

CHAPTER II

LITERATURE REVIEW

2.1 Vanadium Redox Flow Battery (VRFB)

Demands for efficient energy delivery and the anticipated demand for renewable energy have generated a considerable interest in redox flow batteries (RFB) as an energy storage technology. RFB can be classified by several active electrolytes such as vanadium, iron/chromium, bromine/polysulfide, and zinc/bromine. However, VRFB is selected (when compared with other electrolytes) for this work because it displays good compatibility and selectivity of electrolytes. Moreover, the other electrolytes crossover and react irreversibly, not only they induce efficiency loss but also lead to degradation in overall performances of the system (Weber *et al.*, 2011).

Fuel cell and battery are so similar because both of them generate DC electricity and require a proton exchange membrane. The difference is: the fuel cell generate electricity from chemical fuel as shown in Figure 2.1; but the RFB is electricity storage device that can convert electricity energy to chemical energy by the discharge process. Moreover, RFB can convert chemical energy to electricity energy by the charge process as shown in Figure 2.2 (Grot, 2011).

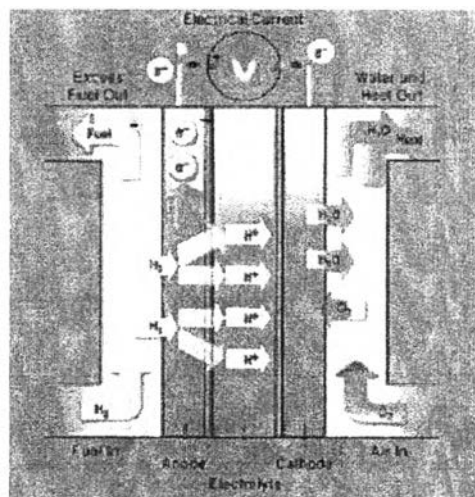


Figure 2.1 Principle of proton exchange membrane in fuel cell (Grot, 2011).

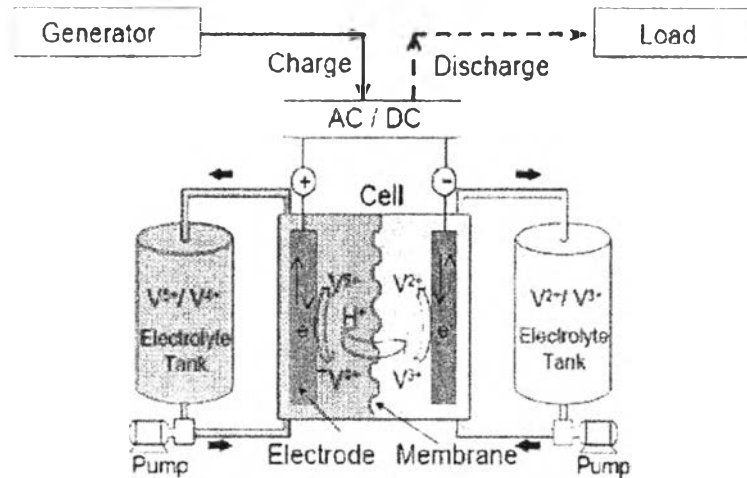


Figure 2.2 Principle of redox flow battery (Grot, 2011).

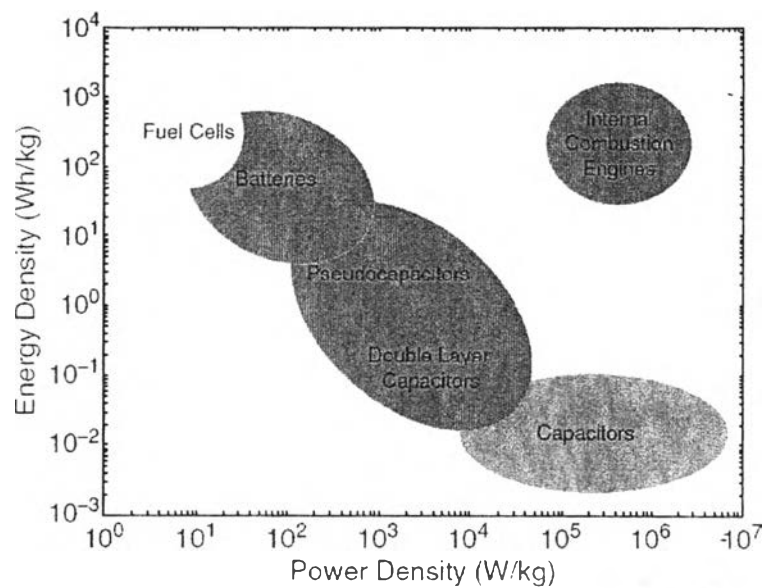


Figure 2.3 Comparison of the power density and energy density for batteries, capacitors, and fuel cells (Whittingham, 2008).

Figure 2.3 shows the energy (the capacity to do work) obtained from any storage device depending significantly on the device but also on the power output (the rate at work is done). Fuel cells have high energy storage, but their power output is limited. Whereas, batteries provide higher energies than capacitors, but capacitors are high-power devices with limited energy storage capability (Whittingham, 2008).

2.1.1 Principle of Vanadium Redox Flow Battery

Specific of the vanadium redox flow battery system, facile regeneration of the electroactive electrolytes is possible because the redox couples can form electrochemicals from a mixture of vanadium species. When the VRFB is charged, the VO^{2+} ions in the positive half-cell are converted to VO_2^+ ions when electrons are removed from the positive terminal of the battery. Similarly, in the negative half-cell, electrons are introduced and convert the V^{3+} ions into V^{2+} ions. The process during the discharge is reversed. The electrons go through the electrical circuit where the protons go through the membrane (Vynnycky, 2011).

2.1.2 Reaction of Vanadium Redox Flow Battery

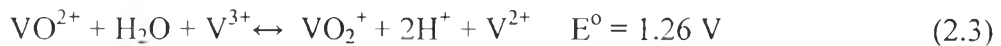
Negative electrode:



Positive electrode:



Overall reaction:



It is known that a VRFB generates a small amount of hydrogen during its operation. Over the lifetime of the battery, this leads to a gradual imbalance in the state-of-charge (SOC) of the positive and negative electrolytes. Not only increasing SOC limitation improves the electrolyte utilization but also increases the rate of hydrogen evolution. The reaction between VO_2^+ and H_2 extends the electrolyte utilization in the VRFB and electrolyte lifetime before rebalancing (Whitehead *et al.*, 2013).

2.1.3 Configuration of Vanadium Redox Flow Battery

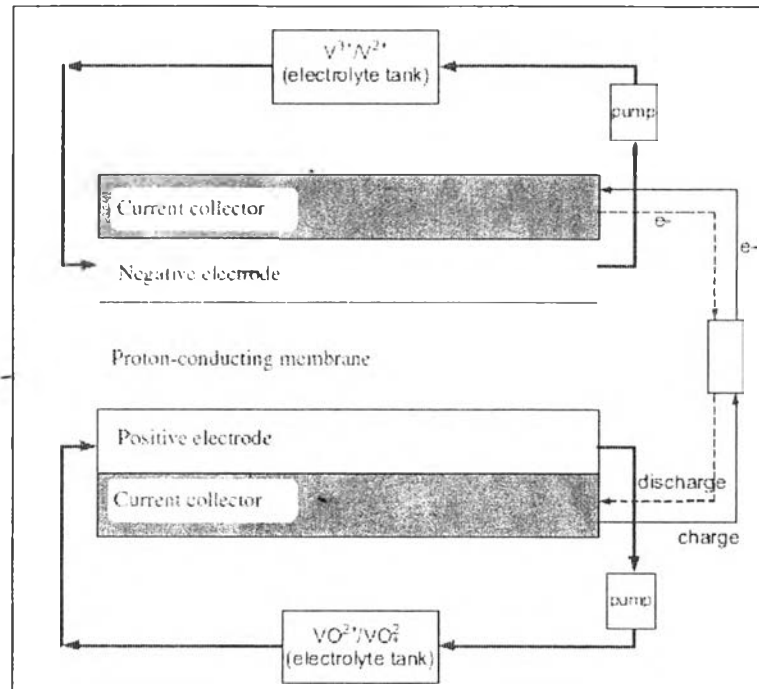


Figure 2.4 A schematic of the overall operation of a vanadium redox battery (Vynnycky, 2011).

Figure 2.4 shows that a VRFB is composed of an assembly of power cells, usually termed stack, although the schematic shows only one cell in which the two electrolytes are separated by a proton exchange membrane. Both electrolytes are vanadium based. The two electrolytes in VRFB are V^{2+}/V^{3+} and VO^{2+}/VO_2^+ redox couples in sulfuric acid. The electrolyte in the positive half-cell (anode) contains VO^{2+} and VO_2^+ ions, while the electrolyte in the negative half-cell (cathode) contains V^{3+} and V^{2+} ions. The electrolyte may be prepared by any one of several processes, including the electrolytic dissolution of vanadium pentoxide (V_2O_5) in sulfuric acid (H_2SO_4). In vanadium redox batteries, both half-cells are connected to storage tanks and pumps, so very large volumes of the electrolytes can be circulated through the cell (Vynnycky, 2011).

2.1.4 Advantages and disadvantages of Vanadium Redox Flow Battery

VRFB is attractive to develop as a stationary energy storage due to several factors including low maintenance cost, quick response time, deep discharge capability, less environment effect, ability to be recharged simply by replacing the electrolyte, and the accidental mixed electrolyte suffers no permanent damage due to electrolytes (Whitehead *et al.*, 2013).

However, VRFB still retains some drawbacks such as poor energy to volume ratio, heavy energy/weight ratio of electrolyte, and system complexity. VRFB is used as a stationary energy storage device, power supply for industrial or integrating wind, and solar to collect electricity. The optimization of vanadium flow battery has been focused on three areas including operation condition, cell geometry, and cell materials (Vynnycky, 2011).

2.2 Proton Exchange Membrane

The proton exchange membrane should provide an effective separation of the positive and negative electrolytes. The gradual exchange of electroactive species automatically through the membrane may lead to a loss of capacity. The function of a membrane does not only prevent the cross mixing of the positive and negative electrolytes, but also allows the transport of ions to complete a circuit during the passage of current.

Chieng *et al.* (1992) suggested that the ideal membrane should possess low permeability of vanadium ions and low water transport in order to obtain a higher coulombic efficiency, longer life cycle, higher proton conductivity, and higher voltage efficiency.

When considering a PEM, an anionic exchange membrane effectively reduces the permeation of the vanadium ions through the membrane owing to Donnan exclusion effect. It does not facilitate the conduction of protons which results in the sacrifice of voltage efficiency of the battery. The use of a cationic exchange membrane is more difficult to prevent the permeation of the vanadium ions with the passage of protons. However, it guarantees a lower resistance of the membrane and the possibility of higher energy efficiency (Chen *et al.*, 2010).

Different materials have been prepared as proton exchange membranes for VRFB. These membranes can be classified into three groups: perfluorosulfonic acid, aromatic polymer, and composite membranes (Park *et al.*, 2011).

2.2.1 Perfluorosulfonic Acid Membrane

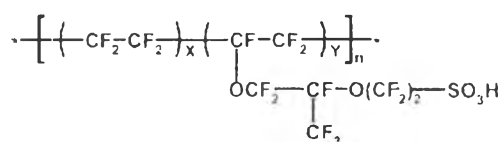


Figure 2.5 Chemical structure of Nafion (Park *et al.*, 2011).

Table 2.1 Nafion117 properties (Dupont, 2009)

Membrane properties	Nafion117
Thickness (mm)	0.183
Base weight (g/cm ²)	360
Specific gravity	1.98
Conductivity (S/cm)	0.10
Acid capacity (meq/g)	0.90
Water content (%)	
23 °C , 50% RH	5
Water uptake (%)	
Soaked at 100 °C for 1 h	38
Tensile modulus (MPa)	
50% RH	249
water soaked, 23 °C	114
Tensile strength (MPa)	
50% RH	43 in MD, 32 in TD
water soaked, 23 °C	34 in MD, 26 in TD
Elongation at break, %	

50% RH	225 in MD, 310 in TD
water soaked, 23 °C	200 in MD, 275 in TD

Perfluorosulfonic acid membrane (Nafion is the most favorable commercial membrane produced by Dupont) has extremely high hydrophilic sulfonic functional groups as shown in Figure 2.5. Protons, water, and vanadium ions can permeate through the membrane easily. Generally, a Nafion membrane is a large ionic cluster membrane yielding high conductivity but also causing high water transport. Additionally, the pristine Nafion exhibits high vanadium permeability that leads to the loss of energy capacity, thus the modification of Nafion is required to reduce the vanadium permeability. For specification of Nafion 117 are shown in Table 2.1.

Xi *et al.* (2007) prepared Nafion/SiO₂ hybrid membrane by in situ sol-gel method that not only displayed very lower vanadium ions permeability over 10 times but also provided nearly the similar proton conductivity compared to Nafion117 membrane as 56.2 and 58.7 mS/cm, respectively.

Luo *et al.* (2008) modified Nafion 117 to form the cationic charged layer using polyethylenimine (PEI) as polyelectrolyte. The results indicated that the crossover of vanadium ions across the membrane decreased significantly as shown in Figure 2.6. While the overall energy efficiency did not change significantly.

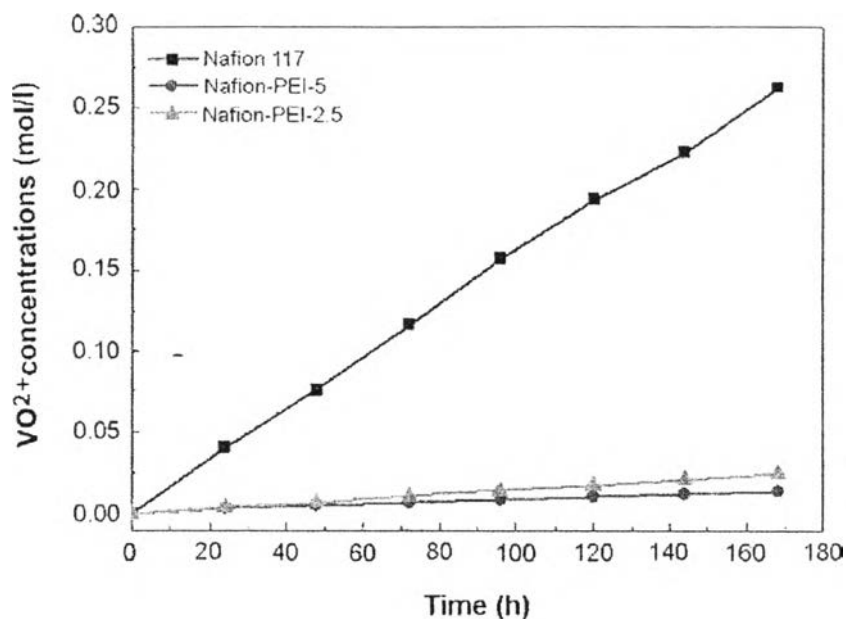


Figure 2.6 The increase of VO^{2+} concentration in the right reservoir (Luo *et al.*, 2008).

Teng *et al.* (2009) proved that the permeability of vanadium decreased (Figure 2.6) because the cluster inside Nafion membrane was filled with organic silica nanoparticles.

Even if perfluorosulfonic acid membrane has high proton conductivity and good chemical stability, but its cost is very expensive compared to other membranes. The perfluorosulfonic acid requires hydration to exhibit proton conductivity. When a Nafion membrane dehydrates, the size of the water clusters within the polymer microstructure decreases and this can diminish proton conductivity. Therefore, the operation temperature of Nafion is limited to the water boiling point (Sancho *et al.*, 2007).

The challenging of research and development on VRFB membranes is to decrease vanadium permeation by replacing nafion with other membranes. Because the vanadium ions could transport through Nafion easily, mix and react with each other, and leading to capacity loss known as self-discharge. For example, anion-conductive membranes (Mai *et al.*, 2013), sulfonated aromatic polymers was lower the vanadium permeability due to their less connected hydrophilic regions (Chen *et al.*, 2010; Chen *et al.*, 2010; Chen *et al.*, 2011; Mai *et al.*, 2011; Macksasitorn *et al.*,

2012). Modification technologies, such as inorganic doping and polymer blending could be used to prepare promising membranes (Sang *et al.*, 2007; Xi *et al.*, 2007; Teng *et al.*, 2009; Teng *et al.*, 2009; Mai *et al.*, 2011).

2.2.2 Aromatic membrane

Aromatic polymer membranes have been developed to replace perfluorosulfonic acid membranes used in the vanadium flow battery due to their high stability and sufficient proton conductivity. Aromatic membranes are certainly low cost membranes. Aromatic membranes have smaller hydrophilic domains than Nafion which has a more polarizable backbone structure. The vanadium permeation of aromatic membrane becomes lower. A number of aromatic polymers have been functionalized to give proton conductive ability by introducing the carboxylic acid group, the phosphoric acid group, or the sulfonic acid group on the polymer backbone or on the pendant chains (Parasuraman *et al.*, 2013).

2.2.2.1 Sulfonation Process

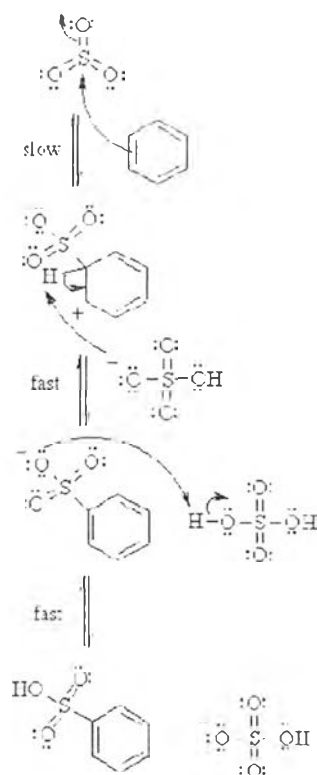


Figure 2.7 The mechanism of sulfonation reaction (Carey, 2000).

Sulfonation is an electrophilic substitution reaction where a sulfonation agent reacts on the aromatic rings and their protons are substituted by sulfonic acid. Unlike the other electrophilic aromatic substitution reactions, sulfonation is reversible. There are 3 steps of sulfonation mechanism as shown in Figure 2.7. First step, the π electrons of the aromatic C=C, which act as a nucleophile, attack the electrophilic S atom and push charge out onto an electronegative O atom (SO_3 can be formed by the loss of water from the sulfuric acid). This step destroys the aromaticity to produce the cyclohexadienyl cation intermediate. Second step, loss of the proton from the sp^3 C atom bearing the sulfonyl group reforms the C=C and the aromatic system. Third step, the sulfonic acid is formed via protonation of the conjugate base with sulfuric acid. The effect of substituent groups on a benzene ring have on both the rate and orientation of electrophilic aromatic substitution reactions. The electron donating groups (EDG) with lone pairs on the atoms adjacent to the π system activate the aromatic ring by increasing the electron density on the ring through a resonance donating effect. While the electron withdrawing groups (EWG) with π bonds to electronegative atoms (e.g. $-\text{C}=\text{O}$, $-\text{NO}_2$) adjacent to the p system deactivate the aromatic ring by decreasing the electron density on the ring through a resonance withdrawing effect (Carey, 2000).

The purpose of sulfonation process is to improve the proton transport via increasing hydrophilicity of polymer. Sulfonation process can be done pre-polymerization or post-polymerization. Pre-sulfonation process offers better control of sulfonation degree but this modification is too complex and impractical for large-scale commercial use. Nevertheless, post-sulfonation, introducing sulfonic acid groups into various types of aromatic polymers, is more widely used due to its simplicity and low production costs (Yee *et al.*, 2013). Sulfonation agents for polymers should be carefully chosen according to the polymer structure. Representative sulfonation agents include strong agents (e.g. concentrated sulfuric acid, fuming sulfuric acid, and chlorosulfonic acid) and mild agents (e.g. acetyl sulfate, sulfur trioxide complexes, and trimethylsilyl chlorosulfonate). Strong sulfonation agents may result in the chain degradation due to their high reactivity,

and excessive sulfonation render the host polymer water soluble. While mild sulfonation agents lead to a more homogeneous reaction, with no polymer degradation, and less side reactions occurring, it is often difficult to achieve a sufficiently high DS with these mild agents (Smitha *et al.*, 2003).

Many promising materials that have been demonstrated in operating cells are based on sulfonated aromatic polymer architectures such as poly(sulfone), poly(phenylene), poly(arylene ether ketone), poly(arylene sulfone), and polyimides as mentioned in following reviews.

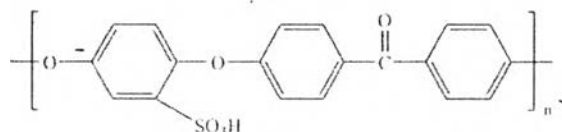


Figure 2.8 Chemical structure of sulfonated poly(ether ether ketone) (Macksasitorn *et al.*, 2012).

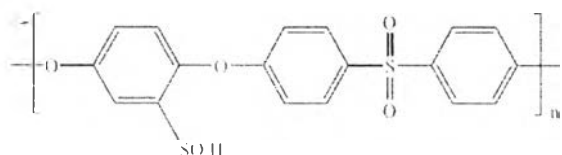


Figure 2.9 Chemical structure of sulfonated poly(1,4-phenylene ether ether sulfone) (Macksasitorn *et al.*, 2012).

A non-fluorinated membrane is low cost, low resistance, and high ion selectivity; (PEEK has less acidic of sulfonic group resulting in highly dispersed sulfonic group and high polarity trend to cluster formation). Moreover, the rigidity backbone prevents the aggregation of the sulfonic group to a large cluster. The permeation of each vanadium ions becomes lower. The vanadium permeability of S-PEEK (Figure 2.8) and S-PPEES (Figure 2.9) membranes were 2.42×10^{-8} and 2.50×10^{-6} cm^2/min , respectively which were significantly lower than that of Nafion117, which was 3.08×10^{-6} cm^2/min (Macksasitorn *et al.*, 2012).

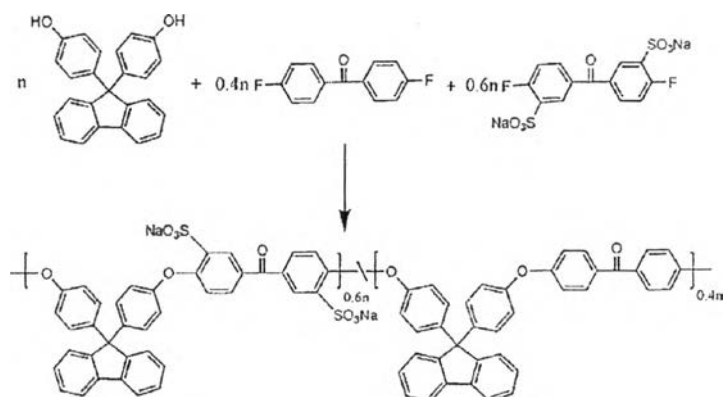


Figure 2.10 Synthesis of sulfonated poly(flourenyl ether ketone) (Chen *et al.*, 2010).

The sulfonated poly(flourenyl ether ketone), SPFEK, membrane as shown in Figure 2.10 displays the VO^{2+} diffusion coefficients (D) lower than Nafion117 that were 24.89×10^{-7} and 9.85×10^{-7} cm^2/min . While SPFEK and Nafion117 had comparable proton conductivity of 1.71×10^{-2} and 3.48×10^{-2} S/cm , respectively (Chen *et al.*, 2010).

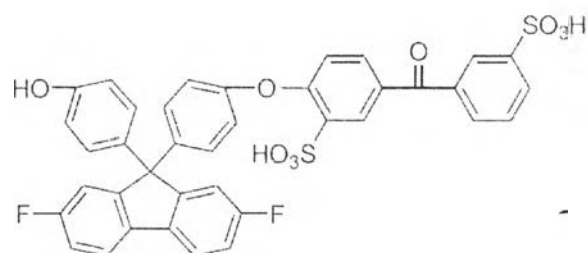


Figure 2.11 Chemical structure of fluorinated sulfonated poly(flourenyl ether ketone) (Chen *et al.*, 2012).

Furthermore, Chen *et al.* (2012) synthesized the fluorinated sulfonated poly(flourenyl ether ketone) (Figure 2.11) which had better proton conductivity (31 mS/cm) than sulfonated poly(flourenyl ether ketone) (19 mS/cm). Moreover, the composite of fluorinated sulfonated poly(flourenyl ether ketone)/3-aminopropyltriethoxysilane (F-SPFEK–APTES) revealed lower proton conductivity

due to its nonhomogeneous phase. After blending with APTES, the VO^{2+} permeabilities of composite polymer was effectively suppressed.

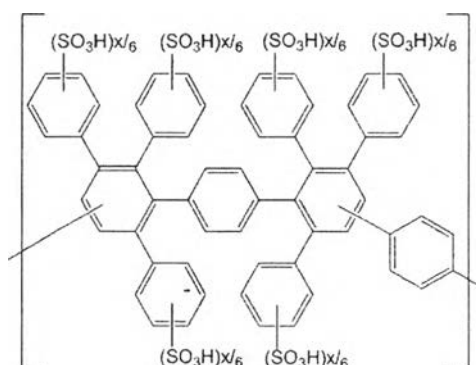


Figure 2.12 Sulfonated Diels Alder Poly(phenylene) (SDAPP) (Fujimoto *et al.*, 2005).

Fujimoto *et al.* (2012) investigated the proton conductivity and VO^{2+} permeability of sulfonated poly(phenylene) as shown in Figure 2.12 which was synthesized from the Diels Alder polymerization (Fujimoto *et al.*, 2005). The ion exchange capacity significantly affected both properties. In all cases, the SDAPP displayed comparable energy efficiencies (88-90%) to Nafion117 (88%).

Kim *et al.* (2010) revealed that the sulfonated aromatic-type membranes showed sufficient ion conductivity at high hydrated state, water permeability, reasonable mechanical, and chemical stabilities in polymer electrolyte fuel cells. Especially, sulfonated poly(phenyl sulfone) membrane had significantly lower vanadium permeability than Nafion117, improved self-discharge and columbic efficiency.

Fluorinated aromatic proton exchange membranes were found to have much higher oxidative stability (Chen *et al.*, 2013), good mechanical properties. But fluorine hydrophobicity did not improve water uptake (Chen *et al.*, 2012).

The important information of previous PEM for VRFB application composed of based polymer, modification approach, chemical structure, proton conductivity, vanadium permeability, and selectivity were summarized in Table 2.2.

Table 2.2 The important information of proton exchange membrane for vanadium redox flow battery application

Membrane	Modification	Proton conductivity (S/cm)	Vanadium permeability (cm ² /min)	Selectivity (S·min/cm ³)	Chemical structure	Reference
S-PEEK	Sulfonation	5.17×10^{-2}	2.42×10^{-8}	2.14×10^6	Figure 2.8	(Macksasitorn <i>et al.</i> , 2012)
S-PPEES	Sulfonation	1.24×10^{-1}	2.50×10^{-6}	4.97×10^4	Figure 2.9	(Macksasitorn <i>et al.</i> , 2012)
S-PFEK	Sulfonation	1.71×10^{-2}	2.49×10^{-6}	6.87×10^3	Figure 2.10	(Chen <i>et al.</i> , 2010)
F-SPFEK	Fluorinated	3.10×10^{-2}	3.30×10^{-8}	9.39×10^5	Figure 2.11	(Chen <i>et al.</i> , 2012)
S-DAPP	Sulfonation	4.90×10^{-2}	4.40×10^{-7}	1.11×10^5	Figure 2.12	(Fujimoto <i>et al.</i> , 2012)
S-PEEK/PVDF	Blend	9.20×10^{-3}	1.14×10^{-8}	8.06×10^5	-	(Li <i>et al.</i> , 2013)

2.2.3 Starting Polymer in Present Work

2.2.3.1 Poly(ether ether ketone)

Poly(ether ether ketone), PEEK, has been widely used as a PEM that provides high proton conductivity. Moreover, PEEK has proper mechanical properties and thermal stability.

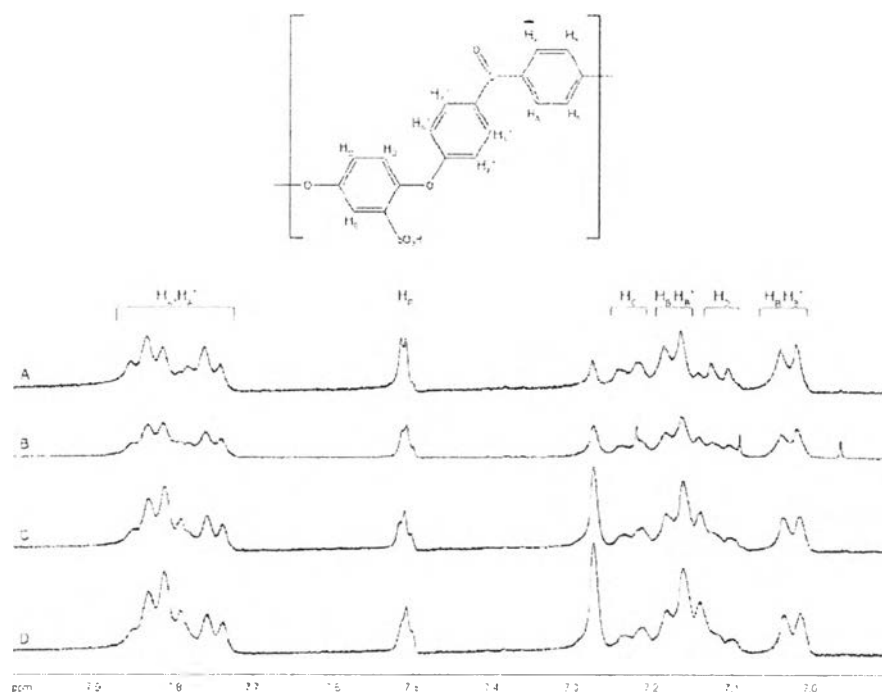


Figure 2.13 NMR analysis of S-PEEK produced at various sulfonation temperatures and reaction times: (A) 60 °C, 6 h; (B) 50 °C, 6 h; (C) 60 °C, 2 h; (D) 50 °C, 2 h (Yee *et al.*, 2013).

Yee *et al.* (2013) determined the structure of S-PEEK by ^1H -NMR analysis as shown in Figure 2.13. The spectrum showed the intensity of the H_E signal provided an estimation of the SO_3H group content at 7.5 ppm.

Jin *et al.* (1985) investigated the crystal structure of PEEK and S-PEEK. The X-ray diffraction of PEEK and S-PEEK showed four intense crystalline peaks at $2\theta = 20^\circ$, 21° , 23° , and 29° . The diffraction profile of PEEK also included an amorphous background with a maximum intensity of $2\theta = 20^\circ$. These

peaks corresponded respectively to reflections from 100, 111, 200, and 211 planes (Rikukawa *et al.*, 2000).

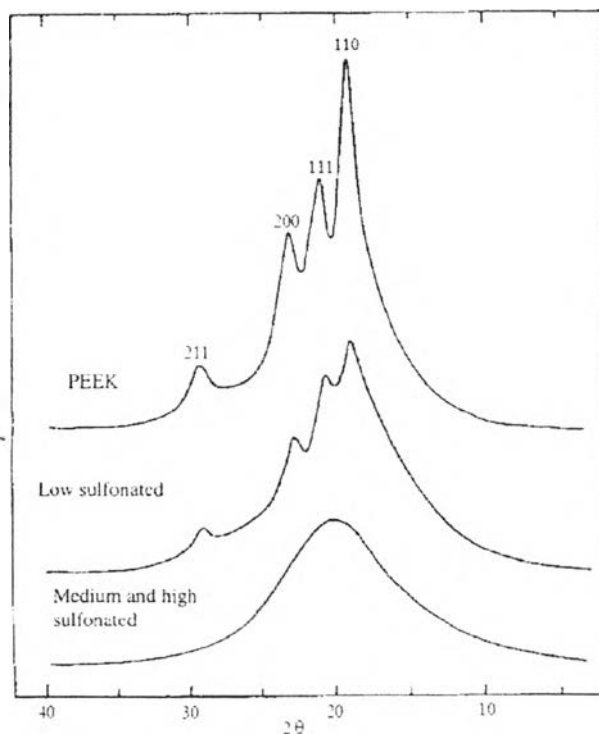


Figure 2.14 X-ray diffractogram of PEEK and sulfonated PEEK (Zaidi, 2003).

Zaidi (2003) concluded that the introduction of SO_3H groups into the PEEK changed the chain conformation and packing, and thus caused loss of crystallinity as shown in Figure 2.14. For low S-PEEK, the XRD pattern showed weaker and less intense crystalline peaks. This indicated that sulfonation strongly decreased the crystallinity of PEEK. While for medium and high S-PEEK sample, The diffractograms showed only a broad amorphous scattering background.

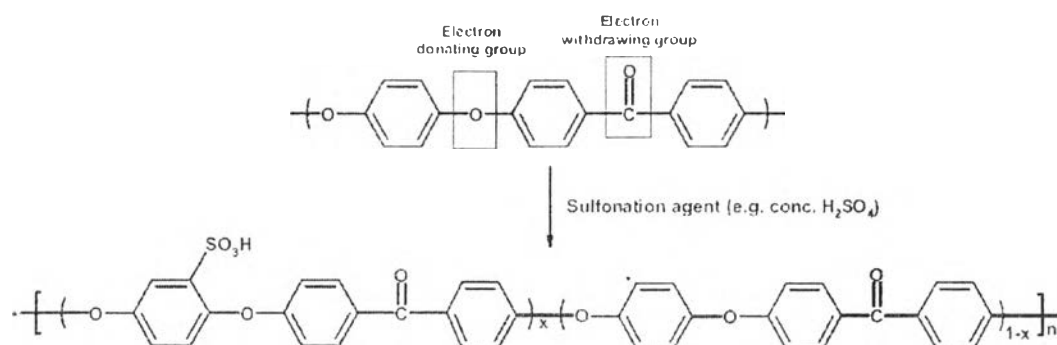


Figure 2.15 The scheme of the sulfonation of poly(ether ether ketone) (Park *et al.*, 2011).

For the PEEK sulfonation, the sulfonic acid group is introduced to the ring located between ether linkages due to their electron donating character as shown in Figure 2.15. Concentrated sulfuric acid is more appropriate as a sulfonation agent than chlorosulfonic acid or fuming sulfuric acid due to polymer chain degradation (Jin *et al.*, 1985; Xing *et al.*, 2004).

Macksasitorn *et al.* (2012) studied a sulfonated poly(ether ether ketone) membrane for VRFB in which the membrane had a vanadium permeability value of $24.95 \times 10^{-7} \text{ cm}^2/\text{min}$, lower than that of Nafion 117, which was $30.84 \times 10^{-7} \text{ cm}^2/\text{min}$.

Li *et al.* (2013) investigated the blend membranes of sulfonated poly(ether ether ketone) (S-PEEK) and poly(vinylidene fluoride) (PVdF) with various mixing mass ratios via solution casting. The addition of PVdF content depressed the swelling behavior of blend membranes that lowered the vanadium permeability. The swelling behaviors of blend membranes were indeed suppressed by PVdF because of the extending of crystalline region in the blend membranes. The prepared membrane with 15 %wt of PVdF provided the highest ion selectivity of $8.06 \times 10^5 \text{ S} \cdot \text{min}/\text{cm}^3$.

2.2.3.2 Poly(phenylene ether ether sulfone)(PPEES)

Poly(1,4-phenylene ether-ether-sulfone), PPEES, is a hopeful PEM because of its high performance thermoplastic having good film forming properties and high thermal stability (Wang *et al.*, 2007).

Unveren *et al.* (2010) studied the sulfonation process of poly(1,4-phenylene ether-ether-sulfone). First, PPEES pellet was dissolved in dichloromethane and precipitated in methanol to get PPEES in powder before sulfonated with concentrated sulfuric acid under nitrogen. After that, sulfonated PPEES membrane was prepared via solution casting with N,N-dimethylacetamide (DMAc).

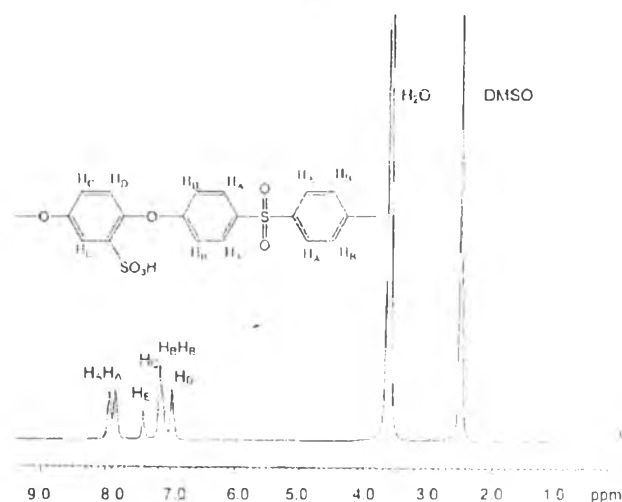


Figure 2.16 ^1H NMR spectrum of S-PPEES in DMSO-d₆ at 25 °C (Unveren *et al.*, 2010).

After the sulfonation process, the ^1H NMR spectrum of SPEES as shown in Figure 2.16 exhibits the presence of a sulfonic acid group causing a significant singlet signal (H_F) at 7.45 ppm.

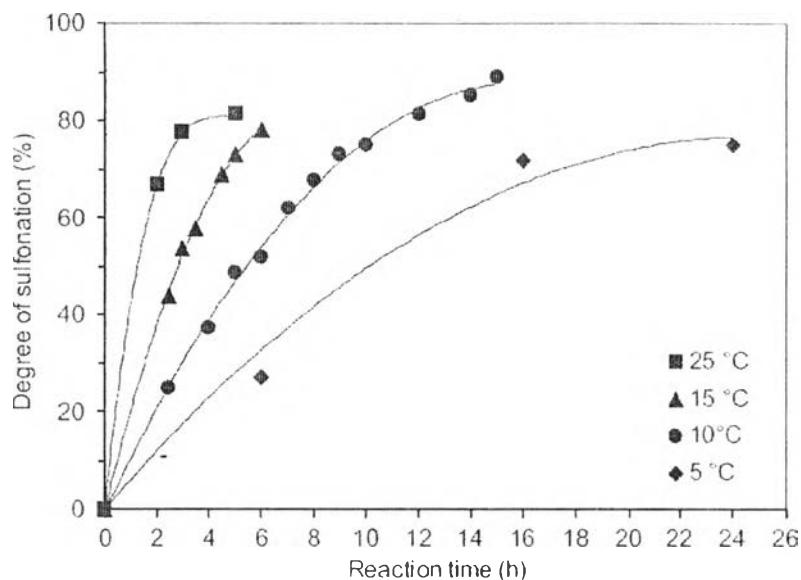


Figure 2.17 The reaction time dependence of the sulfonation degree of S-PPEES at different temperatures (Unveren *et al.*, 2010).

From Figure 2.17, for each sulfonation temperature, degree of sulfonation increases with increasing reaction time. The sulfonation reaction was very slow at low temperature while reaction was faster at higher temperature. For this reason, the degree of sulfonation increased sharply with reaction time at 25 °C. From Figure 2.18, the glass transition temperatures (T_g) of S-PPEES increases with degree of sulfonation because of the ionomer effect and increase in molecular bulkiness. However, T_g decreases with increasing degree of sulfonation at higher sulfonation temperature. The lowering trend can be referred to possible degradation reactions during the sulfonation reaction (Unveren *et al.*, 2010).

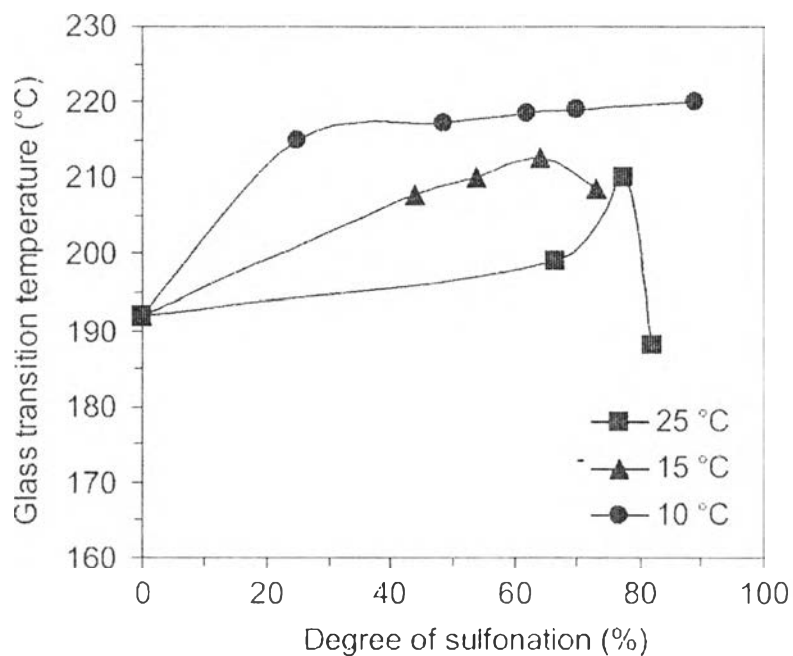


Figure 2.18 The glass transition temperature of S-PPEES versus sulfonation degree (Unveren *et al.*, 2010).

Macksasitorn *et al.* (2012) prepared the sulfonated PPEES powder by adding concentrated sulfuric acid to produce sulfonated PPEES as showed in Figure 2.19. Subsequently, sulfonated PPEES membrane was prepared via solution casting with dimethylformamide (DMF).

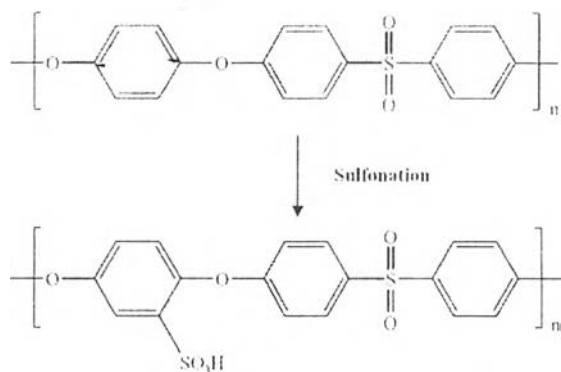


Figure 2.19 The scheme of the sulfonation of poly(phenylene ether ether sulfone).

2.3 Characterization Parameters

2.3.1 Degree of Sulfonation

Sulfonation process is the replacement of a hydrogen atom of an organic compound with a sulfonic acid ($-\text{SO}_3\text{H}$) functional group. In other words, it is an electrophilic substitution reaction where a sulfonation agent reacts on the aromatic rings and their protons are substituted by sulfonic acid. Here, the reaction site selectively occurs on the electron-rich site of benzene rings, such as the ortho-position to the electron donating groups. Electron-withdrawing groups deactivate benzene rings to electrophilic sulfonation. As such, the position of sulfonic acid groups can be controlled by the choice of the monomer or the polymer structure (Park *et al.*, 2011).

2.3.2 Proton Conductivity

The ionic resistance of a polymer electrolyte membrane is an important parameter in determining the mobility of protons through the membrane and the corresponding voltage loss across the membrane. Several techniques, such as Electrochemical impedance spectroscopy (EIS), current interruption, and nuclear magnetic resonance, have been used to measure the proton conductivity of membrane. Of these, EIS is the most powerful and popular. In PEMs, protons can transport in two directions, through-plane conductivity measurement is more important than in-plane because proton transfer occurs in the through-plane direction. The impedance of electrochemical system can be expressed in a Nyquist plot with each point representing the real part (X axis) and imaginary part (Y axis) of impedance as function of frequency. Some typical Nyquist plots for an electrochemical system are shown in Figure 2.20. The usual plot is a semicircle, with the high-frequency part giving the membrane resistance because imaginary part is zero and the width of the semicircle giving the charge-transfer resistance (Yuan *et al.*, 2010).

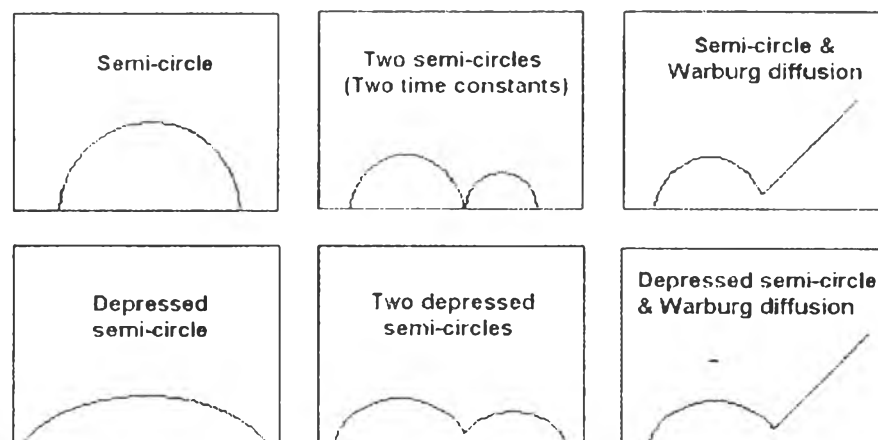


Figure 2.20 Typical Nyquist plots for electrochemical systems (Yuan *et al.*, 2010).

The proton exchange membrane is referred to as proton conduction materials because protons exist in the electrolyte as the main current carriers that can pass through the membrane. Proton conductivity (σ) is defined as the power of the proton conduction. While proton selectivity ($S = \sigma/P$) is defined the ratio between the proton conductivity to the vanadium permeability.

High conductivity is desired which can be facilitated by having more bulk-like water in membrane. Moreover, high concentration and connectivity of sulfonic crosslinking group promote proton transport (Yan *et al.*, 2012). The current department of energy (United States of America) target, proton conductivity larger than 0.1 S/cm at 80 °C is still challenging (Park *et al.*, 2011).

2.3.3 Ion Exchange Capacity (IEC)

The Ion exchange capacity (IEC) is defined as mmol of sulfonic acid groups for 1 g of dry polymer. Ion content can be used to control the hydrophilic domain size. The higher IEC and the degree of sulfonation lead to higher proton/vanadium permeability, coulombic efficiency, and operating cycle times. As the IEC increases, it leads to an increase in water uptake because the $-\text{SO}_3\text{H}$ moiety has a high affinity for water of salvation (Fujimoto *et al.*, 2012).

The content of mobile ions causes a higher electrical conductivity. The membranes with the higher IEC do not necessarily have the lowest diffusivity or lowest resistance (Sukkar *et al.*, 2004).

2.3.4 Water Uptake

Water uptake and swelling ratio are two important properties related to proton conductivity and dimensional stability of the membrane. Water uptake affects the increase in proton conductivity and the decrease of mechanical strength of a membrane. In other words, water uptake can lead to low mechanical properties (Macksasitorn *et al.*, 2012).

Proton and water transport in proton exchange membrane occur within in hydrophilic region (Yan *et al.*, 2012). The water transport is caused by ions moving under a concentration gradient. Water molecules are carried by the charge balancing species and water transport due to the osmotic pressure difference between the two half-cell solutions (Sukkar *et al.*, 2003).

Water molecules transfer across a membrane during the charge–discharge processes of VRB, causing the undesired preferential volumetric change as one half-cell is flooded and diluted while the other becomes more concentrated. Moreover, water transfer across membrane leads to a precipitation of vanadium salts (Parasuraman *et al.*, 2013). Water transfer is determined by the hydration shells of the different vanadium ions and the osmosis pressure difference between the two half-cell solutions. Generally, for cation exchange membranes, the solution transfer is from the negative half cell to the positive half cell. The solution transfer for anion exchange membranes and non-selective membranes is from the positive side to the negative side (Mohammadi *et al.*, 1995).

The SOC leads to different directions of water transport, when the electrolyte discharges from 50% to 0% SOC, the direction of water transfer reverses towards the negative half-cell. These studies are very important, because in long term VRB operation, huge water transfer can cause flooding of the electrolyte reservoir. Figure 2.21 depicts the movement of water and ions for a 2M Vanadium solution in 5M total sulphate at 50% SOC (Sukkar *et al.*, 2003).

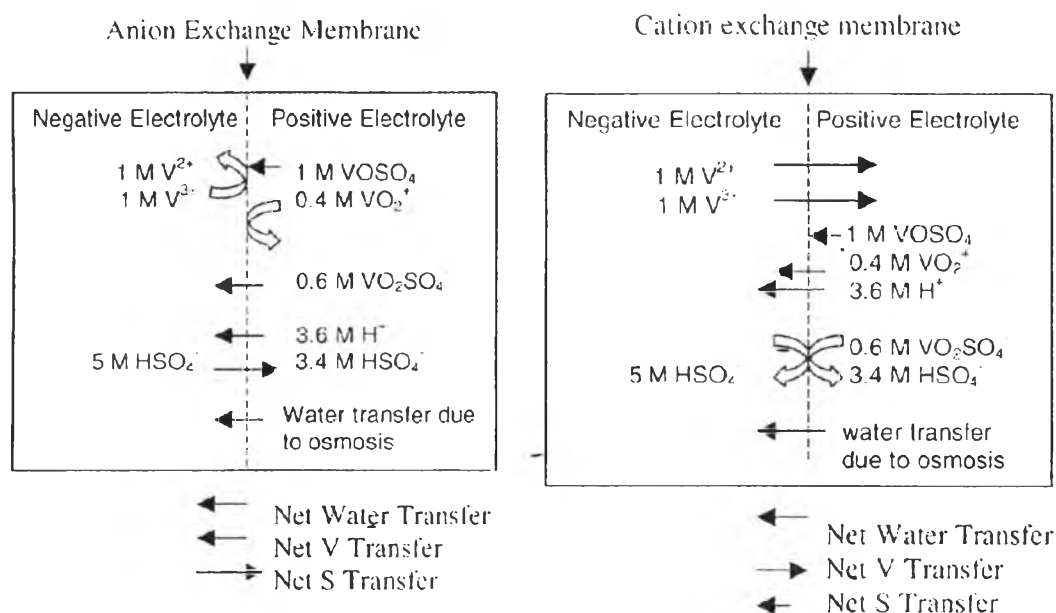


Figure 2.21 Water and ion transfer directions for anion and cation exchange membrane with 50% SOC vanadium solutions (Sukkar *et al.*, 2003).

At higher SOC, the water transfer can be observed significantly. As SOC discharging from 0% to over discharge ($V^{3.5+}$) state displays the most significant level of water transport (Xi *et al.*, 2007).

2.3.5 Vanadium permeability

Vanadium permeability (P) refers to a permeability parameter of vanadium ions. The different vanadium species that can be possibly formed at high concentrations of acid are identified as VO^{2+} , $VO_2SO_4^+$, $VO_2(SO_4)_2^{3-}$, VO^{3+} , VO_2HSO_4 , $VO_2(HSO_4)^{2-}$, V_2O^{3+} , and $V_2O_4^{2+}$. The diffusivity of each of the vanadium ions depends upon the charge of each ion and the nature of the membrane. The diffusivities of the V(IV) and V(V) species were higher than the V(II) and the V(III) species. The different diffusion coefficients and the charges led to different permeability values of each vanadium ions ($V^{5+} > V^{4+} > V^{3+}$, respectively). The vanadium ions of different oxidation states displayed different diffusion coefficients across the membrane due to differences in their sizes and charges as shown in Table 2.3. However, it was not possible to measure the permeability of the V(II) ion across the membranes since the V^{2+} ion could be easily oxidized in the air (Xi *et al.*, 2007).

Table 2.3 The different vanadium ion size (Pauling, 1960)

State of Charge	V ²⁺	V ³⁺	V ⁴⁺	V ⁵⁺
Crystal ionic radii (pm)	93	78	72	68
Effective ionic radii (pm)	79	64	58	54

The permeability of the membrane increased with decreasing selectivity. Initially, this was a result of ions in the electrolyte forming neutral complexes with the counter ions present in the pores of the membrane rendering the membranes neutral. Therefore, their abilities to control the flow of ions were reduced and the level of diffusion of V(IV) ions was increased (Sukkar *et al.*, 2004).

The ions diffusion decreased the cell output voltage due to a mixed potential at the cathode and the fuel efficiency of the device. If vanadium ions with different oxidation states transported to the opposite half-cell and reacted with each other, this led to an increase of self-discharge rate, electrochemical energy loss, and energy efficiency reduction of the battery (Luo *et al.*, 2008).

Less difference between the dielectric constant of the solution and that of the substrate provided the more selectivity of the composite membrane or less diffusion of the vanadium ions through the composite membrane.

2.3.6 Thermal Stability

According to mobile applications, higher vanadium concentrations are required to reduce the size and weight of the battery. The main limitation for the vanadium electrolyte concentration and subsequently its energy density in the VRB is the thermal precipitation of the V(V) ion at elevated temperatures. Although the vanadium concentration improves the energy density of a fuel cell which can be operated at high temperature (Rahman *et al.*, 2009), high temperature operation leads to high vanadium permeability.

2.4 Objectives

2.4.1 To prepare sulfonated polymer membranes for utilizing in a vanadium redox flow battery

2.4.2 To measure the membranes properties composed of the proton conductivity, the vanadium permeability, and the mechanical properties

2.4.3 To compare the membranes properties with those of the Nafion 117 commercial membrane

2.5 Scope of research

This thesis has done cover the topics below:

2.5.1 Two polymers selected are poly(ether ether ketone) and poly(phenylene ether ether sulfone).

2.5.2 The degree of sulfonation is varied to find the optimal membranes for vanadium redox flow battery.