by SPI50 than N115 under 40-160 mA·cm⁻² current density is likely due to the high conductivity and low permeability. The *EE* was maintained at over 75% for 400 cycles at 160 mA·cm⁻². This research group also compared SPI with the aforementioned SPI combined membrane and noted that the SPI50 offered better long-term performance at high current density. However, this comparison is made under different experimental conditions, thus further study needs to be done.

Yan *et al.* [168] introduced a controllable acylation with 4-fluorobenzoyl chloride long side chains onto the PPO backbone and subsequently congealed it with sodium 4-hydroxybenzenesulfonate to form S-L-PPO-51% membrane. Due to hydrophilic/hydrophobic micro-phase separation structure, this membrane keeps a good balance between the conductivity ($44 \text{ mS}\cdot\text{cm}^{-1}$) and permeability ($4.3\times 10^{-9} \text{ cm}^2\cdot\text{s}^{-1}$) which leads to good performance in VRFB system, including higher *EE* than N212 at various current densities. The *EE* was found to be 89.8% at $120 \text{ mA}\cdot\text{cm}^{-2}$, and *CE*, *VE*, and *EE* remained unchanged for 100 cycles at $80 \text{ mA}\cdot\text{cm}^{-2}$.

4.2 Anion exchange membranes (AEM)

Although many methods are applied to decrease the high vanadium ions permeability of CEM, this main shortcoming of the CEM still exists. This shortcoming can be addressed by using AEM.

According to Donnan exclusion effect, the quaternary ammonium groups in anion exchange membranes(AEM) can prevent cation ions including vanadium ions from going through the membrane [113]. In addition to their narrower hydrophilic channel in aromatic-hydrocarbon-based AEM [169], AEM has extremely low vanadium ion permeability and high *CE* in the VRFB system. But comparing to CEM, since the membranes are soaked in the strongly oxidizing electrolyte, AEM have typically lower redox-stability, especially in the positive half-cell. Besides, it may not assist in the conduction of protons, which decreases the *VE*. Thus, relatively, limited number of publications about AEMs for VRFB is found in literature, even other aqueous acid-based redox flow batteries [170]. Thus, researchers are trying to improve the stability and conductivity of AEM by increasing *IEC* and water uptake through microstructure changes.

The performance of Commercial AEMs are compared by Choi *et al.* [171], including ammonium-type AEM AHA and antifouling AEM AFN from the ASTOM of Japan, aminated polysulphone AEM APS from Asahi Glass Co.. Comparing with the larger membrane resistance and instability of AHA, AFN offers constant cell resistance under different *SOCs* and *SODs* (state of discharges). Besides, AFN also offers similar *EE* as N117, which means it can be a suitable

separator for VRFB.

Similar to CEM, AEM also uses the polymer backbones, including poly(arylether), like QADMPEK [159] poly(fluorenyl ether), like QA-PFE [172]; poly(phenylene)s, like QDAPP [173]; cardo-poly(ether ketone) (PEK-C) [174]; poly(phenyl sulfone), like PyPPSU [175]; poly(phthalazinone ether ketone ketone) which also belong to the poly(arylether), such as PyPPEKK [176], QBPPEK [177], QAPPEK [178]. These membranes have lower vanadium permeability, nearly 100% *CE*, similar or lower *VE* and higher *EE* than Nafion membranes due to similar or larger area resistance.

Based on these AEMs, factors affecting the properties of the membrane can be summarized in the following paragraphs.

The density of the functional groups and the monomer units permits are one of the keys to improve the membrane performance. Most of AEMs are using quaternary ammonium group as the functional groups, however, some researchers used other amine-functionalized groups like dimethylamine (DMA) [179], (3-glycidyloxypropyl) trimethoxysilane (GPTMS) [180], trimethylamine (TMA) [181], and further N-(trimethoxysilylpropyl)-N,N,N-trimethylammonium (TMSP-TMA) [169]. It was noted that additive groups can improve *IEC* and water uptake, leading to higher conductivity. Controlling the degree of the functional groups can also lower permeability and enhance the stability of the membrane, resulting in better *CE* and *EE*.

Attaching inorganic additives like nano silica [182], ZrO₂ [183] or BrPPO/Py-56 [184] with different density on the pure AEM can enhance the AEM microstructure. These particles are uniformly formed throughout channel networks which lead to a reduction of free volume for water uptake. Higher *IEC* and conductivity, as well as lower permeability than pristine AEM and Nafion can be achieved. Thus, the composite membranes have higher discharge capacity and *CE*. However, the long-term chemical stability and aging properties still need to be studied in the future.

Cha *et al.* [185] reported a polysulfone-based AEM (CAPSU-x) that could change the microstructure to enhance the membrane durability by crosslinking of the membrane with a primary diamine-based crosslinker at various degrees. Chloromethylated polysulfone is used as a precursor polymer for the crosslink, CAPSU-2.5 shows better performance. the crosslinked membrane offered much lower permeability ($0.272 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$). The conductivity was also improved especially at high temperature. The VRFB using this membrane showed high efficiency ($EE=0.86$) at $50 \text{ mA} \cdot \text{cm}^{-2}$ and excellent CE (almost 100%) up to the 100 cycles.

Moreover, the preparation process of the membrane, including the time, temperature and concentration of the amination process, can affect the membrane properties [70]. With the increase of these three factors, the IEC and water content of the membrane increase while the area resistance decreases. The stability of the membrane depends on the dimension change, which can be affected by high temperature.

Besides, the performance of AEM can be enhanced by their preparation method which can change their microstructure. For example, simultaneous polymerization and quaternization can result in low vanadium permeability due to the high degree of crosslinking, while the dimensional and chemical stability are still retained [186]. And Ma *et al.* [187] used side chain hydrolysis method load anion groups in the porous membrane. They built cross-links to enhance the microstructure by using TMHDA and give quaternary ammonium on a porous membrane and combined the beneficial features of AEM and porous membranes which means high ion selectivity and stability.

Sol-gel method can also change the microstructure of AEM by grafting other polymers, for example, ETFE-g-(VBTAC-co-HEMA) [67]. The degree of grafting (DG) can affect the properties of this composite AEM. With the increase of DG, the concentration of the functional groups and the degree of hydrophilicity are enhanced, respectively. The IEC and water uptake can also be improved. Similarly, the permeability of this composite membrane is also lower than N117 while it keeps stable after long time.

As operating condition can affect the cell performance, Yun *et. al* [168] found that increasing

current density resulted in better ion conductivity of anion exchange membrane.

4.3 Amphoteric ion exchange membranes (AIEM)

CEM has high ionic conductivity and good chemical stability, but the high vanadium permeability led to low *CE* and poor cyclability. For AEM, the vanadium crossover rate is much lower which offers them higher *CE*. But AEM also suffers low ionic conductivity which results in low *VE* and high rate of capacity loss.

The amphoteric ion exchange membrane (AIEM), which combines both properties of AEM and CEM, was proposed by Sollner firstly in 1932 [188]. Since AIEM has both two types of functional groups, it has both two membranes' advantages, including low permeability and high ionic conductivity [189]. However, since the permeability and the conductivity are antagonistic, the improvement will depend on percentages of these two functional groups. Besides, as the preparation of the membrane is complicated and expensive, the main direction of research is to find an easy method to produce low cost and stable AIEM with balanced density functional groups [190].

To introduce the anion functional groups on the CEM, many methods are used. Grafting methods were studied by Qiu *et al.* When combined with other preparation methods like sol-gel and solution phase inversion method, many membranes have been developed including grafting DMAEMA [191], DMAEMA and SSS [192], DMAEMA and AMS [193]. These membranes are prepared simultaneously through irradiation grafting technique on PVDF; or grafting St on ETFE-g-PS to be the ETFE-g-PSSA which can then be grafted by DMAEMA [194], or pre-irradiation induced graft copolymerization on ETFE [195]. Since higher grafting yield brings higher water uptake, *IEC* and conductivity, and higher content of DMAEMA which will lead to lower permeability and conductivity, the properties of the membrane can be controlled by choosing proper grafting conditions. All these membranes have significantly lower permeability and better cell performance than that of N117. They also have superior conductivity compared with PVDF. The long-time performance in which the *OCV* of the system can be maintained over

1.3V also indicates these three AIEMs can be good candidates for VRFB system.

Other methods can also be used to develop the AIEM.

Wang *et al.* [196] developed a solution casting method to control the density of the quaternary ammonium groups on SPEFK in order to decrease the permeability of the vanadium ions. Due to the Donnan exclusion effect, the AIEM-20% has 4.4% vanadium ion permeability of N115 while its stability and proton conductivity are comparable to SPFEK. Similarly, Yan *et al.* [197] also combined SPEEK with imidazolium-functionalized polysulfone (ImPSf) to reduce the permeability. Due to the Donnan repelling effect of the imidazolium cations on the vanadium ions and the low swelling ratio of the amphoteric membranes, the introduction of ImPSf can decrease the migration of vanadium ions efficiently. The amphoteric membrane with an ImPSf mass ratio of 17% shows much lower vanadium permeability and area resistance than NR212. This membrane shows higher *CE* and *EE* than NR212 at high current density. It can also keep *OCV* > 0.8V for twice the duration of NR212, indicating lower capacity decay on the VRFB system.

Lin *et al.* [110] developed a Nafion/amino-SiO₂ hybrid membrane which is filled with amino-SiO₂ nanoparticles (the amino group density is 9.85 nmol·cm⁻²) by electrostatic attraction through the sol-gel process. The membrane has lower vanadium ion permeability and higher *IEC* than Nafion N117 while almost retaining the same conductivity. Because of the additional amino groups on the exposed surface, the contact angle decreased, leading to lower permeability, resulting in higher *CE* (by 3.5%), *VE* (by 1.9%) and *EE* (by 4.2%) than N117's at current density of 80 mA·cm⁻². In the cycling test, the Nafion/amino-SiO₂ hybrid membrane also showed better chemical stability in both vanadium and acid solutions. The detailed data collected from this research group (*SOC* started from 75%, the capacity is 1920 mAh while the current density is 80 mA·cm⁻²) are listed in Table. 13:

Another kind of combined Nafion based AIEM was studied by Kondratenko *et al.* [198]. They combined Nafion membranes with amino groups of AATMS by sol-gel. With a balance between two kinds of functional groups, this combined membrane has improved proton conductivity and

ion selectivity.

Recently, Dai *et al.* [199] grafted zwitterionic SBMA (sulfobetaine methacrylate) onto N115 via SI-ATRP technique to build a novel AIEM named N115-g-PSBMA membrane. The RN_4^+ and SO_3^- enables the membrane to have both kinds of negative and positive exchange groups, leading to lower vanadium ions permeability than the pristine N115 membrane. Although the conductivity is lower than pristine N115, the low permeability contributes to better battery performance, including 2.6% higher *EE* than N115 at current density of 40-80 $\text{mA}\cdot\text{cm}^{-2}$. Further, the polymers used cheaper poly sulfone and poly ether ketone which also led to low cost of the membrane manufacturing.

AIEM with extreme low vanadium permeability known as cross-linked 60SPAEEK-6F-co-15%BI membrane was studied by Liao *et al.* [200]. The permeability of this cross-linked membrane was 1117 times lower than N117 due to narrow ion transporting channels, resulting in longer battery self-discharge time (3 times) and good proton conductivity. The cell performance was also improved or comparable to N117.

To reduce the cost of AIEM, Liu *et al.* developed AIEM by using low-cost backbone SPEEK with QAPEI through the blending method [201]. This membrane also offers a high degree of micro-phase separated structure which is beneficial towards ion transmission. The membrane had lower vanadium permeability and higher selectivity than N115. It was also very stable. The blended N-based functionalized graphene oxide (GO-NH_2) on SPEEK was also studied by this research group [202]. The blending layer which had $-\text{SO}_3$ groups and N-base groups was found to change the ion transport pathway structure of SPEEK, leading to higher conductivity and lower permeability than pristine SPEEK membranes. The combined membrane was tested on VRFB cell for 100 cycles where its capacity remained over 92%. This research group also developed a UiO-66 loaded SPEEK membrane [203] where they found that the ion selectivity and stability were improved due to the presence of micropore sizes of UiO-66 within the radius of protons and the additional material through hydrogen bonding.

Li *et al.* [204] developed a solvent-free strategy to cast poly(VBC-co-DVB)-PEKC-TEPA (ZPPT) onto PETEX between 2 PVC. The combined membrane showed low vanadium permeability, high chemical stability, and ionic conductivity. It also offered higher *CE* than N117 and better cycling ability.

4.4 Non-ionic porous membranes

Beside ion exchange membrane, non-ionic porous membrane with their excellent mechanical, chemical stability and lower cost has also attracted much attention for VRFB application. Without functional groups, they exchange the proton through the pores while the vanadium and other polyhalide ions are rejected because of pore size exclusion effect [205]. However, since its ion selectivity is not as effective as the IEM, these membranes have higher permeability. The high crossover rate will lead to imbalanced transport of vanadium ions between the positive and negative side, in addition to the self-reaction, and finally result in unbalanced concentration, volume change and capacity decay [206, 207] which ultimately leads to bad cell performances.

To address this problem, Zhou *et al.* carried out more research and set a model on how the porous membranes influence ion transport through the porous separator [208]. The factors include the pore size, electrolyte flow rate and membrane thickness and operation mode based on nanoporous polyvinyl chloride (PVC)/silica separator. The transport mechanisms can be divided into three types, namely diffusion, convection, and migration. When the pore size decreases to 15nm, convection, the dominant crossover mechanism is minimized while the other two can only be decreased dramatically after the pore size is close to the size of vanadium ions (2nm). Thus, with the pore size declining, the *CE* increases due to the reduction in the permeability of the vanadium ions, while the *VE* decreases due to the increase in ohmic resistance. Because of the trade-off between the permeability and resistance, the highest *EE* can be achieved at pore size of 5nm. For the same reason, the optimal membrane with pore size of 30nm is 400 μ m. Another important factor is the operation modes, such as flow rate, as it can affect the pressure on the surface of the separator.

Hence, to decrease the permeability of the porous membrane, decreasing the pore size is a good method. This can be done by adding additives like polymer on the surface of and inside the porous membrane. Functional groups can also be added onto the membrane to improve the ion selectivity.

PVDF with its simple production process has been applied in many fields owing to its good stability and low cost. However, because of the super hydrophobic characteristic which leads to the drastic decrease in the porous conduction, and high permeability caused by micro-porous membrane selectivity, the cell performances of PVDF is also not good [209] and thus needs to be improved. .

Many research groups have focussed on improving the performance of non-ionic porous membranes. Cao *et al.* [209] found an effective way to graft PVP on the PVDF while Zhou *et al.* [210] has grafted PSSA and BaTiO₃ on PVDF and Qiu *et al.* [211] grafted styrene and maleic anhydride. Besides grafting, Ren *et al.* [212] used quaternized polysulfone (QAPSF) while Tian *et al.* [213] used functional groups to make the PVDF to be an AEM. All of these modified membranes decrease the permeability by narrowing the transport channels and thus improving *CE*, however, they also increase the area resistance. To find the balance point between these two factors, the grafting density is controlled, and then found to give the higher *EE* than both PVDF and Nafion membranes

Cao *et al.* [214] also analyzed the importance of the experimental parameters such as temperature, the composition of the polymer solution, evaporation time, ambient humidity and the types of supporting material on the structure of the PVDF. However, the group finally concluded that the pore size is still the one that defines the performance of the membrane.

Except PVDF, other combined porous membranes including micro-porous and nano-porous membranes are also studied for VRFB system recently. Like PVDF, researchers combined different materials using various methods to enhance the properties or to reduce the cost of the nano-porous membrane.

Xi *et al.* [215] introduced silica on PES to control the pore size by sol-gel method as well as change the affinity of the membrane while Luo *et al.* [216] combined nanoporous PBI matrix and porous PBI membrane to achieve the properties of a typical nanoporous membrane with low cost Wu *et al.* [217] combined PSF/PVP-50 PSF as skeleton, PVP as functional exchange addition, and based on this porous membrane, GO nanosheet framework [218] was added to decrease the crossover of vanadium ions. Maurya *et al.* [219] combined an AIEM and nanoporous membrane to improve the membrane properties. Chen *et al.* [220] used different percentages of phenolphthalein (FT) in PES/SPEEK to build PES hierarchical porous membranes. The structure of the membrane with phenolphthalein-templating pathway became sponge-like pores, which means high conductivity and stability in strong acid. Z. Yuan *et al.* [221] produced PES-IEC membrane which combined PES with TPA/PVP at low cost. Due to the stable characteristic of porous membranes and high electrochemical performance of IEM particles, the PES-IEC membrane can offer higher *CE* and *EE* than N115 with stable performance over 1200 cycles at the current density of 140 mA cm^{-2} .

Recently, Kim *et al.* [222] combined SPEEK and Engelhard titanosilicate-10 (ETS-10) on PTFE by solution casting method, and found 3 wt% ETS-10 (SE3/P) show the best battery performance. SPEEK–ETS-10 composite dispersing on PTFE, proton exchange groups were added, which led to lower vanadium permeability. Owing to the stable structure of the PTFE, VRFB cell performance test was conducted 40 mA cm^{-2} over 200 cycles with no significant decline in efficiency. Since the swelling ratio of this membrane was lower than SPEEK, the total conductivity ($43.6 \text{ mS} \cdot \text{cm}^{-1}$) was higher than SPEEK, however it was still lower than N115, which led to lower *CE*. But the overall *EE* is higher than Nafion N115, and the cost of material is also lower than Nafion. Besides, this group combined SPEEK and microporous AMH-3 (G-AMH-3) to enhance the performance of membrane [223]. Due to interaction between SPEEK and G-AMH-3, the swelling ratio and mechanical properties are improved, and the membrane can be cycled work for 100 times in VRFB. However, the longer pathways for protons result in lower conductivity and permeability.

Different fabrication methods to decrease the pore size are developed. Sizov *et al.* [224] used

supercritical CO₂ assisted phase-inversion method to create highly selective porous ABPBI membrane for VRFB applications, while Luo *et al.* [225] used phase separation process induced by water vapor by different viscosity solution to manufacture the ABPBI. Low viscosity or supercritical CO₂ assisted phase-inversion method resulted in much more porosity leading to slightly higher vanadium ion permeability but also higher conductivity than PBI resulting in better cell performance.

Beside organic material, flat porous glass membranes with pore sizes in the range from 2 to 50 nm have been applied to VRFB by Mögeli *et al.* [226]. This membrane is prepared by mixing analytical grade SiO₂, B₂O₃, and Na₂CO₃. These materials are which cheaper than Nafion. The chemical, thermal and mechanical stability of these materials are tested and found to be suitable for VRFB operating environment. However, the inner resistance of the membrane is higher than N117, leading to lower efficiency at high current density although the *EE* can achieve up to 76.3% at current density of 20 - 60 mA cm⁻². This study shows the potential of glass membrane application in VRFB. However, further study needs to be done like loading IEM particles or layers to improve the proton conductivity.

All of these membranes improve ion selectivity by narrowing the transport channel or adding IEM particles, and hence achieving higher *CE* at low self-discharge rate which means good stability. But the area resistance is still a problem, which leads to a similar or lower *VE* to Nafion. Comparing with pristine porous membrane and Nafion, they all have better stability and higher *EE* at low current density. Besides, due to the high stability and low cost, the porous material become a basic layer to loading ionic groups [181, 227] or an addition [139] to enhance the microstructure of IEM in the recent membrane development. By combining these two different membranes, the beneficial features can be combined.

4.5 The membrane used on air/Vanadium battery

As a new type of vanadium redox battery, air/V battery also needs a membrane to exchange proton. Till date, it still uses CEM which is also used in VRFB, such as Nafion and Nafion combined

membrane [228, 229], SPEEK and the combined membrane [230, 231]. However, since the air/V battery is not as stable as the VRFB, their efficiency and cell performances are also not so good. Thus, as the key factor, future studies on suitable membranes are still required.

4.6 The diffusion/crossover modelling of VRFB with different membranes

The dynamic model for predicting battery capacity by simulating self-discharge and side reactions would be invaluable in the development of sophisticated control systems for the VRFB. As one of the most important components in the VRFB, membranes are key factor to the diffusion/crossover modelling of the VRFB [232]. The early mathematical modelling of VRFB began around 1970s-80s at NASA, while the first model was published in 1988 at UNSW. [233]. This model explained the VRFB capacity decay caused by the diffusion and self-reactions, which are caused by the vanadium permeability of the membrane as well as the vanadium concentration imbalance between the two electrodes due to different crossover rate for the membrane.

To improve the accuracy of model, more complicated operation and controlled conditions were considered in the model analysis, and Zheng *et al.* [234] summarised different types of methods to VRFB modelling. Tang *et al.* incorporated the heat transfer into Skyras-Kazacos and Goh's model to analyse the capacity of the battery by comparing the VRFB with three different membranes (Nafion 115, Selemion AMV and Selemion CMV) [235]. Ling *et al.* [236] took into account the impact of pulsating flow on the efficiency by using Nafion. Rajagopalan *et al.* [237] combined the effect of temperature change and bulk electrolyte transfer to analyse the working performance of battery with three different membranes. Won *et al.* [238] considered the reacting times and heat transfer in 3-D model to study fresh and degraded membrane in VRFB.

From these models which analysed battery working performance by combining membranes with other operating factors, it can be observed that the membranes which define the crossover rates of four vanadium ions have a fundamental impact to battery including self-reaction [239], permeability and state of health [36]. Besides, Doan *et al.* and Leung *et al.* have estimated that membrane contributes to 20% cost of the whole VRFB system (>USD\$ 200/kWh) [240, 241].

This high cost component has led to research into developing lower cost membrane for all three generations of VRFB systems.

4.7 The summary of membranes

A summary table comparing 84 main types of the membrane in this review is tabulated in *Table.14* where half of these are published within the last two years (2017-2018). The table listed the properties including vanadium ions permeability, conductivity, and energy efficiency and working current density, preparation technologies, stability and cost of these membranes. As the VRFB energy efficiency with respect to membranes reported in these research papers is tested under different experimental conditions (temperature, current density, etc.), thus this table only offers qualitative data when the results are compared with the commonly used Nafion membrane. Furthermore, the membrane cost reported in these research papers are based on comparison with Nafion as a reference. However, they minimize the cost is due to reduction in the dosage of Nafion and using much cheaper materials during the preparation of the membrane product. Thus, fewer papers mention about the production cost such as machine used and the manual work undertaken, especially for the high-performance membrane (such as SPEEK-ETS-10 [222]) which uses over three kinds of material. Also, the method of production might take a large amount of the cost in quantity production. Thus, the cost of membranes summarized in this table is qualitative on material cost. except for Nafion and SPEEK membranes.

Among the membranes used, CEM is still the most commonly used and studied membrane in VRFB. CEM suffers from high permeability which prompts numerous efforts spent to overcome this shortcoming including adding anion groups or porous materials. And these developments lead to much more AIEM percentage in all membranes studied in recent times. The development of porous membrane is also very fast, including development of new materials like glass and PBI. Many research groups have focused on decreasing the pore size or increasing the number of pores channel to improve the conductivity and to decrease the permeability at the same time. In summary, the membrane which can combine the advantages of different ions group with cheap materials in a long life is the main trend of the membrane development. And with the cost

decrease and lifetime improvement of the membrane, the total VRFB systems will become an economical power store system to cooperate with other system like renewables integration in ramping up electric supply capacity in the future.

5. Conclusions

Different types of membranes used in the VRFB system, including their working principles, performance measurement, fabrication, and characteristics are summarized in this paper. The membranes used in VRFB can be classified into ion exchange membrane (IEM) and non-ionic porous membrane based on the ion selection principle. The IEM can be further divided into cation exchange membrane (CEM), anion exchange membrane (AEM) and Amphoteric ion exchange membranes (AIEM).

As a widely used commercial CEM, Nafion membranes have shown high chemical stability and excellent electro-chemical properties, however it suffers from high permeability and cost. Because Nafion membranes are using same material, the performance of them in VRFB is affected by thickness and the preparation methods which define their microstructure. Thicker membranes have lower permeability but higher area resistance, which affects the cell performance and membrane properties. To reduce the crossover rate of membrane, introducing hydrophobic additive and/or polymers have been applied on the Nafion. This leads to even higher Nafion membrane cost. Thus, other low costs CEM such as SPEEK or SPI based CEM have been developed and studied. Although these low-cost membranes show low permeability, they also have low conductivity and stability. Thus, like Nafion membranes, these low-cost CEM have also been modified to improve its desirable properties for VRFB by adding lower swelling ratio matrix. Recently, numerous porous membranes or materials have been used to enhance the stability of CEM and to date, CEM is still the most commonly used membrane in VRFB.

The main shortcoming of these CEM is the high permeability. AEM with the opposite exchanging ions shows much lower permeability. However, the low redox stability and conductivity limit the application of AEM. Researchers have spent efforts to overcome these shortcomings by changing

the microstructure or improving the *IEC* and water uptake through the introduction of additives.

AIEM have both types of functional groups which lead to reasonably better performances. But the complex preparations, which require controlling the balance between the densities of two functional groups, result in high cost. Consequently, most of AIEM researches are focusing on finding an easier method to produce better-balanced AIEM.

With different ion exchange principle, the non-ionic porous membrane offers an excellent mechanical and chemical stability at low cost. However, the ineffectiveness of the ion exchange worsens the performances of the membrane. To overcome this shortcoming, the pore size reduction or even adding functional groups are widely investigated.

Fabrication methods can affect the membrane performance. According to the summary table, most of the particles combined membranes are fabricated by solution casting method, while the multilayer membranes are made by a layer-by-layer self-assembly method. As the fabrication method can change the microstructure and hence its membrane performance and cost.

Hence, to improve the membrane properties, the composite membrane that can combine the advantages of different materials has been the main focus of research in recent years. Since permeability and conductivity are antagonistic, therefore most of the current membrane research is focussing on controlling the density of the additive in order to achieve better performance in the membrane. And to reduce the cost, the cheap materials are used as one of the combined matrices.

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2072

1 Nomenclature

IEC	Ionic exchange capacity, $\text{mmol}\cdot\text{g}^{-1}$
A	The area of the membrane, cm^2
A_0	The initial absorbance of solution A, $\text{L mol}^{-1} \text{cm}^{-1}$
B	The absorbance of solution B, $\text{L mol}^{-1} \text{cm}^{-1}$
CE	Coulombic efficiency, %
EE	Energy efficiency, %
I_c	Charge current in one cycle, A
I_d	Discharge current in one cycle, A
I_j	Discharge current at point j, A
I_k	Charge current at point k, A
l	The thickness of the membrane, cm
L_d	Length of the dry membrane, m
L_w	Length of the wet membrane, m
OCV	Open Circuit Voltage, V
P_0	VO^{2+} permeability, $\text{cm}^2\cdot\text{s}^{-1}$
R	Area resistance, $\Omega\cdot\text{cm}^2$
r	Resistance of membrane value measured, Ω
r_1	Resistance of the cell with membrane, Ω
r_2	Resistance of the cell without membrane, Ω
S	Ion selectivity, $\text{mS}\cdot\text{Scm}^{-3}$
SOC	State of charge
SR	Swelling ratio, %
t	Time of reaction, s
t_j	Reaction time at point j during discharge, s
t_k	Reaction time at point k during charge, s
V_B	Volume of each cell, cm^3
V_c	Charge voltage in one cycle, V
V_d	Discharge voltage in one cycle, V
VE	Voltage efficiency, %
V_j	Discharge voltage at point j, V
V_k	Charge voltage at point k, V
W_d	Weight of membrane after absorption, g

WU	Water uptake, %
W_w	Weight of membrane before absorption, g
x_B	The concentration of crossover species, $\text{mol}\cdot\text{L}^{-1}$
σ	Proton conductivity, $\text{mS}\cdot\text{cm}^{-1}$
$\sigma_{//}$	The in-proton conductivity, $\text{mS}\cdot\text{cm}^{-1}$
AATMS	[N-(2-aminoethyl)-3-aminopropyl] trimethoxysilane
ABPBI	Advanced porous polybenzimidazole membranes
AMS	alpha-methyl styrene
CS	chitosan
DB	degree of branched
DMA	dimethylamine
DMAc	dimethylacetamide
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DS	degree of sulfonation
ETFE	ethylene tetrafluoroethylene
ETS	Engelhard titanasilicate
FT	phenolphthalein
g-C ₃ N ₄	graphitic carbon nitride nanosheets
GO	graphene oxide
HEMA	hydroxyl ethyl methacrylate
HFP	hexafluoropropylene
ImPSf	imidazolium-functionalized polysulfone
NMP	N-Methyl-2-pyrrolidone
PBI	polybenzimidazole
PDDA	poly(diallyldimethylammonium chloride)
PE	polyethylene
PEEK	poly(ether ether ketone)
PEI	polyethyleneimine
PEK	poly(ether ketone)
PEK-C	cardo-poly(ether ketone)
PES	polyether sulfone
PC	Propylene carbonate
PG	Porous glass

PPESK	poly(phthalazinone ether sulfone ketone)
PS	polystyrene
PSf-ABIm	polysulfone-2-amide-benzimidazole
PSS	poly(sodium 4-styrene sulfonate)
PSSA	polystyrene sulfonated acid
PTFE	polytetrafluoroethylene
PVA	polyvinyl alcohol
PVC	polyvinyl chloride
PVDF	polyvinylidene fluoride
PVP	polyvinylpyrrolidone
PWA	phosphotungstic acid
PyPPEKK	poly(phthalazinone ether ketone ketone)
PyPPSU	Poly(phenyl sulfone)
QADMPEK	Quaternized adamantane-containing poly(aryl ether ketone)
QA-PFE	Quaternary ammonium functionalized poly(fluorenyl ether)
QAPFS	quaternized polysulfone
QAPPEK	quaternized poly(phthalazinone ether ketone)
s-MoS ₂	sulfonated molybdenum disulfide
SBMA	sulfobetaine methacrylate
SI-ATRP	surface-initiated atom transfer radical polymerization
S-L-PPO	sulfonated poly(2,6-dimethyl-1,4-phenylene oxide)
SPAEEK	sulfonated poly (fluorenyl ether ketone sulfone)s
SPEEK	sulfonated poly (ether ether ketone)
SPI	Sulfonated polyimide
SPPEK	sulfonated poly (phthalazinone ether ketone)
TCE	tetrachloroethylene
TEPA	tetraethylenepentamine
TMA	trimethylamine
TMSP	trimethoxysilylpropyl
TPA	tungstophosphoric acid
VBTAC	vinyl benzyl trimethyl ammonium chloride
ZGO	functionalized graphene oxide
ZrNT	ZrO _{1.95} nanotube
ZrP	zirconium phosphate

ZrPSPP	zirconium phosphate sulfophenylene phosphonates
PPEK	Poly(phthalazinone ether ketone)
DVB	divinylbenzene

2

3 Table 1: Classify of the membrane

4

Name	Ion exchange membrane (IEM)					Non-ionic Porous Membrane (PM)
	Cation Exchange Membrane (CEM)	Anion Exchange Membrane (AEM)	Amphoteric Ion Exchange Membrane (AIEM)	Bipolar ion exchange membrane	Mosaic ion exchange membrane	
Ion selective methods	functional groups					physical barriers
	negatively charged groups	positively charged groups	negatively and positively charged groups	negatively and positively charged layers	negatively and positively exchange groups over cross-sections	pores or holes with diameters greater than 50-100Å
Advantages	good electrochemical properties	high ions selectivity	low permeability and conductivity		high ionic	much lower cost and high stability
Disadvantages	low ions selectivity	low stability	high cost			low ions selectivity

5

6 Table 2: Comparison of typical Nafion membranes

Types	NR 211	NR 212	N 112	N1135	N115	N117
Thickness(μm)	25	50	50	88	127	183
Equivalent weight (g • mol ⁻¹)	990-1050		1100			
Casting procedure	Dispersion cast		Extruded			
Water uptake (%)	40	47	44.1	32.5	32.1	34.1
IEC (mmol • g ⁻¹)	-	0.88	0.84	0.86	0.87	0.88
Conductivity(mS • cm ⁻¹)	-	70	102	98	100	96

7

8 Table 3: Comparison between N117 and ND

properties	N117	ND	properties	N117	ND
Thickness (μm)	180	183	VE (%)	90.5	85.6
Permeability (cm ² • min ⁻¹)	3.07×10 ⁻⁶	8.64×10 ⁻⁷	EE (%)	85.6	83.4

<i>CE</i> (%)	Current density=1.39 mA • cm ⁻² , and it is tested after 10 cycles	64	52	69
<i>VE</i> (%)		72	65	73
<i>EE</i> (%)		45	34	50
Tensile strength (4 weeks)(MPa)		24	-	140

Table 8: Comparison between N115 and N/[PDDA/ZrP]₃

properties	N115	N/[PDDA/ZrP] ₃	properties	N115	N/[PDDA/ZrP] ₃
Conductivity (mS • cm ⁻¹)	-	12	<i>CE</i> (%)	82	93
Permeability V ⁴⁺ (10 ⁻⁷ cm ² • min ⁻¹)	10.5	0.154	<i>VE</i> (%)	93	91
Hours of <i>OCV</i> >0.8V (h) <i>SOC</i> =0.5	31	42	<i>EE</i> (%)	77	83

Table 9: Comparison between N117 and N/[PDDA-PSS]₅

properties	N117	N/[PDDA-PSS] ₅	properties	N117	N/[PDDA-PSS] ₅
Conductivity(mS • cm ⁻¹)	58.7	50.3	<i>CE</i> (%)	81.8	90.9
Permeability V ⁴⁺ (10 ⁻⁷ cm ² • min ⁻¹)	V(III)	35.6	<i>VE</i> (%)	90.2	92.3
	V(IV)	30.0			
	V(V)	7.02			
Hours of <i>OCV</i> >0.8V (h) <i>SOC</i> =0.75	12	45	<i>EE</i> (%)	73.8	83.9

Table 10: Comparison between NR212 and Nafion-[CS-PWA]₃

properties	NR212	Nafion-[CS-PWA] ₃	properties	NR212	Nafion-[CS-PWA] ₃
Conductivity(10 ⁻² S • cm ⁻¹)	13	5.5	<i>CE</i> (%)	60	65
Permeability(V ⁴⁺) (10 ⁻¹⁰ cm ² • h ⁻¹)	12.2	2.9	<i>VE</i> (%)	96	96
Hours of <i>OCV</i> >0.8V (h) <i>SOC</i> =0.80	50	70	<i>EE</i> (%)	58	63

Table 11: Comparison between N117 and SPEEK48

properties	N117	SPEEK48	properties	N117	SPEEK48
Thickness(μm)	175	100	<i>CE</i> (%)	91	92
Water uptake (%)	14	41	<i>VE</i> (%)	81	83
Electrolyte uptake (%)	11	14	<i>EE</i> (%)	73	77
Conductivity(mS • cm ⁻¹)	11.92	10.67	<i>IEC</i> (mmol • g ⁻¹)	0.91	1
Area resistance(Ω • cm ⁻²)	0.71	0.45	Swelling ratio (%)	11	21

Table 12: Comparison between N117 and HSPAEEK

properties	N117	HSPAEEK	properties	N117	HSPAEEK
Thickness (μm) (wet)	215	60	<i>CE</i> (%)	91	92
Water uptake (%)	33.0	38.5	<i>EE</i> (%)	73	77

<i>CE</i> (%)	97.4	94.7	<i>EE</i> (%)(current density = 20mA • cm ⁻²)	82.8	87.6
Cell resistance (Ω)	0.1	0.15	Capacity retention (after 100 cycles,%)	14.3	84.6

9

10 Table 4: Comparison between N117 and ZNM-5

properties	N117	ZNM-5	properties	N117	ZNM-5
Thickness(μm)	~183	~120	<i>CE</i> (%)	92	94
IEM resistance(Ω)	0.81	0.55	<i>VE</i> (%)	80	88
			<i>EE</i> (%)	73	83

11

12 Table 5: Comparison between NR212 and P/N

properties		NR212	P/N	properties	NR212	P/N
Thickness(μm)		50	45	<i>CE</i> (%)	89.2	94.1
VO ²⁺ Permeability (cm ² • s ⁻¹)	4.5 M H ₂ SO ₄	2.80×10 ⁻⁸	1.09×10 ⁻⁸	<i>VE</i> (%)	88.8	90.9
	1.5 M H ₂ SO ₄	6.67×10 ⁻⁸	4.62×10 ⁻⁸	<i>EE</i> (%)	79.2	85.5
Conductivity (mS • cm ⁻¹)		33	71	<i>IEC</i> (mmol • g ⁻¹)	0.88	0.69
Water uptake (wt%)		30.8	24.9	Weight(mg • cm ⁻²)	10.1	7.5
Hours of <i>OCV</i> >0.8V (h) (after 45 cycles)		58	140	Swelling radio (%)	15.1	10.0

13

14 Table 6: Comparison between P/N and P/N/S with different preparation

properties	P/N	P/N/S (casting)	P/N/S (sol-gel)
Si content (%)	0	3	7
Thickness (μm)	45	30	25
Water uptake (wt%)	19.5	12.3	21.1
Conductivity (mS • cm ⁻¹)	57	52.1	61.1
Permeability (cm ² • cm ⁻¹)	2×10 ⁻⁷	1.1×10 ⁻⁷	0.95×10 ⁻⁷
Hours of <i>OCV</i> >0.8V (h) (after 89 cycles)	11	13	-
<i>CE</i> (%)	79.4	87.3	92.8
<i>VE</i> (%)	87.7	87.0	89.6
<i>EE</i> (%)	69.6	75.9	83.1
Area resistance (Ω • cm ⁻²)	1.3	1.6	-

15

16 Table 7: Comparison of NR212, AHA and Celgard

properties	NR 212	Neosepta AHA	Celgard
Thickness (μm)	50	203	60
Electrolyte uptake (wt%)	17.1	27.7	80
Swelling ration (%)	9.3	3.5	0.6
Conductivity (mS • cm ⁻¹)	10.7	5.27	49.1
Permeability (cm ² • s ⁻¹)	7.32×10 ⁻⁸	8.50×10 ⁻⁹	6.00×10 ⁻⁹

Swelling radio (%)	18.6	11.6	IEC (mmol • g ⁻¹)	0.86	1.72
Conductivity (mS • cm ⁻¹)	90.0	33.4	Swelling radio (%)	11	21

27

28 Table 13: Comparison between N117 and N/SiO₂

properties		N117	N/SiO ₂	properties	N117	N/SiO ₂
Thickness(μm)		186	188	CE (%)	92.5	96
Permeability(c m ² • min ⁻¹)	VO ²⁺	8.65×10 ⁻⁷	2.32×10 ⁻⁷	VE (%)	75	77
	VO ₂ ⁺	2.73×10 ⁻⁷	0.85×10 ⁻⁷	EE (%)	65	69
area resistance (Ω • cm ⁻²)		3.36	3.45	Hours of OCV>0.7V	33	71
Contact angle (°)		89.8	79.5	IEC (mmol • g ⁻¹)	0.96	1.05
Water uptake (wt%)		36.5	35.1			

29

30 Table 14: Summary table

31

2	1	No
60SPAEEK-6F-co-15%BI	[Nafion/(WO3)0.329]	membrane name
70	NA	EE tested current density (mA cm ⁻²)
1.4X10-5	23.1	V(IV) permeability (10 ⁻⁷ cm ² min ⁻¹)
73.4	NA	EE (%) or size comparing with Nafion
1.35	24.5	Conductivity(mS·cm ⁻¹)
casting and solvent evaporation method	solution casting method	technology
lower	NA	cost comparing with Nafion
higher CE, VE and EE to that with Nafion117 over 200-cycles at 70 mA cm ²	no significantly change in the subsequent 60 days when exposing them to an environment closely mimicking.	Life stability testing
200	129	reference
AIME	CEM	Membrane types
2017	2018	published year

9	8	7	6	5	4	3
bSPI/M oS2-ns	bSPI (BAPP)	BrPPO/Py- 56	AIEM with pendant quaternary ammonium groups (10%)	ABPI	AATMS(z=0.2)	6F-s-bSPI
40	30 to 120	100	50	180	20	60
0.65	2.89	around 0.25	1.56	1.4	8.5	1.18
74	61.6 -80.7	around 92	NA	62	83	78
50.4	35.5	24	11.9	36	90	20.6
solution casting and heating	polycondensat ion and post-sulfonatio n method	solution casting and hot pressing	solution casting method	phase separation process	sol-gel	post-sulfonation method
lower	lower	NA	NA	much lower	NA	lower
capacity decay fast on first 100cycl e	500-time cyclic charge-dischar ge test while the CE slightly decreased	cycled over 537 cycles with a capacity decay rate of 0.037% per cycle	NA	NA	No pronounced performance degradation and changes in efficiency were observed after 12 repetitive charge-discharge cycles	the surface of the 6F-s-bSPI membrane facing the positive and negative electrode shows almost no change after the 100 testing cycles
161	163	184	196	225	198	163
CEM	CEM	AEM	AIEM	porous membrane	AIEM	CEM
2018	2017	2016	2014	2018	2017	2017

18	17	16	15	14	13	12	11	10
N115-g-PSB MA	ImPSf/SP EEK 17%	HSPA EK(60)	ETFE-g-PSSA/DM AEMA	EFFE-g-(VBTAC- co-HEMA)	CSPI-DM DA	CSOPBI- NH2(9/1)	CAPSU-2.5	BVSN-por ous-3
40	200	80	40	60	200	60	50	80
13.6	0.15	around 6	0.029	0.49	0.93	0.0599	0.272	0.777
89.6	77.3	84	75.1	57.7	75.3	0.85	0.86	82.7
63.8	144	33.4	24	NA	39.2	32	7.5	77
grafting via SI-ATRP technique	solution casting and hot pressing	solution casting method	grafting method	ion sputtering method	solution-ca sting method	solution casting method (DMSO)	solution casting method	casting and hydrolysis
slightly higher	NA	lower	NA	NA	NA	NA	lower	lower
$CE > 96.2\%$ with no decay over 100 time	efficiency keep constant for 50 cycles	super stable CE and EE as well as excellent discharge capacity retention (83%) during 100 cycles life test	no efficiency decline is observed for 40 cycles	keeps stable during 10 cycles	no obvious decay over 1000 charge-disc harge test under 160 mA cm^{-2}	little decay was observed after 300 cycles test	exhibits an excellent CE of almost 100% up to the 100th charge-dischar ge cycle	EE despite some fluctuations during 100 cycles
199	197	137	194	67	166	190	185	224
AIEM	AIEM	CEM	AIEM	AEM	CEM	AIME	AEM	AEM
2018	2017	2015	2009	2012	2019	2017	2017	2018

27	26	25	24	23	22	21	20	19
Nafion/silica te D-AMH-3	Nafion/P VA	Nafion/PTFE/Silic a(solution casting)	Nafion/PTFE/ Silica(sol-gel)	Nafion/P TFE	Nafion/porous ZrNT	Nafion/colloi dal silicalite	Nafion/amino-SiO2 hybrid membrane	Nafion (N117)
20	1.39	50 and 80	50 and 80	50	40	20	20	40
8.64	5.1	1.1	0.95	2	0.036	10.44	2.32	34.9
87.6	32	75.9	83.1	85.1	78.5	around 85	74.6	77
NA	49.1	52.1	61.1	68.5	95.2	23	NA	11.92
solution casting and hot pressing	solution casting method	solution casting method	sol-gel	solution casting or sol-gel	solution casting method	solution casting method	solution casting method	casting method
higher	higher	higher than PTFE	higher than PTFE	higher	higher	higher	higher	\$200/m ²
no efficiency decline after 100 charge-disch arge cycles	keeps stable during 10 cycles	keeps stable during 89 cycles	better than Nafion/PTFE/ Silica (solution casting)	keeps stable during 50 cycles	discharge capacity was 3.5 times higher than N117 100 charge-dischar ge cycles.	keeps stable during 50 cycles	EE decreased only 1% for 150 cycles	good chemical stability electrolyte after being soaked for 30 days.
122	128	32	32	124	127	123	110	135
CEM	CEM	CEM	CEM	CEM	CEM	CEM	CEM	CEM
2014	2016	2015	2015	2013	2017	2015	2015	2014

35		34	33	32	31	30	29	28
PES (with proper hierarchical morphology) (20%)	PC-Nafion/P	OPBI	Nafion212/graphene oxide(GO)	Nafion117/graphene oxide(GO)	Nafion-[PDDA-PSS] ₅	Nafion-[PDDA/ZrP] ₃	Nafion-[CS-PWA] ₃	
80	NA	100	NA	40	20	30	60	
39.8	3	lower than 0.01	32-60% of N212	5	2.85	10.5	around 16.8	
81.66	NA	81.87	NA	82.5	83.9	around 84	around 71.5	
NA	11	around 10	10.56	around 25	50.3	around 15	around 52	
Radiation grafting method	solution casting method	solution casting method	spin coating method	solution casting method	layer-by-layer self-assembly	layer-by-layer self-assembly	layer-by-layer self-assembly	
	much lower	NA	higher	higher	much higher	much higher	much higher	
stable cyclic efficiencies over 70 cycles	NA	capacity over 77.6% after running 500 cycles	NA	NA	efficiency does not tend to decline after 50 cycles	NA	no efficiency decline after 35 cycles	
	220	121	62	102	126	96	131	132
porous membrane	CEM	membran	CEM	CEM	AIEM	CEM	AIEM	
2017	2018	2018	2010	2014	2008	2017	2014	

43	42	41	40	39	38	37	36
PVDF-g-PMAODEMAC-co-PAMSSA	PVDF/St/DM AEMA(0.88)	PS-IPA	P-sHCP10	PSF-PVP/GO(0.05)	p-Nafion-1:1-PBI5	PG10	PES-IEC
NA	NA	80	150	60	80	20	140
0.69	0.73	much lower than N115	16	around 1.5	similar to Nafion 212	NA	around 17
expected higher	expected higher	90.4	77	87	80	75.3	81.61
around 52	46	much higher than N115	24	35	0.4	NA	NA
simultaneous irradiation grafting technique	radiation grafting approach	phase inversion method (casting)	solution-casting method	grafting method	solution-casting method and spraying method	pre-heating and solution casting method	solution casting and hot pressing
lower	NA	lower	NA	lower	higher	much lower	lower
NA	NA	keep a stable performance without obvious efficiency decay during over 500 cycles	no cracks, holes or other signs of degradation could be observed after 8 days	high efficiencies are maintained for 100 cycles	low loss in charge capacity over 45 cycles	NA	stable performance after more than 1200 cycles
193	191	46	227	218	47	226	221
AIEM	AIEM	porous membrane	CEM	CEM	CEM	porous membrane	CEM
2012	2009	2018	2018	2017	2018	2018	2017

52	51	50	49	48	47	46	45	44
S/DHNTs 3%	S/CNT@PD A MMM	QPEK-C/TMSP- TMA+Cl-(20%)	QDAPPs(3)	QAPSF/PV DF (15%)	QAPPEK -5	QADMPEK- 3	Q/P/S-3:2	PyPPSU- 2
120	200	30	NA	NA	40	80	40	100
3	8.7	0.318	1.8	around 3.5	0.69	7.64	0.7	0.15
84.9	75.4	78–80	80–90	higher	85.9	84	84.5	80.2
91.6	97.7	5.6 ± 0.5	NA	NA	than	NA	10.27	NA
rapid deposition method(DH NTs)	solution casting method	solution casting method	solution casting method	solution casting method	solution casting method	solution casting and hot pressing	solution casting method	solution casting and hot pressing
higher than	lower	NA	NA	much lower	NA	NA	NA	lower
CE>97.9% for over 300 cycles under 80 mA cm ⁻² .	CE >98.5%) with extremely low capacity fading rate (0.04% per cycle) over 1000 cycles	stable work for 20 cycles	stable energy efficiencies for 400 cycles	NA	NA	good chemical stability electrolyte after being soaked for 30 days,	NA	stable work for 42 cycles
	152	174	173	213	178	159	189	175
CEM	CEM	AEM	AEM	AEM	AEM	AEM	AEM	AEM
2018	2018	2014	2014	2016	2010	2016	2018	2015

60	59	58	57	56	55	54	53
SPEEK(48)	S-L-PPO-51%	silica nanocomposite anion-exchange membranes	SE3/P	scABPBI	S67-DMF	S/HNTs 3%	S/GO-NH2
40	120	40	40	40	120	120	50
10.44	2.58	around 4.24	7.1	0.41	around 2	4.4	2.04
73	81.85	60	88	88	78.4	83.2	89.5
10.67	44	NA	42.6	27	7.5	89.1	39
casting method	Friedel-Crafts acylation and solution casting method	sol-gel	solution casting method	supercritical CO2 assisted phase inversion method	solution casting method with S67 -DMF	solution-casting method	blending
\$50/m2	\$64/m ²	lower	NA	much lower	lower	lower	NA
good chemical stability electrolyte after being soaked for 30 days.	unchanged <i>CE</i> , <i>VE</i> , and <i>EE</i> for 100 cycles under 80 mA cm ⁻²	good chemical stability electrolyte after being soaked for 120 h	no significant decline in efficiency at 40 mA cm ⁻² over 200 cycles	NA	stable <i>CE</i> and <i>EE</i> during 150 cycles	<i>CE</i> fluctuate sharply at 178th cycle, and drop rapidly at 185th cycle	92% capacity retention after 100 cycles, 97.2% <i>CE</i> , 89.5% <i>EE</i> and stable cell efficiency after 100 cycles.
135	168	182	222	224	151	139	201
CEM	CEM	AEM	CEM	porous membrane	CEM	CEM	AIME
2014	2018	2013	2018	2018	2015	2018	2017

68	67	66	65	64	63	62	61
SPEEK/PVD F	SPEEK/P(VDF-c o-HFP) (15%)	SPEEK/mesoporous silica hybrid membrane (S/SBA-15 20)	SPEEK/L 15	SPEEK/g- C3N4-1.5	SPEEK/G -AMH-3	SPEEK/carboxy lic acid groups	SPEEK/5% TiO2
60	80	60	120	60	40	80	50
around 2	19	6.2	0.19	around 4	9.6	much lower than Nafion 115	around 2.8
81	83.8	88.1	83.5	77.7	85	over 85	82.9
9.2	around 14	6.4	29.56	7.9±0.3	19.7	NA	17.8
solution casting method	solution casting method	solution casting method	solution casting method	solution casting method	solution casting method	solution casting method	solution casting method (DMSO)
lower	lower	lower	much lower	NA	NA	NA	lower
no obvious <i>CE</i> and <i>EE</i> declines are observed after 80 cycles cell test	stable <i>CE</i> and <i>EE</i> during 100 cycles	<i>EE</i> no obvious decline over 120 cycles	retains 15% capacity after 900 cycles under 80 mA cm ⁻² .	no obvious decrease in energy efficiency after 300 cycles	After 100 cycles, the capacity decay 15.3%	keeps stable during more than 100 cycles	The capacity decay of VRFB with the composite membrane over 20 cycles (0.11% per cycle)
148	146	143	141	145	223	150	140
CEM	CEM	CEM	CEM	CEM	membran	CEM	CEM
2013	2014	2014	2019	2017	2017	2014	2017

76	75	74	73	72	71	70	69
SPI/functionalized graphene oxide(ZGO-4)	SPI/boehmite(A LOOH-10%)	SPFEK/5 ZrPSP	SPEEK36-100	SPEEK-15	SPEEK/UiO-66-OH	SPEEK/S GO-3	SPEEK/Q APEI-15
60	60	50	20	80	50	30	50
around 10	1.14	6.3	0.0015	NA	2.37	6.7	1.3
73	around 72	around 53	90.2	89.8	91.4	81.1	88.45
9.2	30.5	21.9	2.4	than	around 25	17.6	47.37
solution casting method	solution casting method/coating	solution casting method	casting method and porogen-leachin g-out method	heat and solution casting method	solution casting method	solution-casting	blending
lower	lower	lower	lower	lower	lower	NA	lower
<i>EE</i> over 78% for 100 charge-discharge cycles	stable performance during 100 cycles	no catastrophic failure is observed after 50 cycles	The <i>CE</i> and <i>EE</i> show no significant decline over 50 cycles	350 cycles at 180 mA cm ⁻² , while no fade in <i>CE</i> was founded	performance up to 100 cycles without significant decline in <i>EE</i>	a longer self-discharge time (56.6 h) against Nafion 117	shows no obvious decline after running for 100 cycles
27	156	144	149	153	203	125	201
CEM	CEM	CEM	CEM	CEM	porous membrane	CEM	AIME
2015	2014	2013	2018	2018	2017	2018	2015

84		83	82	81	80	79	78	77
ZPPT-6		TMA-5	SPPEK-P-90	SPPEK/T PA-17	SPPEK with WO ₃	SPI50	SPI/ZrO2 (15%)	SPI/sulfonated molybdenum disulfide (s-MoS2)
50		160	60	60	50	80	70	80
around 1.89		NA	through the membranes	5.75	3.97	2.2	2.18	1.23
73.4		80	83	74.58	78.6	81.2	around 67	66.89
NA		NA	NA	19.04	NA	56.9	34.1	27.5
solution casting method		phase inversion method	solution casting method	solution casting method	solution casting and hydrothermal method	solution casting method	solution casting method	solution casting method
much lower		NA	lower	lower	lower	much lower	lower	much lower
good chemical stability electrolyte after being soaked for 20 days.		EE of around 80% was maintained after 1500 cycles	EE over 83% for 100 charge-discharge cycles	EE no obvious decline after every 32 cycles	no obvious CE and EE declines are observed after 100 cycles cell test	EE>75.0 % for 400 cycles under 160	steadily lasts for 50 cycles with no attenuation	exhibits stable operation performance up to 500 cycles with no significant decline in CE and EE
204		181	155	138	154	166	158	162
AIEM		AEM	CEM	CEM	CEM	CEM	CEM	CEM
2015		2018	2017	2013	2012	2018	2014	2015

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Fig 3. Schematic of water transport experiment. Reprinted with permission from ref[19] Copyright Elsevier,

Fig 4. Schematic of the ion exchange process of an anion exchange particle

Fig 5. Schematic of the ion exchange process of a cation exchange membrane in VRFB

Production Process

Fig 6. Solvent cast process on a belt line. Reprinted with permission from ref [54] Copyright Elsevier, 2005.

Fig 7. Sol-gel process on a belt line. Reprinted with permission from ref[68], 2008.

Fig 8. Representation of Molecular deposition. Reprinted with permission from ref [4] Copyright Elsevier, 2006.

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