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Membranes for all vanadium redox flow batteries

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ABSTRACT

Battery storage systems become increasingly more important to fulfil large demands in peaks of energy consumption due to the increasing supply of intermittent renewable energy. The vanadium redox flow battery systems are attracting attention because of scalability and robustness of these systems make them highly promising. One of the Achilles heels because of its cost is the cell membrane. Exposure of the polymeric membrane to the highly oxidative and acidic environment of the vanadium electrolyte can result in membrane deterioration. Furthermore, poor membrane selectivity towards vanadium permeability can lead to faster discharge times of the battery. These areas seek room for improvement to increase battery lifetime. The high costs of the currently used membranes substantially contribute to the price of the vanadium redox flow battery systems. Therefore, the reduction of the cost of the membrane by using alternative materials can reduce the overall battery costs substantially, thereby increasing the prospects of the industrial use of these systems. In this report different membrane types are reviewed and the important factors determining membrane performance are analysed. An overview of potential new membranes is presented which could boost the performance of these systems in future and reduce costs substantially.

1. Introduction

Battery storage systems are emerging as one of the key solutions to effectively integrate high shares of solar and wind renewables in power systems worldwide. Solar photovoltaics produced 1.8% and wind turbines produced 4.4% of the global electricity production in 2017 [1]. The share of renewables in power generation capacity expansion reached 72% in 2019. Most of the new capacities (nearly 90%) came from solar and wind projects. Consequently, more electricity is generated from renewable energy than in the previous year. Energy Information Administration (EIA) projects that renewables will collectively increase to 49% of global electricity generation by 2050 [2]. The growing share of variable renewable energy sources (VRE, i.e. solar and wind), calls for a more flexible energy system to ensure that the VRE sources are integrated in an efficient and reliable manner to electricity grid. A wind turbine can peak at night when the demand is low, and its output may vary from GW to MW during the day depending on the wind speed. Similarly, the output of a solar PV plant could vary when clouds pass by. These intermittent gaps in power supply need to be compensated by conventional power plants, which introduce challenges to electricity grid operators.

Electrical energy storage (EES) will be a key component in future grid and in a low-carbon society, enabling VRE generation to provide electricity not only for residential and industrial use but also feed electrical vehicles. Battery storage systems are emerging as one of the potential EES solutions to complement VRE by providing system flexibility due to their unique capability to quickly absorb, hold and then reinject electricity. Unlike conventional EES, such as pumped hydro storage, batteries have the advantage of geographical flexibility and can therefore be deployed closer to the location wherever they are needed.

Cost is probably the most important hurdle for a battery system for a broad market penetration. For stationary applications, long-lasting capacity may not be needed but long cycle life, high discharge rates and high current densities are important, because multiple daily discharges could be needed to regulate frequency. Electrochemical energy storage systems have the potential to release their energy rapidly if needed and redox flow battery (RFB) systems have the advantage of scalability and therefore they are among the most promising EES options. Various redox couples i.e. Fe/Cr, Cr/Ti, V/Sn, V/Fe, Sn/Cl [3, 4] were investigated in RFBs. The all-Vanadium RFBs (VRBs) (Fig. 1) received more attention because most other systems suffer from cross contamination due to the use of different elements in catholyte and anolyte which results in self-discharge and capacity loss. Moreover, electrolytes can be reused to reduce the operating cost of the system.

To date, many VRB demonstration plants have already been realized, ranging in sizes up to a 60 MWh system in Japan [5–9]. The relatively high capital and maintenance costs of VRBs are the major setback for their further implementation [5]. Membranes are costly components of the VRBs. The operational lifetime and their limited conductivity at high current densities adversely affect the VRB systems.

At present, commercial perfluorinated polymeric ion exchange

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Fig. 1. Schematic representation of a VRB system.

membranes (i.e. Nafion) are the most widely used ones because of their high ion conductivity and stability in the acidic and oxidising electrolyte solutions of VRBs [10–12]. The high cost and undesirable crossover of active species makes the low-cost porous membranes more promising alternatives for industrial VRB applications [13]. The main challenge of porous membranes is their relatively low voltage efficiencies at higher current densities [14]. This is related to the membrane's ion conductivity. In general, larger pore size, higher pore interconnectivity, lower thickness and higher hydrophilicity contribute to higher ion conductivity. However, there is a trade-off between high ion conductivity and selectivity. The modifications on membranes for improving the voltage efficiency should not sacrifice the high columbic efficiency at elevated current densities as well.

Various approaches in literature have been applied to improve the performance of membranes. Most methods involve parameter optimisation in synthesis which includes introducing hydrophilic inorganicbased nanoparticles or charged groups. This often leads to higher membrane resistance or weaken the chemical stability. Identifying novel membrane materials is another approach, which is usually coupled with further structural modifications. The ideal membrane should have high ion exchange selectivity, high ion conductivity, low water uptake, low swelling ratio, high conductivity, high chemical and thermal stability, as well as low cost. This review focuses on the most recent advancements of investigations on the structure design and optimization to improve the selectivity and conductivity of membranes and describe the development of future trends of VRB membranes. Additionally, this review will provide effective ideas and methods to direct further improvements in the power density and energy density of VRB systems.

2. All vanadium RFB principles

The all Vanadium Redox Flow Battery (VRB), was developed in the 1980s by the group of Skyllas-Kazacos at the University of New South Wales [1–4]. The explorative work by the Skyllas-Kazacos group provided new insights for improvements to improve its long-life cycle, flexible design, fast response time, deep-discharge capability and low polluting emissions [1, 5].

In order to store electrical energy, vanadium species undergo

chemical reactions to various oxidation states via reversible redox reactions (Eqs. (1)–(4)). The main constituent in the working medium of this battery is vanadium which is dissolved in a concentration range of 1–3 M in a 1–2 M H₂SO₄ solution [1]. To avoid mixing of the charged V species separation of the cathode and anode half-cell via a membrane is essential to prevent battery self-discharge. Membranes must be permeable and conductive to enable charge transferring H⁺ species to move to the two half cells. The standard potential E₀ at the cathode is 1.0 V whereas the negative electrode contains a standard potential of -0.26 V. The equilibrium potential is determined using the Nernst equation and depends on the concentrations of the ions present in the cell (Eq. (5)) [15].

Cathode reactions

 $VO_{(aq)}^{2+} + H_2O_{(1)} \rightarrow VO_{2(aq)}^+ + 2H_{(aq)}^+ + e^- \text{ (charging)}$ (1)

$$VO_{2(aq)}^{+} + 2H_{(aq)}^{+} + e^{-} \rightarrow VO_{(aq)}^{2+} + H_2O_{(l)}$$
 (discharging) (2)

Anode

 $V_{(aq)}^{3+} + e^- \rightarrow V_{(aq)}^{2+} \text{ (charging)}$ (3)

$$V^{2+} \rightarrow V^{3+}_{(aq)} + e^-$$
 (discharging) (4)

$$E = E^{+} + E^{-} = E_{0} + \frac{RT}{nF} \ln \left(\frac{C_{H^{+}} C_{VO_{2}}^{+} C_{V}^{2+}}{C_{VO}^{2+} C_{V}^{3+}} \right)$$
(5)

In contrast to other battery systems the electrodes in this system are non-participating and are therefore not affected by metal deposition or metal decay and enables the use of graphite electrodes [16, 17]. This provides high robustness to the system and enables the production of custom made electrodes for its purposes from graphite [18]. Similarly, the same electrolyte is used in the two half-cells which helps improving the overall energy efficiency [18].

The energy storage capacity of the battery is directly proportional to the volume and concentration of electrolyte. The capacity of the battery is defined as State-Of-Charge (SOC). A value of 100% indicates that the complete capacity is used for storage of electrical energy while a state of 0% indicates a fully discharge battery.

The comparison of the performance of different battery systems requires defining efficiency. The most commonly used definitions of efficiency of a battery are coulombic (CE), voltage (VE) and energy (EE) efficiency shown in Eqs. (6)-(8) [16].

Coulombic efficiency (CE) =
$$\frac{\text{total charge}_{\text{discharge}}}{\text{total charge}_{\text{charge}}} \times 100\%$$
 (6)

$$Voltage \ efficiency \ (VE) = \frac{average \ voltage \ during \ discharge}{average \ voltage \ during \ charge} \times 100 \ \% \ or$$

$$VE = \frac{EE}{CE} \times 100 \%$$
 (7)

$$Energy \ efficiency \ (EE) = \frac{energy \ density_{discharge}}{energy \ density_{charge}} \times 100\%$$
(8)

3. Types of exchange membranes

3.1. Cationic exchange membranes

From the mid-80's large effort has put into developing cation exchange membranes (CEM) which would only transport cations. The early membranes in the late 80 s consisted of pore filled ion exchange membranes (IEMs). In these kinds of membranes, a porous support is filled with an ion-exchange resin or polyelectrolyte together with a cross linking agent. The mixture is than cured to obtain the crosslinking reaction.

The early membranes prepared accordingly were sulfonated porous polyethylene and polystyrene materials. A comparison of these materials by Skyllas-Kazacos et al. [19] in VRB showed the influence of the molecular composition of the polymer materials. The polyethylene material revealed a coulombic efficiency of 87% using a current density of 15 mA•cm⁻², while the polystyrene material possessed a coulombic efficiency of 90% at a current density of 40 mA·cm⁻². These high CE values were obtained due to the low levels of cross-mixing. On the other hand, the polystyrene material outperformed the polyethylene material leading to an overall energy efficiency of 81% over the 10-90% SOC range for the polyvinyl material. The large difference between charge and discharge curves leading to a poor voltage efficiency of the sulfonated polyethylene membrane are likely due to a high membrane resistivity. Valuable screening work by Grossmith et al. [20] in the early years of VRB research revealed potential challenges when various materials are used as membrane in VRB. For instance, microporous PVC and ultra-microporous Durapore GMV (PVC polymer) membranes showed high volumetric cross-over rates and thus let to self-discharge. The Aqua pore membrane did not get wetted by the solution, preventing cations to flow through the membrane. A membrane provided by the RAI, Inc showed not to be chemically stable leading to the formation of pinholes. The Gellman NFWA membrane showed poor chemically stability becoming very brittle over time leading to rupture. They also studied Nafion N324 and N423 (polyfluoroethylene sulfonic acid) and Selemion CMV (polystyrene sulfonic acid) membranes which showed high chemical stability and permeation rates. An overview of various parameters measured for membranes are collected in Table S1.

The studies tabulated in Table S1 indicated that variety of parameters should be carefully considered when developing a membrane material: i) the cross-over rates should be low in order to prevent selfdischarge, ii) wettability should be high and resistivity should be low to enable cationic transport through the membrane iii) the durability of the membrane is crucial which is mostly determined by the chemical stability. The Selemion and Nafion membranes possess suitable properties for VRB applications. However, the long-term stability of the Nafion membranes are limited and the main disadvantage of Nafion is its high price. To overcome the drawbacks of early membranes, various materials were studied extensively which are described below.

3.1.1. Polyethylene based membranes

The use of polyethylene has been studied extensively in the 1990s because of its commercial availability and ease of manufacturing with desired properties. The proton conductivity in these materials often arise by the introduction of sulfonic acid groups as cation exchange sites. To introduce the sulfonic groups various reactants can be considered such as concentrated sulfuric acid and sulfuryl chloride [21–23]. The properties of the membrane pores can also be modified by introducing various types of polymers which enables the use of cheaper support materials while the pores can be filled with Nafion type polymers. In this way, the material costs can be reduced. An example of such cheap commercially available membrane support is Daramic which is an ultrahigh molecular polyethylene providing exceptional strength to the material. Furthermore, the material possesses high resistivity against oxidation compared to other commercially available membranes such as Selemion. However, the large pores of Daramic causes poor membrane selectivity when being applied untreated in VRB applications. To increase membrane selectivity the pore can be filled with polymers introducing high conductivity and membrane selectivity in VRB applications. An early example is work from the group of Skyllas-Kazacos where they impregnated the Daramic membrane with a divinyl benzene (DVB) mixture containing methanol and Amberlite 400CG. After introduction of the DVB the hybrid material was treated in a polymerization reactor containing an aqueous solution of NaS₂O₈ for the direct introduction of sulfonic acid groups [23]. The obtained membrane showed a CE of 90% as compared to 77% for the untreated Daramic separator. Also the area resistance was lower than 3 Ω cm², accompanied by a reduced hydraulic permeability and diffusion coefficient [24]. Hydro permeability can be problematic since this increases pressure on one site of the half cells. In another approach the DVB pore filled membranes were treated after cross linking with concentrated sulfuric acid to directly introduce sulfonic acid groups. It was possible to obtain lower area resistivities by conducting a short cross-linking time. This led to somewhat decreased diffusivity but still acceptable for VRB applications [25]. It was however shown that shorter polymerization times improved the membranes resistance against oxidation and improved its stability [26]. A similar approach was used to obtain sulfonated AMV but led to cross contamination of V through the membrane [27]. In an alternative route a polyelectrolyte in the form of polysodium 4-styrene-sulfate (PSSS) was introduced into the pores of Daramic to include the cation-capacity upon cross-linking with DVB. The use of PSSS improved solvent transport trough the membrane due to its hydrophilic properties [28].

More recently in 2013 another membrane based on microporous PE as support was presented. In this work the pores of the PE membrane support were filled with poly-4-vinylbenzyl chloride (VBC) [29]. In their work they showed that the incorporation of 10 wt. % of VBC led to a reduction in vanadium permeability of 48% compared to that of Nafion 117 while the area resistivities were similar. This type of membrane showed a good selectivity when it comes to ion cross-over, high proton permeation and a low vanadium cross diffusion. The EE is 5.4% higher than the EE of Nafion 117 [29].

3.1.2. Fluorocarbon based membranes

The current generation of membranes applied in VRB applications, but also in fuel cells are largely based on fluorinated carbon backbone polymers. The use of such materials as base material is of interest because of their high chemical stability under the oxidative conditions of the VRB battery [30]. Nafion produced by the DuPont company and the Nafion 117 is made up from a fluorocarbon polymer, consisting of hydrophobic Teflon-like backbone with hydrophilic side chains, decorated with sulfonic acid groups [31]. The number in the polymer name (e.g. Nafion 117) indicates the equivalent weight and thickness of the Nafion membrane. Jiang et al. investigated the effect of Nafion membrane thickness [32] on various membrane parameters important for VRBs. It was shown that a thicker membrane led to a lower vanadium ion permeability which improves the CE and the self-discharge rate. Looking at these two parameters, the order of the membranes would be: N112 < N1135 < N115 < N117. Discharge capacity, fading rate and

electrolyte volume, increased with decreasing membrane thickness, while the membrane resistance decreased. All these parameters lead to an optimal thickness for the EE which was determined to be Nafion 115 [32].

The current understanding is that the sulfonic acid groups are organized in such way that 2.5 nm channels are formed which enable the transport of small ions. The fluorocarbon polymer provides the mechanical strength of the membrane. This model is known as the water channel model [33, 34]. Currently, this material is often used in batteries and fuel cells because of the high proton conductivity and good chemical and thermal stability [35]. However, the untreated Nafion membrane itself is prone to substantial vanadium ions to crossover when used to separate the electrolytes in the VRB [11, 35]. In addition, the high binding ion strength of V⁴⁺ leading to membrane fouling is a driving force to decrease vanadium permeation through the membrane [36]. Since the Nafion membrane makes up a large part of the cell cost [11] various modification methods of Nafion have been investigated in literature.

3.1.3. Nafion based polymeric composite membranes

By exchanging a part of the Nafion material with cheaper alternatives it is possible to reduce costs [37]. Tian et al. reported a method to impregnate Nafion into a cheap microporous polyethylene Daramic membrane by soaking it in a 5 wt. % Nafion solution. Compared to the parent Daramic membrane the impregnated material showed reduced water uptake and lower vanadium permeability resulting in a lower self-discharge. The results were however not compared to a pure Nafion membrane [38]. Another example to reduce on Nafion material costs is to laminate a poly (ether ketone) SPEEK membrane with a Nafion membrane. Despite the excellent conductivity properties of SPEEK, its chemical stability in the oxidative VO^{2+} environment. By covering the SPEEK material with the highly stable Nafion layer the material is protected without losing substantial performance in VRB applications [39].

Recently, commercial Nafion hybrid membranes are on the market such as VANADion [40]. In this unclassified composite membrane a thin layer of Nafion 115 is combined with a porous layer [40]. The non-Nafion part of the composite consists of a porous layer possesses a high proton conductivity increasing further when in contact with strong acids. The dense Nafion membrane part acts as the V resistant membrane reducing permeability. Comparing the performance of the membrane in VRB applications it was shown that the VANADion material showed improved EE (71.3%) compared to that of Nafion 115 (76.2%). Also, the electrolyte utilization increases from 54.1% to 68.4%, even at a high current density of 240 mA•cm⁻² [40]. Moreover, the durability of the hybrid VANADion membrane in multiple charge/ discharge cycling was shown to be similar to that of Nafion 115 and VANADion over the 80–240 mA•cm⁻² current density range [40].

3.1.4. Nafion based inorganic hybrid membranes

Another point for further improvement is to reduce permeability of V through the membrane. The surface of the Nafion consists of polar clusters in the membrane which enhances the V cross-over. By filling these polar clusters using inorganic nanoparticles the polar nanocluster become blocked. An example of such hybrid material was presented by Xi et al. [35]. In their study a Nafion 117 membrane was treated with SiO₂ sol-gel to fill the polar clusters of the Nafion membrane. Results showed that the IEC and proton conductivity properties of the composite Nafion/SiO₂ membrane were preserved. The V crossover, however, was dramatically reduced leading to higher CE (~93%) and EE (~80%) compared to that of Nafion-117 (CE = ~92%; EE = ~74%) values and a lower self-discharge rate. Also, the membrane was shown to be stable showing perseverance of the VRB after 100 charge-discharge cycles [35]. Replacing sol-gel silica precursor with tetra ethyl ortho silicate (TEOS) and diethoxydimethylsilane (DEDMS) to form the Nafion/ORMOSIL membrane. This ORMOSIL membrane contained

even higher efficiencies (CE = ~96%; EE = 88%) values compared to the Nafion and Nafion/SiO₂ membrane and a further reduced self-discharge rate. These improved properties were attributed to the improved vanadium ion blocking characteristic of this hybrid membrane [41]. Teng et al. attempted to further improve the Nafion/ORMOSIL membrane by treating with TiO₂, but this did not lead to further performance improvement [42].

The conductivity of the Nafion-117 membrane upon introduction of SiO₂ leads to a small decrease in conductivity. To improve conductivity of the Nafion/SiO₂ membrane Nafion can be impregnated with amine functionalized SiO₂ nanoparticles [43]. The amino groups of amino functionalized SiO₂ nanoparticles resulted in improved conductivity while the SiO₂ particles increased the membrane selectivity. The efficiencies (CE = 96%, VE = 83% and EE = 74%) increased and are comparable to that of the reference Nafion membrane [43].

3.2. Nafion surface polymerization

Lamination of a polymer layer on top of Nafion or the deposition of polyelectrolytes is an alternative to reduce V permeability, but these systems can also be prone to swelling of the membrane. Swelling is detrimental since it leads to reduction of membrane lifetime. To reduce swelling it is possible to grow the polyelectrolyte polyimine layer on top of the Nafion surface via interface polymerization. In this way a cationic charged layer can formed on the surface of Nafion which is strongly bonded to the Nafion surface. As a result of the repulsive layer the membrane showed a lower vanadium ion crossover rate, at the cost of a higher area resistance. Due to the lower permeability, the membrane shows less water transfer and a reduction in self-discharge rate [44].

Graphene materials have gained attention in recent decades because of its high conductivity, mechanical strength and barrier properties [45, 46]. By introducing graphene oxide (GO) in a blend with Nafion followed by spin-coating, a well oriented material is formed with a high barrier effect preventing V to cross-over [47]. Because of the reduced permeability higher CE and EE were obtained for the GO/Nafion membrane compared with the pristine Nafion membrane due to the improved barrier properties. Because of the conductive properties of GO proton conduction was preserved.

3.3. Poly aryl ether membranes

A promising cheaper membrane material as an alternative to Nafion is the use sulfonated aryl backbone polymers such as SPEEK, SPES and SPESK. These materials possess good thermal and mechanical stability and proton conductivity which can be easily achieved by introducing sulfonic acid, imidazole and quaternary ammonium groups. By doing so the SPEEK, SPES, and SPESK membranes are potentially suitable for VRB application because of their reasonable price, good ionic conductivity, and strong mechanical properties. The proton conductivity of these materials depends on the degree of sulfonation; however, it is generally lower than that of Nafion [48]. With a higher degree of sulfonation the SPEEK membrane can take up more water leading to swelling, and thus, higher V permeability, discharge lifetime and membrane oxidation [49-51]. Nevertheless, these membranes possess lower V permeability compared to Nafion membranes. This is attributed to the fact that the channels in the Nafion membranes are more continuous compared to those in sulfonated hydrocarbon membranes [52]. For instance, a SPEEK-40 (40 indicates the degree of sulfonated monomers [53]) membrane showed an order of magnitude lower V cross over compared to Nafion 115 resulting in substantial higher CE and EE values for the SPEEK membrane [54]. The Achilles heel of SPEEK membranes are their susceptibility to swelling due to bulk water uptake in the large hydrophilic regions. Furthermore, the arylether linkages are susceptible to oxidative degradation [55].

3.3.1. Organic hybrid polyarylether membranes

Because of the high degree of sulfonation SPEEK has excellent conductivity properties while possessing strong mechanical stability and resistance to acidic conditions. However, high degree of sulfonation (DS) leads to swelling of the membrane and increased V permeability decreasing the stability of the membrane and performance in VRB. To increase chemical stability, combinations of polymeric membrane materials with SPEEK to form a hybrid membrane have been explored. One of the first hybrid SPEEK membranes was a composite material with Nafion [39]. Using SPEEK as filler material reduced the price of the membrane substantially and reduced V permeability. The application of Nafion at the surface of SPEEK improved the chemical stability due to its antioxygenic properties and proton conductivity.

Jia et al. [17] have reported a layered composite membrane consisting of stacked layers of SPEEK, PP and perfluorosulfonic acid sulfonated (PFSA) abbreviated as S/P/P membrane. The PFSA layer improved the oxidation properties of the membrane and, thus, the chemical stability of the material. The PP layer is applied to support the PFSA and SPEEK layers. Furthermore, the SPEEK and PP contribute to the reduction in V permeability, while the SPEEK layer still imposes good conductivity. The composite membrane showed a slightly higher area resistance but a significantly lower vanadium ion permeability, compared with Nafion 212. The CE of the S/P/P membrane was higher compared to Nafion 212. Due to the higher are resistance the VE of the S/P/P membrane was lower compared to that of Nafion 212 [17].

Blending the SPEEK monomer with polymer monomers which are less susceptible to swelling like sulfonated poly(ethersulfone), can also improve the stability of the material, but still possessing the advantageous properties of SPEEK such as high conductivity. The SPES/SPEEK membrane showed a strong mechanical strength, high water uptake and a low permeability of V ions. These properties where attributed to a lower degree of swelling due to incorporation of SPES into the SPEEK matrix. Compared with Nafion 212, the CE and EE of this SPES/SPEEK hybrid membrane were higher (CE: 98% vs. 91% and EE 84% vs. 79.5%). When being applied in a VRB, the system showed a lower charge capacity loss. Even after 100 cycles, there was no significant decline in CE and EE [17].

3.3.2. Polyarylether crosslinking

As mentioned before, hydrocarbon membranes such as SPEEK are more susceptible to swelling compared to PTFS materials such as Nafion. As a result of swelling SPEEK membranes are more prone to ether linkage oxidation with VO^{2+} species [55] when diffusing trough the membrane. One way to reduce SPEEK membrane swelling and improve mechanical stability is to introduce crosslinking between polymer chains thereby introducing covalent bonds. The introduction of crosslinks can be done by introducing functional groups in the monomers which can later be activated to form interchain cross-links. As an example, the crosslinking of SPEEK with diallyl bisphenol A group in the SPEEK main chain was investigated by Zhang et al. [56]. The allylic groups were cross polymerized via UV polymerisation. The result is a sulfonated poly (diallyl-bisphenol ether ketone) (SDPEEK) membrane. It was also shown that high degrees of sulfonation (80%) still lead to substantially lower V^{4+} permeability (2.4 × 10⁻⁸ cm^{2} •min⁻¹) compared to Nafion 115 (1.04 × 10⁻⁶ cm²•min⁻¹). Although somewhat lower increased ion selectivity was observed at SD value of 100% resulting in an even higher CE and EE. Also, the SDPEEK membrane with a SD of 80% showed a higher CE (98% vs. 92%) and a longer self-discharge time (180 h vs. 50 h) [56].

3.3.3. Polyarylether graphene hybrid materials

To reduce V permeability trough the SPEEK membrane Dai et al. [45] incorporated graphene oxide into the polymer blend. Graphene oxide is an interesting material due to its mechanical strength, a thickness of only one or a few carbon atoms, high electrical conductivity and excellent barrier properties [57]. The material with a DS

of 75% outperformed the Nafion 117 material especially at higher current densities. For instance, the material contained a CE of 97% at a current density of 200 mA•cm² compared to 94% for that of Nafion 117. Also, EE and VE being both 70% for the S/G membrane, which are higher compared to that of Nafion 117. The composite membrane also contained substantial lower permeability compared to SPEEK and Nafion 117. Due to the lower permeability, the membrane was less susceptible to degradation under VRB conditions.

In another study, it was attempted to increase mechanical stability further by embedding short-carboxylic multi-walled carbon nanotubes into SPEEK membranes (SPEEK/SCCT) [50]. This composite membrane had been prepared with a high DS. This treated SPEEK membrane containing a DS of 50% showed enhanced mechanical strength. In this paper the performance was compared to that of Nafion 212 membrane in VRB and it showed an increase of the CE by 7% and 6% for the EE. Overall, the membrane showed a good cell performance, a reduced vanadium ion permeability compared to pure SPEEK membranes, and compared to Nafion 212 it showed a lower capacity loss rate [50].

3.3.4. Hybrid organic/inorganic sulfonated polyarylether membranes

Besides polymeric hybrid materials also the application of organic/ inorganic hybrid SPEEK materials have been investigated. The use of inorganic fillers can have beneficial effects on the properties of such hybrid membrane by the formation of dynamic cross-links [58, 59]. As a result of such interactions the proton conductivity, mechanical and vanadium permeability properties potentially can improve [60]. Sun et al. have shown the beneficial effect of the introduction of H₃PW₁₂O₄₀ or WO₃ into SPEEK materials resulting in improved proton conductivity and reduced V permeability. The ion selectivity of the SPEEK/ $(WO_3)_x$ hybrid membrane is more than three times higher than that of recast Nafion, 2.1×10^4 S•min•cm⁻³ instead of 6.5×10^3 S•min•cm⁻³, respectively. The water uptake as well as the conductivity improved. Also, when the most promising SPEEK/(WO₃)_x membrane (with the best NPs concentration) was mounted in a VRB cell operating at realistic conditions, the CE and cyclability were improved over a system operated with a Nafion 212 membrane [60]. The improved conductivity was attributed to the formation of better connected channels in the membrane material [61]. The reduced permeability is attributed to the increased cross-linking of the membrane thereby reducing the size of the hydrophilic domains leading to less water uptake which eventually leads to less swelling of the membrane [62]. Various other applications of tungsten type nanoparticles have been reported in literature on sulfonated polyarylethers [63,64].

Another sulfonated poly (phthalazinone ether ketone) (SPPEK) has also been considered for VRB applications after modification with tungstophosphoric acid (TPA). The SPPEK-TPA-17. The PPEK is interesting because of its higher glass transition temperature and thermal stability [65]. Despite the promising properties of this material, it is also prone to swelling due to water uptake. To reduce swelling a composite membrane consisting of SPPEK was prepared with 8 wt.% to 25 wt.% tungstophosphoric acid (TPA). The SPPEK-TPA-17 (containing 17 wt.% TPA) showed the best results. The composite membrane had a higher CE (98.75% vs. 92.81%) and EE (74.58% vs. 73.83%) compared with a system using a Nafion 117 membrane. Cycling test showed that the SPPEK/TPA membrane has a high chemical stability [64, 66].

Comparable to the Nafion/SiO₂ hybrid membranes a similar approach was followed to reduce V membrane permeability in a poly ether sulfone (PES) membrane [67]. It was reported that the pore size and pore size distribution can be easily adjusted by controlling the amount of silica gels in the pores of the pristine PES membrane. The CE, VE and EE of this membrane were substantially increased to that of the pristine PES membrane. This modified PES membrane has a high oxidation stability demonstrated by a long-term VRB operation [67].

As has been discussed earlier the introduction of SiO_2 nanoparticles has a negative effect on the conductivity of the membrane material [43]. Research on SPES membranes showed that the incorporation of conducting AEM materials for VRB.

4.1. Novel AEM materials

membrane with inorganic fillers in the form of sulphated zirconia $(SeZrO_2)$ additive in sulphated poly (ether sulfone) (SPES) in order to increase proton conductivity while inhibit the crossover of vanadium ions. SPES/SeZrO₂ is a membrane which performs better than Nafion 212 in this area. Because of this enhanced vanadium permeability, the self-discharge time was prolonged by four times the value than that of Nafion 212. But also, the CE and EE were higher, reaching 98.89% and 86.78% at a current density of 100 mA•cm⁻², respectively. At this current density, the EE of over 86% is maintained after 70 charge-discharge cycles. The efficiencies are higher than the pristine SPES membrane [68].

WO₃ particles can decrease membrane permeability without decreasing

the conductivity of the material. Therefore, researchers doped the SPES

The examples discussed in this section on cationic exchange membranes describe ways to improve the performance of cationic membranes in VRB applications. The cationic exchange membranes are susceptible due to interaction with the V electrolyte thereby causing cell discharge and lower membrane lifetime. The most promising methods are based on treatment of commercial membranes with inorganic nanoparticles, graphene oxide. The current standard in VRB membrane science is Nafion 117, which is prone to high V permeability and high costs. To reduce membrane costs also the combination of membrane materials has been investigated such as the Nafion/SPEEK hybrid. Another promising method is to use relatively cheap membranes such as polyethylene and polypropylene and fill the pores with highly conductive and V impermeable polyelectrolyte or Nafion type polymers.

4. Anionic membranes

An alternative membrane type class is the Anionic Exchange Membrane (AEM). Due to their positively charged functional groups they repulse positively charged V species (Fig. 2) from the membrane [69]. This effect is also described as the Donnan effect [70]. Although, the reduced V permeability of AEM is of high interest, they have drawbacks for application in VRB. The AEMs show reduced proton conductivity as well as poor chemical stability thereby hampering the commercial application in VRB [71-73]. Comparisons of various commercially available membranes by Hwiang et al. [74] reported that conductivities are lower compared to that of Nafion 117. Higher SO₄²⁻ and HSO4⁻ permeability is usually observed in AEMs than CEMs, leading to preferential water transfer trough the membrane [75]. The prevention of the degradation of anionic groups of the membrane remains challenging and several studies have investigated the mechanism of AEM degradation [74,76]. It was found that, the stability of these membranes' are affected largely by the molecular structure of the polymer backbone and the functional groups [55, 77-80]. More recent research focusses on the preparation of more stable and better

Qui et al. described the preparation of 2-(dimethylamino)ethyl methacrylate (DMAEMA) functionalized ETFE via y-radiation induced grafting [81]. After grafting DMAEMA the material was further functionalized using di-methylammonium chloride to introduce conductive properties to the material. The final material was abbreviated as ETFE-g-PMAOEDMAC. Results showed that with increasing grafting yield, the water uptake as well as the IEC increased while the area resistance decreased. As a result, this membrane contained a higher IEC, but lower area resistance than Nafion 117. The permeability towards V was substantially lower so it could maintain the OCV for more than 50 h compared to 17 h for Nafion 117. The vanadium ion permeability was as low as 1/20 to 1/40 than that from Nafion likely due to the Donnan effect.

The application of polybenzimidazole (PBI) anion membranes has attracted high attention for their application as a membrane in VRB's [82, 83]. The use of PBI is advantageous because of its highly chemical stable backbone which can withstand the highly acidic and oxidative conditions of VRB. Furthermore, the narrow pore size of PBI helps to reduce V permeability [84, 85]. The PBI materials are not conductive from themselves but can interact with acids such as sulfuric acid also known as acid doped membranes. The PBI materials are highly stable under VRB conditions whereas most of the non-fluorinated hydrocarbon are prone to degradation as a result of reaction with highly charged V ions [76]. The conductivity of the PBI membrane can be further improved when blending with FAA3i, which is a commercially available anion exchange polymer consisting of a poly(phenylene oxide) chain structure decorated with quaternary ammonium groups [86]. When blending PBI with FAA3i, CE will slightly decrease from 99.7 to 97.8%, while the VE will strongly increase with 5.7% to 88.22% which results in a higher EE of 86.2% (at $80 \text{ mA} \cdot \text{cm}^{-2}$) when more FAA3i is introduced. This performance in EE is comparable to that of meta-PBI (82.2%) and Nafion 212 (83%). The chemical stability of the membrane becomes lower against VO₂⁺ with more FAA3i introduced in the polymer blends.

Another AEM was prepared based on ether-free bond poly(p-phenylene)-based membrane functionalized with quaternary ammonium and imidazole groups. The results revealed the membrane prepared with quaternary ammonium groups to provide the best performance and properties [87]. The membrane showed an IEC of 2.1 meq•g⁻¹ with a high anion conductivity for OH⁻, SO₄²⁻, and Cl⁻. The diffusion coefficient for VO²⁺ was low, with 2.12×10^{-9} cm²•min⁻¹ compared to 2.88×10^{-6} cm²•min⁻¹ for Nafion 115. Also, its chemical and operational properties were excellent. Operated in a VRB, the CE was 99%, VE 87%, and EE 86% after 100 cycles at 80 mA•cm⁻² [88].



Fig. 2. Schematic representation of an anion exchange membrane.



Fig. 3. Schematic representation of amphoteric ion-exchange membranes.

The use of Anionic Exchange Membranes (AEM) has high potential for VRB application. Especially the highly repulsive character towards V-species due to the positively charged functional groups reduces V permeability substantially. The low stability of the functional cationic charged groups results in a relatively lower lifetime compared to CEM. Large research attention goes to improve stability of these groups which can be achieved by modifying the molecular structure of the polymeric membrane. By modification of the chemical environment it is attempted to increase steric hindrance thereby reducing oxidation of the cationic groups in AEM.

5. Amphoteric ion-exchange membranes (AIEM)

The Amphoteric Ion-Exchange Membranes (AIEM) contain both anionic and cationic exchange groups and provide the properties of both AEM and CEM membranes (Fig. 3). The CEM contain better stability against chemical degradation and higher conductive properties, while the AEM show lower V cross over rates. However, both membrane types suffer from water transfer trough the membrane due to cross-over of V, SO_4^{2-} and HSO_4^{-} species [75]. By introducing simultaneously AEM and CEM properties permeabilities of vanadium and sulphate species can be lowered.

Nafion materials are highly susceptible to V permeability. By alternating adsorption of the Nafion membrane with positively polycation poly(diallyldimethylammonium chloride) (PDDA) and negatively charged polyanion poly(sodium styrene sulfonate) (PSS) an electrostatic repellent force exists between vanadium ions and the positively charged polyelectrolyte layers covering the surface [89]. Experimental results indeed showed that less V was transferred through the Nafion-[PDDA-PSS]_n membrane compared to the regular Nafion membrane. As a result, higher Coulombic efficiency and energy efficiency were obtained and a slower self-discharge rate, the latter due to reduced V cross-over [89].

The group of Skyllaz et al. [75] did a comprehensive study on the effect of polyelectrolyte modification Gore Select L-01854 cationic exchange membrane. In this study various types of cationic and anionic electrolytes were studied in order to prevent preferential water transfer due to V, HSO_4^- and SO_4^{2-} crossover. In this procedure the Gore Select membranes were soaked for 10 days in a poly electrolyte solution after which they were washed with distilled water. Testing the permeability of V and SO_4^{2-} trough the polyelectrolyte modified Gore Select L-01854 membranes, showed that the diffusivity during short exposure times was reduced. However, over extended exposure times the polyelectrolyte modified membranes showed increased V, HSO_4^- and SO_4^{2-} permeability and preferential water transfer. Therefore addition of polyelectrolytes should be considered carefully since the cationic and anionic groups in the polyelectrolytes can increase V, HSO_4^- and SO_4^{2-} transfer rates [75].

Another example of polyelectrolyte modification is the surface modification of Nafion 117 with polypyrrole via various preparation methods. The best results were obtained with the membrane prepared by electro-deposition showing a reduction in V ion permeability of 5 times and a decrease in the water transfer property by over 3 times [41]. In a later study Schwenzer et al. [90] compared the effect of the amine-type incorporated into the polyelectrolyte. To study this various Nafion membranes were modified with polypyrrole and polyaniline. The variance in polymerization behaviour between aniline and pyrolle caused the V transport to be higher trough the polyaniline modified membrane, while the membrane resistance was lower compared to that to the polypyrolle modified Nafion membrane.

Another approach for the modification of fluorinated membrane materials is to introduce molecular functionalities by grafting precursor molecules to the membrane surface. The advantage of such procedure is that these functionalities can be introduced homogeneous trough the material. An example was described by Qiu et al. [91]. Their method consisted of a two-step radiation-induced grafting technique was used in which ETFE is first grafted with styrene followed by a sulfonation treatment (ETFE-g-PSSA). In the second grafting step dimethylaminoethyl methacrylate (DMAEMA) was grafted and protonated. This resulted in the AIEM membrane which both has anionic and cationic groups. As a result, the membrane contained high IEC, high conductivity, and reduced vanadium ion permeability compared to Nafion 117. The VRB equipped with this membrane could maintain an open circuit voltage (OCV) of more than 1.3 V after a 300 h placement. Also, the CE and EE of this AIEM membrane were higher than that of the Nafion 117 membrane. Because of the lower conductivity of the ETFEg-PSSA-g-DMEAMA membrane compared to that of Nafion 117 the VE, however, is somewhat lower compared to Nafion 117. After 40 cycles of charge and discharging, the AIEM membrane showed no declines in efficiency indicating good chemical stability.

In recent years the preparation and use of polyarylether based AIEM materials has been extensively studied. Similar to the Nafion materials the cationic exchange properties of SPEEK membranes makes it still susceptible to V permeability. Additionally, the hydrophilic character makes the material susceptible to swelling thereby increasing V permeability causing the aryl ether linkages to be oxidized. To reduce V permeability further, researchers treated the SPEEK polymer with an imidazolium-functionalized polysulfone (PSf) polymer thereby creating an amphoteric membrane abbreviated as ImPSf/SPEEK. The addition of PS reduces the large hydrophilic regions while the imidazole functionality introduces anionic properties introducing the Donnan effect repulsing V ions [92]. The performance of the ImPSf/SPEEK membrane was compared to that of Nafion 212. Because of the low V permeability of the membrane, the battery could keep an OCV of 0.8 V for 43 h, which is almost twice as long compared to that of Nafion 212 (23 h). Due to the lower permeability the capacity decay rate of this membrane was lower than Nafion212. The ImPSf/SPEEK membrane showed a low area resistance ($0.48 \Omega \text{ cm}^{-2}$) comparable to that of Nafion212 ($0.41 \Omega \text{ cm}^{-2}$). Furthermore, the efficiencies of ImPSf/SPEEK (CE = 97.5% and EE = 77.3%) were slightly higher to that of Nafion 212 (CE = 92.4% and EE = 73.4%) even at current densities as high as 200 mA cm⁻². Swelling can be problematic in polymer combined membranes but crosslinking between the imidazolium and sulfonic groups prevents swelling of this amphoteric ImPSf/SPEEK membrane.

An alternative way is to introduce anionic properties into the arylic backbone of the membrane as demonstrated by Jian et al. [93]. They prepared their membrane based on chloromethylated poly (phthalazinone ether sulfone ketone) (CMPPESK). The material was prepared by using chloromethyl octyl ethers (CMOE) on poly (phthalazinone ether sulfone ketone) (PPESK) forming a material abbreviated as CMPPESK. Then this CMPPESK was modified with a quaternary ammonium salt, as quaternized poly (phthalazinone ether sulfone ketone) (QAPPESK) was made. This prepared membrane showed excellent resistance when exposed to the solvents, being not dissolved in sulfuric acid (98%) and it was partly swollen in N, N-dimethylformamide. This membrane showed higher EE than a cell executed with a Nafion 117 membrane. Later work attempted to improve the synthesis method of the QAPPESK membrane to improve the VRB performance. Work by Zhang et al. describes an improved more environmental friendly synthesis preparation method to synthesize the membrane under milder conditions [56]. Others tried to improve the anionic properties by introducing more amine groups by treating the membranes with trimethyl amine and ethylene amine [94]. The effect of the degree of chloromethylation (DCM) was investigated by Zhang et al. [95] investigated revealing that V permeability substantially decreased with increasing DCM.

In the light of costs and availability of membrane materials Lee et al. [96] prepared an AIEM via impregnation of a microporous PE with vinylsulphonic acid, (vinylbenzyl)trimethylammonium chloride and N,N'-ethylene bisacrylamide monomers which were then UV polymerized after being sandwiched by PET film layers. The resulting membrane contained an ammonium functionalized sulfonated polyaryl keton material with AIEM properties. The prepared material showed lower vanadium permeability and higher conductivity compared to Nafion 117. The lower self-discharge rate and cycle performance test have proven that this AIEM crosslinked pore-filled membrane is suitable for VRB applications.

Another AIEM membrane from fluoro-methyl sulfonated poly(arylene ether ketone) bearing content-controlled benzimidazole moiety was produced. The ion diffusion is ultra-low, the vanadium-ion cross over is 638 times lower and the VO^{2+} permeability is 1117 times lower compared with Nafion 117. This resulted in a nearly 3 times longer battery self-discharge time. These low diffusion rates are owed to the fact that the ion transporting channels are narrower because of the acidbase interactions: there is the positively charged structure (benzimidazole) and the VO^{2+} ions. This resulted that all three efficiencies (CE, VE and EE) are equal or higher than that of Nafion 117 [97].

The use of Amphoteric Ion Exchange Membranes (AEIM) has currently a wide attention because of its cationic and anionic exchange properties. Thereby, it combines the advantages from both worlds bringing lower permeability for V, HSO_4^{-1} and SO_4^{2-1} species. Thereby it has the potential for less spontaneous discharge and preferential water transfer between half cells. Especially the modification of cationic membranes such as Nafion and SPEEK with polyelectrolyte or single functional groups containing anionic exchange species is of main interest in many studies.

6. Design constraints

The extensive research performed on polymeric membranes over the last decades improved our understanding on several important aspects to determine the final performance of membranes in VRB applications. These insights provided guidelines for producing novel membrane chemistries from various types of materials.

6.1. Membrane conductivity

The ease of proton transport through the membrane is determined by the ease of which charge balancing ions (H^+, SO_4^{2-}) and HSO_4^{-} can be transported through the membrane. High conductivity of these species is important to close the cell circuit. The greater the conductivity the more efficient and faster the discharge cycles can be performed. A high conductivity is needed to transport the charge balancing ions through the membrane at a fast rate. Fast rates are needed to obtain decent charge/discharge rates in case of high energy demand or energy production [98]. Membrane conductivity is introduced by introducing functional groups such as sulphonic acid, quaternary ammonium, or imidazole . Often the concentration determines the conductivity of the material and is expressed as the Ion Exchange Capacity (EIC) expressed in mmol/g. A higher concentration of these functional groups leads to a higher conductivity of the membrane. To measure proton conductivity Electrochemical Impedance Spectroscopy (EIS) is used and is expressed as $mS \cdot cm^{-1}$.

6.2. Membrane resistance

The area resistance indicates the internal resistance of the battery and should be as low as possible to minimize the loss in internal energy. However, an increased current density goes accompanied with an increase in resistance in the membrane resulting in loss in power and a loss in voltage efficiency over the charge/discharge cycle. Operating at lower current densities has to be compensated with larger cell stacks and, thus, electrolyte increasing the costs of the installation. [14] Higher hydrophilicity and a higher degree of interconnected channels can lead to a reduction in the internal resistance of a membrane [99]. The well interconnected water channels in Nafion membranes explains the relatively low resistance of these membranes [33]. To measure this, the membrane separated half cells are filled with V and H₂SO₄ from which area resistance is determined [96, 100-103]. Another common way to report conductivity is the resistivity of a membrane which is expressed as area resistance $\Omega \cdot cm^{-2}$. The resistance is measured by subtracting the resistance of the cell equipped without membrane from the cell equipped with membrane.

6.3. Vanadium permeability

Diffusion of the V ions from one half-cell to the other leads to discharge of the battery and, thus, determines the energy storage time of the battery. Extensive research has shown that the cationic membranes are susceptible to V permeability due to their attraction of the V species. To reduce permeability, pure anionic functionalized membranes and amphoteric membranes (combination of cationic and anionic functionalized groups) have been introduced. The introduction of anionic groups introduces repulsive forces hampering V ions to diffuse into the membrane pores thereby reducing V permeability.

Vanadium permeability can be measured by separating a reservoir with the membrane followed by filling one half-cell a sulfuric acid solution with the correct concentration of V species present [104]. The other half cell can be filled with a $MgSO_4$ solution of a similar ion concentration to reduce osmotic pressure [105]. From both reservoirs' samples can be taken over constant time intervals which can be analysed using elemental analysis, for instance ICP-AES to determine their V concentration. From these results it is possible to calculate cross-over rates [105].

Energy is also discharged by V permeating through the membrane and thus can reduce storage lifetime. To test the energy storage lifetime, the Open Circuit Voltage (OCV) is tested. The open circuit voltage in VRB systems is described as the difference in equilibrium potentials between the positive and the negative electrode [106–108,109] and depends on the concentrations of the various V species. The OCV is measured to investigate the susceptibility of the membrane to self-discharge which caused by cross-over of V ions trough the membrane. In typical experiments to test OCV of the VRB batteries the battery is charged to 1.7 V using a current density of for instance 20 mA·cm⁻² until full State-Of-Charge (SOC) is obtained. A higher current density leads to a faster discharge of the electrical energy resulting in higher charge and discharge capacities because V ions have less time to diffuse trough the membrane [35].

6.4. Preferential water transport

Hydrophilic properties of the membrane can promote a water flux to the membrane from one half cell to the other. This can be disadvantageous, because it can lead to flooding of the VRB reservoirs [15]. Due to concentration differences because of water transport from one half-cell to the other the storage capacity becomes lower. The drive for preferential water transport is when water in the hydration shell of V^{2+} , V^{3+} , SO_4^{2-} and HSO_4^{-} ions species diffuse through the membrane during charging and discharging events. In the cationic membrane permeation of V^{2+} and V^{3+} species mainly cause water transport, whereas in the anionic membrane SO_4^{2-} and HSO_4^{-} are responsible for water transfer [15]. Because of a difference in molecular concentrations over the membrane an unequal balance in osmotic pressure occurs which is equilibrated by transport of water from one to the other halfcell. This effect occurs upon charging and discharging events but becomes highly pronounced during deep discharging of the battery. This effect is closely related by V permeability and solving this problem will also contribute to a reduction in preferential water transport.

6.5. Membrane stability

Membrane stability is an important factor since it determines the lifetime of the whole battery. The battery working medium, which consists of sulfuric acid and V-species, generates a highly oxidative environment causing fouling and erosion. Also, the concentration of the dissolved V species can create problems and becomes more pronounced when membranes are more susceptible to swelling. For example, Nafion 112E/H⁺ showed an outstanding stability in 1.0 M V⁵⁺ but the worst in a 0.1 M V⁵⁺ solution [105]. This is attributed to the fact that more dilute vanadium concentrations lead to more V species to enter the pores which results in the swelling of the membrane [105].

Another issue determining the lifetime of a battery is the overcharging and discharging of a battery. At overcharge the battery will start to generate heat and produce hydrogen and oxygen gas leading to loss of water and pressure build up in the cell and eventually mechanical stress [110]. Also, the graphite electrode can react with the formed O_2 to generate CO_2 gas [110]. Therefore, commercial applications prevent charging and discharging of the complete battery capacity limiting the operation window in the 20–80% SOC. In commercial battery systems, software monitors the SOC to guarantee that batteries are operated in the 20–80% SOC window [111, 112]. The formation of gas can lead to overpressure on the battery cell, leading to deformation and mechanical stress on the membrane. Furthermore, heat generation can contribute further to mechanical stress and membrane decomposition. Therefore, the membranes should be able to withstand some mechanical stress to prevent rupture.

6.6. Morphology of membranes

Nafion membranes are the most used membranes in VRBs because of their high stability and proton conductivity. However, they suffer from the cross-mixing of vanadium ions. The membrane has the important task to transfer the charge balancing species between the half cells, at the same time to be selective enough to separate Vanadium species, where their mixing leads to auto battery discharge [75, 113].

The morphology of ion exchange membranes is another important factor which effects the ion-selectivity [114]. Ideally membranes consist of a homogeneous phase made up of a polymeric backbone decorated with functional ionic groups capable of exchanging cations [115]. To increase the mechanical strength and prevent dissolution into the water, polymer chains are often interconnected via cross-links [115]. Therefore, the morphology of a typical ion exchange membrane consists of hydrophobic and hydrophilic regions introduced by the polymer backbone and ionic groups, respectively [16]. The distribution of these two regions will largely affect the properties of membranes, namely ion selectivity, ion conductivity, mechanical and chemical stability. The hydrophobic polymeric backbone provides the materials strength, whereas the hydrophilic part introduces conductivity to the membrane [16]. Microscopic phase-separated morphology of membranes is mostly affected by the nature of the polymer chains. In particular, the length of the side chains has a strong effect on the morphology of the membrane [116] .Water channels in the membranes are formed in areas rich in hydrophilic ionic groups forming the walls of the channels and facilitate charge transport trough the membrane [117]. Another important function of the cross-linking in the polymeric backbone is to prevent extensive swelling of the membrane by water uptake [118]. In Nafion, the ionic side-chains and perfluorinated backbone makes up of continuous networks of ion channels. This leads to low ion selectivity in VRB. Conversely, SPEEK is a rigid aromatic polymer where the continuous ion channels are hard to occur. In depth understanding and characterization of the hydrophilic and hydrophobic phases and the morphology of a typical ion exchange membrane can help to reveal the working mechanisms and pathways for improvement.

7. Other chemistries

Innovative membranes are needed for vanadium redox flow batteries, in order to achieve the required criteria; i) cost reduction, ii) long cycle life, iii) high discharge rates and iv) high current densities. To achieve this, variety of materials were tested and reported in literature.

7.1. Zeolite membranes

Zeolite membranes have been considered in a wide range of applications such as catalysis and separation. The zeolite frameworks often used in acid catalysis are ZSM-5, zeolite Y, chabazite and zeolite B. The molecular structure consists of Si and Al coordinated in a tetrahedral fashion to oxygen atoms and are built in a highly ordered manner thereby creating a porous network. The high degree in pore size uniformity of these materials makes these materials suitable for molecular separation by means of shape and size selection of penetrating molecules. Zeolites can contain a large concentration of protons in their porous systems due to the presence of Brønsted Acidic Sites (BAS). These sites arise when Si-O-Al linkages are formed as part of the framework. Recently the use of zeolite as membrane in VRBs has drawn attention. Work by Xu et al. [119] showed the application of a zeolite T grown over an α -alumina substrate as membrane in VRB. The material showed high conductivity due to the high proton concentration inside the zeolite and the low thickness. Furthermore, the material has a high membrane selectivity resulting in a low V permeability due to its pore size (0.31 nm x 0.51 nm). Yang et al. [120] have evaluated the use of non-ionic silicalite-1 membranes, which shows low V permittivity. The absence of BAS and thus protons results in a relatively high resistance and a low conductivity compared to Nafion 117. When introducing Al into the zeolite framework the conductivity increases tremendously resulting in substantially higher CE, VE and EE values compared to Nafion [121]. Furthermore, the membrane shows very low V permeability resulting in virtually no self-discharge even after 650 h. The low permeability can be attributed to the fact that the smaller pore size of ZSM-5 channels (0.56 nm) compared to that of V and its hydration shell (Fig. 4).



Fig. 4. Schematic representation of a zeolite membrane.

7.2. Application of porous MOF membranes

Like zeolites, metal-organic frameworks (MOFs) are regarded as feasible materials for membrane-based separations, which are usually grown on substrates. MOFs, which are composed of metal ions and bridging organic ligands, have substantial variability resulting from the diverse possibilities of the combinations of metals and ligands. This provides opportunity to design and tune the chemical and structural properties of the MOFs, such as pore size, pore shape, permeability, selectivity, and conductivity. The introduction of functional groups through covalent bonding with the bridging organic ligands, makes it much easier to control the functionality at the molecular level than zeolites. Their stability, hydrophobicity/hydrophilicity, permeability, and conductivity should all be considered when designing a MOF for a membrane application [122] and makes them promising materials for electrochemical energy storage [123]. The metal-ligand bonds in MOFs are mostly vulnerable to hydrolysis, and therefore the earlier reported MOFs are instable in aqueous chemical environments. The vulnerability of metal-ligand bonds made these earlier MOFs mostly considered for gas separation rather than liquid-liquid separation. Nevertheless, in the recent years, variety of water stable MOFs have been reported, particularly as solid electrolytes [124-126]. Similar to MOFs, the covalent organic frameworks (COFs) are attractive candidates for advanced membrane applications owing to their high porosity, highly organized channels and enhanced stability [127] and employed in electrochemical applications [128].

The development of water-stable MOFs has opened the way for electrochemical applications. Zhang et al. [129] reported the water and acid stable MOF-801 used as a proton exchange membrane (PEM). MOF-801 is combined with poly(vinylpyrrolidone) (PVP) and poly(vinylidene fluoride) (PVDF) in a post synthesis method. The mixed matrix membranes (MMMs) combining polymers with other materials, such as MOFs is a common method applied in literature. This approach enables joining the advantages of both materials, such as the chemical and thermal stability of the host polymer with the ionic selectivity and/or conductivity of the guest material. MOF-801 on PVDF matrix shows high proton conductivity ($1.88 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$) at room temperature and at 98% relative humidity (RH) as well as stability to hydrochloric acid or diluting sodium hydroxide aqueous solutions and boiling water. Qin et al. [130] reported an alternative material, ferrocenyl carboxylate framework (FCF). Their FCF materials show proton conductivity of 1.17×10^{-1} S·cm⁻¹, at 100 °C and 98% RH, which is comparable to the commercial Nafion membranes and it is one of the highest among MOFs. Another two highly stable MOFs were reported by Xie et al. [131] which uses imidazole dicarboxylate as organic linker and Sr and Cd as metals. MOFs were tested in boiling water for 24 h and immersed in water for one week, which did not bring about any damage to their structure. In these MOFs, the nitrogen containing imidazole ligands enhances the proton conductivity by promoting hydrogen bonding. Another approach to utilise the N containing (e.g., imidazole, triazole, histamine) molecules is to incorporate them into the pores of a substrate. Luo et al. [132] achieved high proton conductivity by encapsulating imidazole molecules into a proton conducting MOF-808. MOF-808 possesses high proton $(10^{-3} \text{ S} \cdot \text{cm}^{-1})$ and chemical stability to water and acids. The replacement of DMF and water in the pores of MOF-808 with imidazole improved its proton conductivity further, which makes it a promising membrane material. In a similar synthesis approach, Zhang et al. [133] impregnated the pores of zeolitic imidazolate framework (ZIF) type MOF, ZIF-8, with an ionic liquid (BMIMCl) and used it as a filler to PVP and PVDF type polymer. A sulphated Zr-MOF-808 [134] mixed with Nafion has been shown recently to improve the stability, surpassing the performance of pure Nafion. Zhang et al. [135] compared the co-synthesis and post-synthesis approaches of the addition of imidazole on a MOF-801. Both materials showed stability in water and in acidic solutions with similar proton conductivities. By modifying the ligands in a MOF with functional groups (e.g. $-SO_3H$, $-NH_2$) may also effectively enhance the protonic carrier concentration and provide new ion transfer pathways. Dong et al. [136] prepared UiO-66 MOF materials modified with $-SO_3H$ and -NH₂ and prepared a mixed matrix membrane by incorporating them with chitosan. The hybrid membranes showed high proton conductivity, and stability under anhydrous conditions However, the longterm stability of these hybrid membranes is not clear. In addition, the hybrid MOF/Polymer material usually have lower proton conductivity than the parent MOF. The flexible nature of the polymers makes them convenient for practicality. Another advantage is their lightweight structure. Bai et al. [137] reported a Nickel 1,4-benzenedicarboxylic acid mixed with polyacrylonitrile, (Ni-BDC/PAN) nanofibrous membrane with incorporated imidazole molecules. Although imidazole improved the conductivity (6.04 \times 10⁻⁵ S·cm⁻¹) of this 1D MOFs/ polymer fibres, it remained relatively lower than others reported in literature. Ru et al. [138] functionalized MIL-101 type MOF with ammonia (-NH₂) and sulphate groups (-SO₃H) and mixed is with sulfonated poly(arylene ether ketone) (SNF-PAEK) type polymer matrix which contains naphthalene and fluorine moieties. This mixed matrix possessed remarkably high proton conductivity membrane (0.192 S cm⁻ , 80 °C), which was much higher than those of the pristine membrane $(0.145 \text{ S} \cdot \text{cm}^{-1})$ and even higher than recast Nafion $(0.134 \text{ S} \cdot \text{cm}^{-1})$ at 80 °C. It showed a power density of 125.7 mW·cm⁻² and an open-circuit voltage (0.839 V) in direct methanol fuel cell. The superior performance on adsorption, transport, and separation of molecules in MOF and in related porous structures are due to their unparalleled flexibility in adjusting the composition and geometry of the framework and its pores. Therefore, they remain as an important candidate for electrochemical separation applications. The cost of their large-scale production, their long-term stability, and their

cycle life should be addressed in an attempt for their commercial utilisation.

8. Conclusions and prospects

This review on the various approaches to prepare polymeric membranes for the application in Vanadium Redox Flow Batteries (VRB) reveals various factors which should be considered when developing new membranes materials with or without the addition of non-polymeric materials. Important factors are high conductivity, low vanadium permeability and high stability. The high conductivity is important to maintain a descent voltage efficiency during charge-discharge cycles at descent current densities. Cationic membranes have had large attention in the past because of the ease of sulfonic acid group incorporation thereby introducing high conductivity. However, cationic exchange membranes have the disadvantage that they are prone to V permeability leading to shorter discharge periods compared to anionic and amphoteric types of membranes. The permeability of VO²⁺ species into the membrane leads to oxidation of the membrane leading to lower mechanical strength and swelling. The use of anionic or amphoteric functionalities can reduce V permeability due to the Donan effect. Also, the cost of Nafion has prompted the search for other polymeric membrane materials. One of such group of materials are the aromatic polyether sulfonic materials. Another group of materials which could be useful for future application in VRB systems are Metal Organic Framework membranes which potential can be prepared with highly selective membrane separation and chemical properties.

Declaration of Competing Interest

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

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Supplementary materials

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