CHAPTER II

LITERATURE REVIEW

2.1 The Basic Principles of Vanadium Redox Battery

Vanadium redox flow battery (VRB) is a type of rechargeable battery that has been successfully put in use in many countries. In contrast, conventional batteries store all of their reactive materials within the cells but a flow battery stores the electrolytes in tanks. The advantages of VRB are long cycle life, quick response time, deep-discharge capability, flexible design, and low maintenance cost. The VRB composes of two electrolyte tanks equipped with sufficiently electrochemical V^{3+}/V^{2+} and VO^{2+}/VO_2^+ redox coupled in a sulfuric acid solution. The electrolytes are pumped through the cells when electric current flows out and back into the same tanks. In this case, it provides an electromotive force to drive the redox (oxidation-reduction) reaction needed to charge and discharge the cell. Both electrolytes do not mix together but are separated in the cells by an extremely thin membrane which allows selected ions to pass through. Besides, the internal of the cells are very stable porous carbon electrodes where the critical reactions take place. As the reactions only involve the dissolved salts, the electrodes do not change physically or chemically. Therefore, the large number of charge and discharge cycles possibly is carried without decreasing in capacity. Previously, the problem of cross-contamination has been solved by several vanadium compounds; VCl_3, V_2O_5, $VOSO_4$ have been investigated in different solutions (HCl, NaOH, H_2SO_4) and at different concentrations. To avoid problems of the chlorine generation, there is a need to eliminate the compounds such as VCl_3 and HCl. Because of slow solubility of V_2O_5 in the acids, this has made the preparation of electrolytes difficult. Thus, a vanadyl sulphate solution in a sulfuric acid has been selected as the electrolyte for both half-cells (Rychcik and Skyllas-Kazacos, 1988).
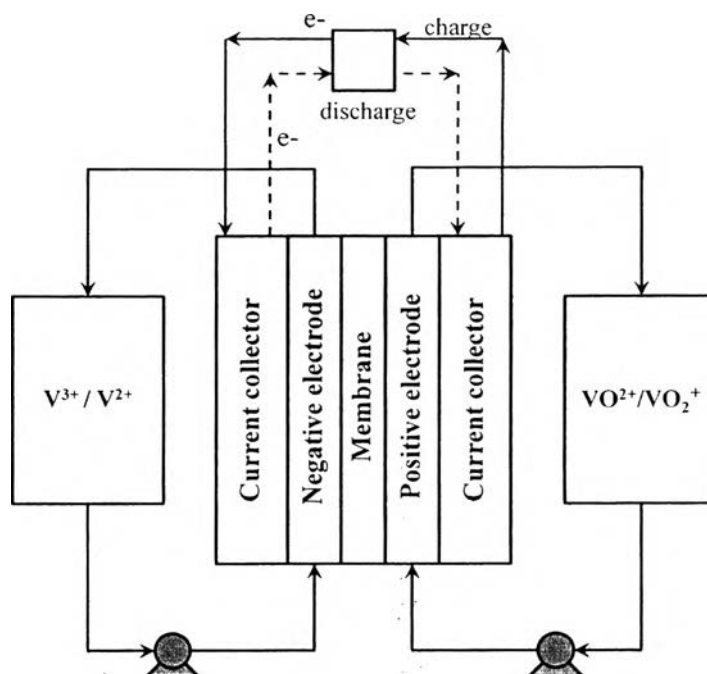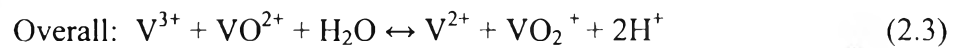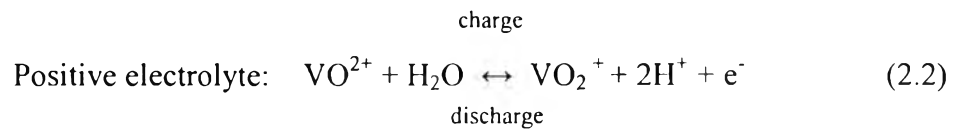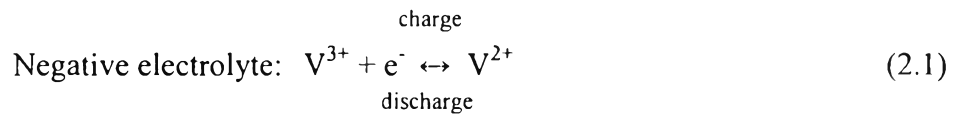
Figure 2.1 Schematic of vanadium redox battery.

Generally, a variety of flow batteries modules exist including the redox flow battery in which all active components are liquefied in the electrolyte. This is distinct from hybrid flow batteries such as the zinc-bromine or cerium-zinc systems, which have only reactive electrodes and suffer from the limitations of conventional batteries. The VRB uses vanadium salts in the electrolytes. Besides, the electrolytes contain a sulfuric acid similar to the lead-acid battery. Vanadium is a relatively common metal, used to make vanadium steels and dietary supplements and is often found in many common foods. Though, vanadium is present in both the positive and negative electrolytes, but in different oxidation states. In addition, the oxidation state measures how far a reaction has proceeded. For instance, unreacted vanadium has an oxidation state of zero, when it is fully reacted it has an oxidation state of +5. Furthermore, the oxidation state may have values in between if the vanadium is only partially reacted, although not every value is possible. Vanadium is an unusual metal in term of stability, concentrated solutions with four different oxidation states, a property shared only by uranium and some other heavy, radioactive elements. Charging and discharging the battery changes the average oxidation state of the vanadium in the electrolytes (Vanadium Redox Flow Battery Technology, 2009).

The electrochemical reactions that take place in the battery are:

$$\text{Negative electrolyte:} \quad V^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\longleftrightarrow}} V^{2+} \tag{2.1}$$

$$\text{Positive electrolyte:} \quad VO^{2+} + H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\longleftrightarrow}} VO_2^+ + 2H^+ + e^- \tag{2.2}$$

$$\text{Overall:} \quad V^{3+} + VO^{2+} + H_2O \longleftrightarrow V^{2+} + VO_2^+ + 2H^+ \tag{2.3}$$

2.2 Commercial Membrane (Nafion®)

Nafion® is a sulfonated tetrafluoroethylene copolymer which is produced by Dupont. It is highly conductive to cations and suitable for many membrane applications. Nafion® consists of perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) chain. Furthermore, Nafion® has a good thermal and mechanical stability which is used as a proton conductor for proton exchange membrane (PEM). The proton transfer mechanism in fuel cells is due to the protons on the SO_3H (sulfonic acid) groups jump from one acid to another (Grotthuss Mechanism) (Agmon et al., 1995).
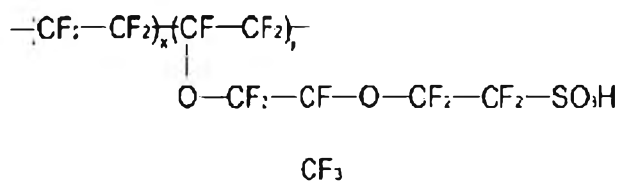
$$-[CF_2-CF_2]_x-[CF-CF_2]_y-$$
$$|$$
$$O-CF_2-CF-O-CF_2-CF_2-SO_3H$$
$$|$$
$$CF_3$$

Figure 2.2 Nafion® chemical structure.

2.3 Sulfonation of Aromatic Compound

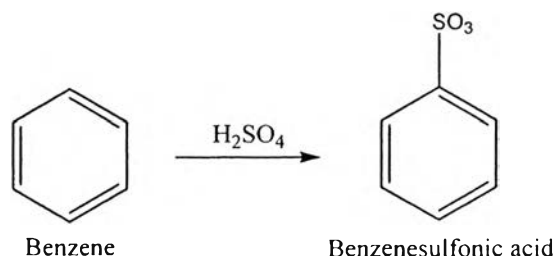Benzene   Benzenesulfonic acid

Figure 2.3 Sulfonation reaction of benzene ring.

The sulfonation of aromatic compounds can be achieved by a number of methods. Basically, this involves the reaction with sulfur trioxide in various organic solvents and the reaction with the sulfuric acid. Fuming sulfuric acid, a chlorosulfuric acid, the dioxane adduct of SO_3, and an amine adducts of SO_3 are mainly used as the agents for sulfonation aromatic compounds by introducing a sulfonic acid group into the aromatic ring of the compound (Earle *et al.*, 2006). Sulfonation is an efficiency method for the modification of polymers to introduce sulfonic acid functionality improving the transport of protons. This leads to the structure of the polymer hydrophilic and increases the solubility of the polymers. Indeed, a sulfonation of hydrocarbon polymers causes the proton exchange which leads to the high proton conductivity of 10^{-2} S/cm and enhance the performance of aromatic compounds (S.M. Javaid Zaidi, 2003).

In 1995, Mohammadi and Skyllas – Kazacos, studied an ion-exchange membrane which was prepared by soaking the micorporous separator, Daramic, in a solution of poly(sodium 4-styrenesulfonate or PSSS) and crosslinked with divinylbenzene. The method decreased the capacity of loss and reservoir flooding during the operation of a vanadium redox battery and also improved the battery performance compared with the cross linked Daramic separator that had not been soaked in the PSSS solution. The area resistance of the PSSS composite membrane was reduced to a value of 1.36 Ωcm^2 from a value of 2.68 Ωcm^2.

Mohammadi and Skyllas – Kazacos (1995) studied Daramic which consisted of ultrahighmolecular polyethylene, amorphous silica, and a mineral oil and was crosslinked with divinylbenzene (DVB) as a crosslinking agent and further sulfonated to obtain a cation exchange membrane for the vanadium redox cell. Subsequently, the average pore size of Daramic was reduced from 0.1 to 0.02 μm after the crosslinking. Although, slight differences in vanadium ion permeability, the area resistance and the cell performance were achieved after the sulfonation. In addition, the water transport properties were reduced, such as the capacity loss and the reservoir flooding during operation of the vanadium battery.

In 2003, Li *et al.*, investigated the sulfonated poly(ether ether ketone) membranes for a direct methanol fuel cell. Sulfonated poly(ether ether ketone) (SPEEK) membranes with various degrees of sulfonation (DS) were prepared. The SPEEK membranes with the DS 39% and 47% were tested in a single DMFC. The proton conductivity of two SPEEK membranes exceeded 10^{-2} S/cm above 80 °C, which was similar to that of the Nafion® 115 membrane under the same condition. Their proton conductivity and methanol permeability as a function of temperature were investigated.

In 2005, Li *et. al.*, studied the electrochemical properties of a sulfonated PEEK used for ion exchange membranes. S-PEEK membranes showed the increase of IEC at 0.712, 1.312, 1.421, and 1.521 as well as the degree of sulfonation (DS) at 0.4, 0.8, 1.0, and 1.2. In addition, the increase in DS the S-PEEK was accompanied with increasing water content from 13% to 54%. In addition, the S-PEEK membranes showed better mechanical properties.

Schauer *et al.*, (2005) investigated poly(1,4-phenylene sulfide) sulfonated with chlorosulfonic acid in 1,2-dichloroethane. The product (IEC = 2.38 meq./g) was ground and sieved to obtain small particles. The particles and linear polyethylene were mixed in various ratios and the resulting blends were press-molded at 150 °C to obtain the membranes. Membranes containing up to 66 wt% of sulfonated particles could be conveniently prepared with good mechanical strength. The membrane containing 66 wt% of sulfonated particles was similar to the Nafion® 117 which

showed the proton conductivity of 905 mS/cm^2. Conversely, the membrane has a much lower diffusive permeability to methanol.

In 2007, Qiu *et al.*, studied an ETFE-based anion exchange membrane (AEM) for the application in the VRB. The membrane was prepared successfully by a radiation grafting technique. Comparing with the Nafion$^®$ membrane, at ca. 40% GY, the AEM processed a higher ion exchange capacity, a lower area resistance, and significantly a lower permeability of vanadium ions. In addition, the open circuit voltage of the VRB with the AEM led to an efficiency improvement and a lower cost than the Nafion117 membrane.

In 2008, Luo *et al.*, investigated the surface modification of Nafion membrane using an interfacial polymerization which severely reduced the permeability of vanadium ions across the membrane and accompanied by a little higher area resistance. Therefore, the columbic efficiency (CE) VRB-modified Nafion$^®$ was obviously higher than that obtained with VRB-Nafion. In contrast, due to the higher area resistance of the modified Nafion membrane, the voltage efficiency (VE) obtained with VRB-modified Nafion$^®$ was lower than that obtained with VRB-Nafion. In addition, the water transferred across the modified Nafion membrane was minimized to just half of the value that transferred across the unmodified membrane.

Luo *et al.*, (2008) studied a Nafion/sulfonated poly (ether ether ketone) (SPEEK) layered composite membrane (N/S membrane), from chemically crosslinking between the sulfonic acid groups of Nafion ionomer and SPEEK ionomer. As a consequence, the N/S membrane showed a lower permeability of vanadium ions accompanied by higher area resistance compared with Nafion membrane. Then, the VRB single cell using N/S membrane possessed a higher coulombic efficiency (CE) and a lower voltage efficiency compared with those of the Nafion membrane. Hence, the overall energy efficiency of VRB single cell with N/S membrane was slightly lower. However, it had a good chemical stability and a lower cost membrane in VRB system.

Win and Oo (2008) studied the preparation of a membrane as a proton exchange membrane. Polystyrene resin was prepared from commercial grade polystyrene beads using two solvents, namely acetone and methyl ethyl ketone to solubilize the polystyrene beads. Subsequently, sulfuric acid was used as the sulfonating agent. As a result, the resin prepared using the 30 min sulfonation reaction time at 100 ± 5 °C in acetone (SPR-2) and 90 ± 2 °C in methyl ethyl ketone (SPR-4) showed the highest values of cation exchange capacities 2.95 meq/g and 3.215 meq./g, respectively. The thickness of the prepared membrane was 0.02 mm and apparent diffusion coefficients for SPR-2 and SPR-4 membranes were 2.8×10^{-7} and 3.9×10^{-7} cm^2/s, respectively. The diffusion coefficient of SPR-4 membrane was larger than that of SPR-2 membrane. Thus, SPR-4 membrane was more suitable to use in the assembly of fuel cell.

In 2009, Rahman and Skyllas-Kazacos studied the stability of supersaturated V(V) solutions as a function of V(V) concentrations, sulfuric acid concentration, temperature, density, viscosity, conductivity and the presence of V(IV) ions. All in all, the evaluation of the experiments, density, viscosity and conductivity measurements, and electrochemical behavior of V (V) were carried out to indicate that a 3.0- 3.5 M V(V) solution in 6 M total sulfate/bisulfate may be appropriate for the VRB up to a temperature of about 40 °C. Thus, an increase in the vanadium concentration to 3 M allowed a 50% increase in the energy density compared with the 2 M solutions.

Qiu *et al.*, (2009) prepared an amphoteric ion exchange membrane (AIEM) through a two-step radiation-induced grafting technique. ETFE film was first grafted with styrene (St) (denoted as ETFEg-PS), followed with a sulfonation treatment to obtain a cation exchange membrane (ETFE-g-PSSA). The ETFE-g-PSSA membrane was subsequently grafted with dimethylaminoethyl methacrylate (DMAEMA) and then protonated. As a consequence, an AIEM exhibited advantages over both anion exchange membranes and cation exchange membranes in VRFB: significantly a lower permeability of vanadium ions than cation exchange membranes due to the Donnan exclusion effect; higher conductivity comparing to anion exchange membranes.

Teng *et al.*, (2009) improved the selectivity of a Nafion membrane, reduced the crossover of vanadium ions and decreased the water transfer across the membranes used in VRB systems. The sol–gel method was employed to obtain a composite membrane of Nafion/organic silica modified TiO_2 (Nafion/Si/Ti hybrid membrane). The permeability of vanadium ions and the water transfer were all reduced due to the clusters inside Nafion membrane which was filled with organic silica modified TiO_2 nanoparticles. As a result, the VRB with the prepared composite membrane had a higher coulombic efficiency and energy efficiencies than those of the VRB with Nafion membrane. Nevertheless, the higher area resistance of the Nafion/Si/Ti hybrid membrane, the voltage efficiency with Nafion modified membrane was lower than that of the VRB with Nafion membrane. In addition, the decrease of the vanadium crossover caused the self-discharge rate of the VRB single cell with the modified membrane was also lower than that of the VRB with Nafion membrane.

Choi *et al.*, (2009) examined the proton conducting composite membranes comprising of sulfonated poly(1,4-phenylene sulfide) and zeolite for fuel cell. Sulfonated poly(1,4-phenylene sulfide or S-PPS) was prepared from poly(1,4-phenylene sulfide) and the fuming sulfuric acid. Then, the sulfonated poly(1,4-phenylene sulfide) membrane with varying concentrations of zeolite were synthesized. With an increase in the zeolite concentration to 10 wt%, the proton conductivity of composite membrane decreased from 0.075 to 0.02 S cm^{-1} at room temperature due to the sturdy interaction between sulfonic group of S-PPS and the zeolite particles. Moreover, the water uptake of the composite membrane was reduced from 255% to 150% with the increase in the zeolite concentration to 10 wt%. As a result, the thermal stability analysis showed no enhancement of thermal stability of the composite membranes with increasing zeolite concentration.

Li *et al.*, (2009) studied the synthesis and property of a novel sulfonated poly(ether ether ketone) with a high selectivity for direct methanol fuel cell applications. C-SPEEK1, 2, 3 and 4 exhibited the DS of 0.2, 0.4, 0.5, and 0.6 respectively. The highest proton conductivity of 0.16 S/cm was obtained from C-SPEEK4 (IEC = 1.44mequiv/g) at 80 °C, higher than that of the Nafion[®] 117 (0.12

S/cm). The methanol permeability coefficients of C-SPEEK membranes were in the range of 3.54×10^{-7} cm^2/s to 5.9×10^{-9} cm^2/s, which were essentially lower than that of the Nafion117 (1.61×10^{-6} cm^2/ s). As a consequence, the C-SPEEK membranes exhibited a much higher selectivity compared with that of the Nafion[®] 117 membrane.

Devrim *et al.*, (2009) studied the preparation and the characterization of sulfonated polysulfone/titanium dioxide composite membranes for proton exchange membrane fuel cells. Polysulfone (PS) was sulfonated with trimethylsilyl chlorosulfonate in 1,2-dichloroethane at ambient temperatures. The work showed that the degree of sulfonation was increased with increasing molar ratio of the sulfonating agent to PS repeat unit. The degree of sulfonation was defined by the elemental analysis. Furthermore, 1 H NMR was performed to verify the sulfonation reaction on the PS. Sulfonation levels from 15 to 40% were achieved by varying the capacity of the sulfonating agent. The water uptake of the S-PS membranes also increased from 1 to 33% with increasing degree of sulfonation. At the same sulfonic acid content, the water uptake of the S-PS/TiO$_2$ composite membranes was lower than that of the S-PS membrane since the presence of inorganic substance reduced the membrane free volume and swelling ability. The proton conductivity of S-PS membranes increased with sulfonic acid content and the maximum conductivity of 0.12 S/cm was reached at 100% relative humidity and at 90 °C. Proton conductivity of the S-PS/TiO$_2$ composite membrane increased with temperature, relating to high thermal stability in the structure and sulfonic acid group. The S-PS/TiO$_2$ composite membrane proton conductivity was 0.098 S/cm at 90 °C.

In 2010, Chen *et al.*, synthesized the sulfonated poly(fluorenyl ether ketone) or S-PFEK. The S-PFEK membrane properties were compared with those of the Nafion[®] 117 membrane. The S-PFEK membrane showed a lower permeability of vanadium ions than Nafion[®] 117 membrane the same thickness. Both energy efficiencies (EE) and power densities of the VRB single cell based on the S-PFEK membrane were higher than those of the VRB with Nafion[®] 117 membrane at the same current densities. As a result, the highest coulombic efficiency (CE) of VRB with S-PFEK membrane was 80.3% while the highest CE of VRB with Nafion[®] 117

membrane was 77%. Thus, from the membrane life test, it can be concluded that the SPFEK membrane was stable in the VO_2^+ electrolyte.

Buquet *et al.*, (2010) constructed new hybrid membranes for fuel cells. Sulfonated laponite particles were used to prepare polysulfone and sulfonated polysulfone composite membranes for the fuel cell application. Sulfonated polysulfone membrane gave a proton conductivity of 0.09 S/cm. After the addition of modified laponite, the conductivity was significantly increased to 25% leading to membrane of correct conductivity for fuel cell use. PSU (7.2 g) was dissolved in 1,2-dichloroethane (DCE) (75 ml) by stirring at 80 rpm under a reaction temperature of 60 °C. The solution containing chlorosulfonic acid in DCE was added drop by drop for 1 h. The reaction mixture was stirred for 6 h. As a result, the conductivity of PSU composite membranes remained at 20% of laponite particles, the proton conductivity of the sulfonated polysulfone (SPSU) composite membranes increased with the modified laponite contents, due to additional SO_3H groups and the improvement of water retention properties of the membranes allowing the diffusion of the protons through the membranes.

Jia *et al.*, (2010) developed the sandwich-type sulfonated poly(ether ether ketone) (S-PEEK)/tungstophosphoric acid (TPA)/polypropylene (PP) by hybrid solution casting. The vanadium ion permeability of the S/T/P composite membrane was significantly lower than that of a Nafion 212 membrane. The VRB with an S/T/P membrane showed higher CE, EE values and a lower self-discharge rate than the Nafion® 212 membrane.

Xing *et al.*, (2010) studied the effects of amine conditions on the properties and prepared two types of anion exchange membranes using different amination agents, namely trimethylamine (TMA) and ethylenediamine/trimethylamine (EDC/TMA). The study found that with an amination reagent of TMA (33 wt.%), the ion exchange membrane (IEC) = 1.69 mmol/g, water content (Wc) = 28%, area resistance (R) = 0.53 Ωcm^2 and VO^{2+} ions permeability (Ks) = 2.79×10^{-5} cm/min. Then, the property of water stability of TMA membrane was improved by EDA/TMA compositions. Thus, the properties of EDA/TMA membrane were IEC =

1.40 mmol/g, Wc = 22%, R = 1.00 Ωcm^2 and Ks = 4.30×10^{-6} cm/min. In addition, the vanadium redox battery with TMA and EDA/TMA membrane showed higher CE and EE values than those of Nafion membranes under the same testing conditions. EE of TMA values attained were 87.9%, while EDA/TMA achieved was 83.4%.