REPUBLIC OF TURKEY
YILDIZ TECHNICAL UNIVERSITY
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SURFACE MODIFICATION AND APPLICATION OF POROUS MEMBRANES FOR ALL-VANADIUM REDOX FLOW BATTERIES

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A thesis submitted by Dilek YALÇIN in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE** is approved by the committee on 21.12.2017 in Department of Chemistry, Analytical Chemistry Program.

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LIST OF SYMBOLS

A Absorbance
C Concentration
Co Initial concentration of vanadium in $VOSO_4$ compartment
Ct Vanadium concentration in $MgSO_4$ compartment
D Diffusivity coefficient
dC/dx Concentration gradient
ε Molar absorptivity constant
I Current
J Diffusion flux
L Thickness of kuvette or membrane
Q_{dis} Discharge capacity
Q_{ch} Charge capacity
t Time
V Voltage
v Volume of solutions in both side
W Power
Wd Dry weight of membrane
Ws Swelling weight of membrane
$1/\sigma$ Proton conductivity
Ω Resistance

LIST OF ABBREVIATIONS

DSA	Dimensionally Stable Electrode
EDX	Energy Dispersive X-Ray Spectroscopy
IEM	Ion Exchange Membrane
PVDF	Polyvinylidene Fluoride
PEEK	Poly(ether-ether-ketone)
PTFE	Poly(tetrafluoroethylene)
PAN	Polyacrylonitrile
PVC	Polyvinyl chloride
RFB	Redox Flow Battery
SEM	Scanning Electron Miscroscope
VRB	Vanadium Redox Battery
UV-VIS	Ultra Violet Visible Spectroscopy

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ABSTRACT

SURFACE MODIFICATION AND APPLICATION OF POROUS MEMBRANES FOR ALL-VANADIUM REDOX FLOW BATTERIES

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The porous membranes are well known with their cost advantage which is also meant an alternative for further commercialization of redox flow batteries in the future in the literature. However, they suffer from the cross-over of redox active species despite their cost advantages. Correspondingly to these factors, the aim of this thesis is to develop the permeability decrease of Amer-Sil FF60 porous membrane via surface modification.

FAP® 450 (FuMA-Tech, Germany) (as anionic ion exchange membrane), Nafion® 117 (DuPont, the USA) (as cationic ion exchange membrane) and Amer-Sil FF60 porous membrane (Amer-Sil, Luxembourg) were employed in this study. Amer-Sil FF60 porous membrane's one face was modified with two different proportions of Nafion® (5, 7%, wt) dispersion such as (0,5:1) and (1:1). Spraying technique was utilized as modification method.

According to the characterization values, the diffusion of V^{4+} ions could be declined with upon the addition of Nafion (5, 7%, wt). It was observed that the improvement of Amer-Sil FF60 membrane's selectivity could be achieved with the addition of Nafion (5, 7%, wt) dispersion and correspondingly to this, it was reported that it could remarkably be provided a capacity increase through the modified membranes. However, it couldn't be maintained the ionic conductivity as same as possible. With the addition of Nafion® (5,7 %, wt) dispersion, both proton conductivity and hydrophilicity degrees were decreased owing to the hydrophobic group of polytetrafluoroethylene (PTFE) which is the characteristic group of Nafion® (5,7 %, wt) dispersion. The chemical stability test was only applied to the Amer-Sil FF60 membrane and observed that it was stable in the highly acidic environment. Moreover, it was observed that the coloumbic, energy efficiency and power performances of modified porous membranes were approximately increased 10-15 % more than unmodified Amer-Sil FF60 porous membrane.

According to the cell tests, it was denoted that the modified Amer-Sil FF60 membrane's performances could be accomplished circa 15% compared to the unmodified Amer-Sil FF60 porous membrane. As a result, it might be claimed that the modification of Amer-Sil FF60 may be considerable. According to the result of Nafion® (5,7%, wt) stability test, it was reported that the Nafion® (5,7%, wt) dispersion couldn not be stayed on the surface of the membrane as it was interacted via highly acidic vanadium electrolyte medium.

Keywords: Vanadium redox flow battery, porous membrane, anionic ion exchange membrane, cationic ion exchange membrane, spraying.

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ÖZET

POROZ MEMBRANLARIN YÜZEY MODİFİKASYONU VE TÜM VANADYUM REDOKS AKIŞKAN BATARYALAR İÇİN UYGULANMASI

Dilek YALÇIN

Analitik Kimya Anabilim Dali
Yüksek Lisans Tezi

Danışman: Prof. Dr. Yücel ŞAHİN

Bu çalışmanın amacı ekonomik avantajından kaynaklı olarak vanadyum redoks akışkan bataryaların ticarileşmesi için alternatif olabileceği düşünülen Amer-Sil FF60 poroz membranın redoks aktif türlerin karışmasına neden olan geçirgenlik özelliğinin yüzey modifikasyonu ile iyileştirilmesi ve uygulamasına yöneliktir.

Bu çalışmada FAP® 450 (FuMA-Tech, Almanya)(anyonik iyon değiştirici membran), Nafyon® 117 (DuPont, USA) (katyonik iyon değiştirici membran) ve Amer-Sil FF60 (poroz membran) (Amer-Sil, Luksemburg) membranları kullanılmıştır. Amer-Sil FF60 poroz membranı Nafyon® (5,7 %, g) ile iki farkli oranda, (0,5:1) ve (1:1), poroz membranın tek yüzü kaplanarak modifiye edilmiştir. Modifikasyon yöntemi olarak spreyleme tekniği kullanılmıştır.

Karakterizasyon sonuçlarına göre V^{4+} difuzivite katsayısının Nafyon® (5,7 %, g) eklendikçe düşürülebildiği gözlenmiştir. Nafyon® (5,7 %, g) eklendikçe poroz membranın seçiciliğinin geliştirilebildiği buna bağlı olarak modifiye poroz membranın belirgin ölçüde bir kapasite artışı sağlayabildiği görülmüştür. Ne var ki Nafyon® (5,7 %, g) eklenisi ile iyonik iletkenliğin düştüğü gözlenmiştir. Hidrofobiklik sağlayan (PTFE) miktarı arttıkça hidrofiliklik ve proton iletkenliği düşmüştür. Kimyasal stabilite testi yalnızca Amer-Sil FF60 poroz membrana uygulanmıştır ve yüksek asidik ortamda stabil olduğu gözlenmiştir.

Hücre testlerine göre Amer-Sil FF60 poroz membranın modifikasyonu sayesinde performansının %15 civarında geliştirilebildiği gözlenmiştir. Buna baglı olarak, ekonomik olarak daha avantajlı olan Amer-Sil FF60 membranın modifikasyonu anlamlı olabilir. Nafyon stabilite testi sonucları Nafyon (5,7 %, g)'un yüksek asidik ortama sahip vanadyum elektroliti ile etkileştikçe yüzeyde kalamadığını göstermiştir.

Anahtar Sözcükler: Vanadyum redoks batarya, poroz membran, katyonik iyon degistirici membran, anyonik iyon degistirici membran, sprey.

CHAPTER 1

INTRODUCTION

1.1 Literature Review

The human life has been eased more than past thanks to the technological advancement and various types of products such as transport facilities, convenience food. However, it has disturbed ecological balance and damaged the environment, which has been meant more damaged for global life and has resulted in tremendous critical issues such as global warming, ozone layer depletion, excessive pollution and photochemical smog, especially in and around the urban areas. Therefore, it seems to find new ways to satisfy our energy demands in an eco-friendly manner by utilizing decentralized renewable energy sources such as solar power, wind, geothermal energy, biofuel and biomass. Furthermore, these sources are more efficient, abundant, and affordable (available free of cost). Both developed and developing countries should adopt the above-mentioned sustainable resources to build their enegy capacity and improve their regulatory for clean, safe, and renewable energy [1]. Renewable-energy sources, such as, solar and wind are being deployed in larger numbers than ever before, but these sources are intermittent and often unpredictable [2]. Owing to the fact that sustainable energy sources are mainly intermittent and dispersed, large-scale energy storage equipments are required to utilize the best of these sources. However, the present energy storage capacity only store around 1% of the energy consumed worldwide, and the current trend seems to be requiring more energy storage devices at the grid scale to increase the penetration of renewable energy [3]. One effective solution is to connect the power station and the grid with the electrical energy storage (EES) devices such as pumped hydro, compressed air technology and flywheels [4]. Another possible solution for intermittent energy sources, such as sun and wind power, is redox flow batteries (RFB). Below is a table of popular energy storage technologies [5]. One effective solution is to connect the power station and the grid with the electrical energy storage (EES) devices such as pumped hydro, compressed air technology and flywheels. Another possible solution for intermittent energy sources, such as sun and wind power, is redox flow batteries (RFB). Below is a table of popular energy storage technologies [5].

Table 1.1 Energy storage systems classifying to the energy conversion method [5]

Mechanical Systems	**Electrical Systems**	**Chemical Systems**
Pumped Hydro	Super Conducting Magnet	Li-ion Battery
Compressed Air Storage	Super Capacitors	Sodium-Sulphur Battery
Flywheel		Flow Battery

Unlike tradational batteries, RFBs utilize redox couples that can be stored in independent tanks and only brought together when power is needed through an energy-conversion cell stack as shown in Figure 1.1 [6].

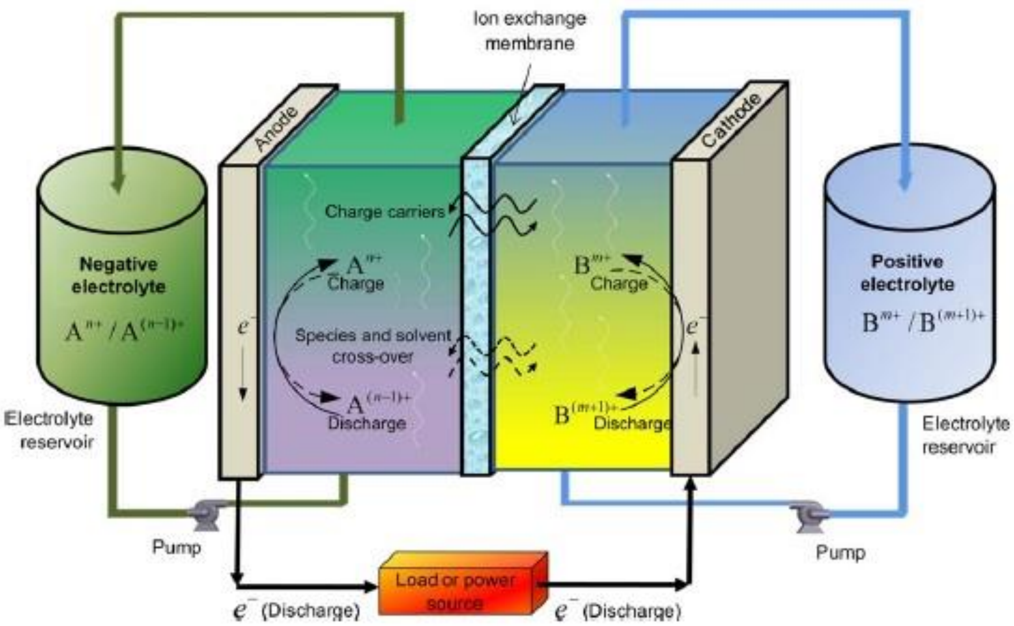

Figure 1.1 Schematic of a RFB system [6]

RFBs are inherently well suited for large scale applications since they scale-up in a more cost effective manner than other batteries. Since the energy and power capacities of RFB system are independent variables, the required capacities for any application can be met using correctly-sized energy and power-modules. RFBs also possess other compelling attributes for stationary EES applications, especially long duration applications. For example RFB architecture enables long lifetimes since the electrodes are not inherently required to undergo physicochemical changes during charge/discharge cycles [6]. Compared with traditional batteries, the reactants of flow battery are stored in external tanks instead of within electrode. A stack including series single cells acts as the reactor, the electrochemical electron-transfer reactions in single cells as their reactants flow through. The power of flow batteries is determined by stacks (electrode area, cell numbers) whereas the energy is dependent on the volume and concentration of active species [4].

Similar to other batteries, there are various flow battery chemistries, including zinc-bromine batteries, polysulphide-bromide batteries, iron-chrome batteries, soluble lead-acid batteries, zinc/nickel flow batteries, sodium sulphur batteries and vanadium flow batteries (VFBs) [4], [7]. Compared to other batteries such as zinc bromine battery, sodium sulphur battery and lead-acid battery, as the data were listed in Table 1.2, the VFB performs higher energy efficiency, longer operation life as well as the lower cost, which made it the most practical candidates for energy storage purposes [8].

Table 1.2 Comparison of competing storage technologies [8], [9]

Technology	**Efficiency full cycle (%)**	**Size range (MW)**	**Cycle life charge/ discharge**	**Operation temp (° C)**	**Effective Energy Density (W hL^{-1})**	**Gree n**	**O& M costs ($/ KWh)**
VRB	78	0,5-100	13000	30	24	Yes	0,001
ZBB	68	0,05-1	2500	50	33	Yes	0,015
NAS	65-70	0,15-1	3000	350	40	No	0,02
Lead acid	45	0,001-40	1000	Ambient	12	No	0,02

The vanadium redox flow battery (VRFB) system consists of two electrolye tanks filled with electrolytes of V (II)/V (III) and V (IV)/V (V) in sulfuric acid solution, respectively, two electric pumps and a battery stack [8]. The electrolytes are pumped into the stack where electrochemical reactions occur. The electron exchange takes place at the electrodes in the aqueous phase according to the following reactions [7], [8] :

Negative electrode reactions:

$V^{3+}{}_{(aq)} + e^- \rightarrow V^{2+}{}_{(aq)}$ (charge) (1.1)

$V^{2+}{}_{(aq)} + e^- \rightarrow V^{3+}{}_{(aq)}$ (discharge) (1.2)

Positive electrode reactions:

$VO^{2+}{}_{(aq)} + H_2O \rightarrow VO_2^{+}{}_{(aq)} + 2H^{+}{}_{(aq)} + e^-$ (charge) (1.3)

$VO_2^{+}{}_{(aq)} + 2H^{+}{}_{(aq)} + e^- \rightarrow VO^{2+}$ (aq) $+ H_2O$ (discharge) (1.4)

Overall cell reactions:

$V^{3+}{}_{(aq)} + VO^{2+}{}_{(aq)} + H2O \rightarrow V^{2+}{}_{(aq)} + VO_2^{+}{}_{(aq)} + 2H^{+}{}_{(aq)}$ (charge) (1.5)

$V^{2+}{}_{(aq)} + VO_2^{+}{}_{(aq)} + 2H^{+}{}_{(aq)} \rightarrow V^{3+}{}_{(aq)} + VO^{2+}{}_{(aq)} + H_2O$ (discharge) (1.6)

Under standard conditions , the overall cell potential is 1.26 V at 25 °C, but for an electrolyte composition of 2 M vanadium in 5 M sulfuric acid open-circuit potentials of 1.4 and 1.6 can be measured at 50% and 100% state-of-charge (SOC) , respectively [9].

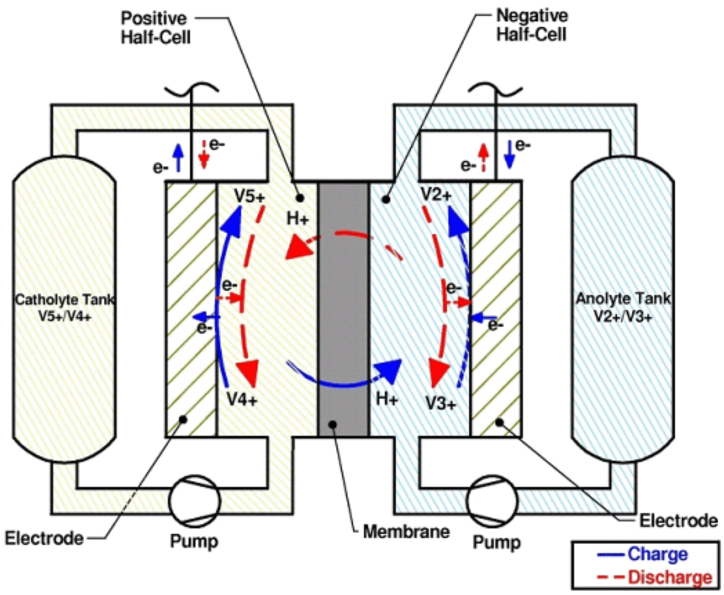

Figure 1.2 Vanadium redox flow battery schematic

As illustrated in Figure 1.2 a VRB comprises a cell or cell stack where the electron transfer reactions take place at inert electrodes, and two electrolyte reservoirs that store the half-cell solutions [9]. When the battery is being charged or discharged, the solutions are pumped through the cell stack via a series of pipes and manifolds at an appropirate flow rate that ensures adequate supply of the electroactive vanadium ions for the electron transfer reactions. The two-half cells in each cell are seperated by a membrane that prevents the mixing of half-cell electrolytes,while simultaneously permitting the movement of the charge carrying hydrogen ions [9].

One of the important components of a VRFB is bipolar plates. They possess many functions in a VRFB cell such as the delivery of the reactants to the active surface areas, the transportation of the current from cell to cell. It is preferred that bipolar plates should be possessed good ionic conductivity, chemically stable, resistant to the corrosive effects. Generally, graphite plates are utilized for bipolar plates. Besides, carbon-filled materials are being develeoped since graphite materials are more expensive [4].

As the key part of a VRB, an ion exchange membrane (IEM) is responsible for transferring ions from anode to cathode as well as for preventing cross-mixing of the positive and negative electrolytes [11]. The properties of the IEM greatly affect the resulting performance of the VRB. The membranes traditionally used in VRB are perfluorosulfonic acid polymers such as Dupont's Nafion®. Although they show both high proton conductivity and chemical stability, the extremely high cost and low ion selectivity of these membranes (high vanadium cross-over) have limited their further commercialization in VRBs [11], [12] . Hence, alternative IEM materials are being sought [11], [12].

In short, an ideal membrane for VRB applications should exhibit: 1) low permeation rates of water and vanadium ions to minimize self-discharge ; 2) high ion conductivity for the transport of charge-carrying ions to maintain the electric circuit, including excellent proton conductivity ; 3) low area resistance to minimize efficiency loss resulting from ohmic polarization ; 4) good chemical stability during operation- lifetimes of several years are minumum requirement ; and 5) low cost [10], [11], [12].

Nafion®, which is sulfonated fluorocarbon polymer developed by Dupont, has been accepted widely as a suitable material in vanadium redox flow batteries (VRFBs). The high price of Nafion membranes (10-15 % total cost of the battery system, with ~ 41 %

of the total cost of VRFB cell stack) is the one reason that the technology has not yet been implemented more widely [12], [13]. Also, many types of commercial membranes, e.g, the Asahi Glass, Selemion series (AMW, DMW, CMW) and microporous Daramic membranes, were proved to be unsuitable for VRB application due to their poor chemical stability or ion selectivty [14], [15], [16]. Hence, extensive research on novel membrane materials are intensified on porous membranes which are possessed lower cost. Recently, porous membrane seperators have attracted wide attention and were firstly reported in VRB [14]. They can preclude vanadium ions transport based on pore size exclusion via Stokes radius difference while permitting the transportation of protons [11], [14]. Besides, their performance can be adjusted via tuning the morphology and by membrane modification [14], [17]. Different kinds of porous membranes were studied up to now such as poly (ethersulfone), polyvinylidene difluoride (PVDF), polyacrilonitrile (PAN), Daramic, polyvinyl chloride/silica (PVC/Si) [11], [14], [18], [20]. Briefly, to develop more economic membrane materials for VRBs is a crucial attempt to commercialize the VRB applications for utilizing these batteries in a more widespread area. In this research, it was studied on different commercial membranes and was focused on the most feasible membrane material's improving via surface modification which was based on earlier literature studies, too.

1.2 Objective of the Thesis

The goal of this thesis work was based on developing the porous membrane which is well known its feasibility in the literature via surface modification for the further commercialization of VRFBs.

Briefly, the main objectives of this thesis were:

- to provide the enhancement of the membranes' permselective properties against vanadium ions and protons while maintaining its ionic conductivity.
- to improve an alternative membrane, porous membrane, for further commercialization of redox flow battery applications.

1.3 Hypothesis

Renewable energy sources are being paid more attention and improved nowadays [1]. On the other hand, it is being developed new energy storage technologies to store the excess energy or release when it is in demand [19].

For this work, it was determined to characterize, test and evaluate different commercial membranes such as anion exchange membrane, FAP 450® (FumaTech, Germany), cation exchange membrane, Nafion® 117 (Dupont, France), porous membrane, Amer-Sil FF60 (Amer-Sil , Luxembourg).

In general, porous membranes are known the lack of ionic permselectivity [21]. The coloumbic efficiency is a perfomance criteria to evaluate the capacity of all-VRB systems and is closely associated with the volume of the vanadium electrolytes. As the coloumbic efficiency is higher, it may be provided a higher energy efficiency since the energy efficiency is a result of multiplying coloumbic efficiency and voltage efficiency [11]. These notions are related to a VRB system's performance [10]. For this thesis, the hypothesis was correspondingly based on preventing the cross-mixing of vanadium ions as much as possible through surface modification of the membrane by coating . Thereby, it was hypothesized to provide the less loss of vanadium electrolyte volume and to gain higher coloumbic efficiencies as a proof of keeping standard volume amount.

CHAPTER 2

ELECTROCHEMICAL ENERGY STORAGE TECHNOLOGY

2.1 The Current Status of The Electrochemical Energy Storage Technology

Renewable energy sources such as solar and wind are paid more attention nowadays [1], [4]. However, their intermittent characterization are not allowed that is utilized in a more widespread area due to lack of developed storage technologies. As a more effective solution it is reported to connect the power station and the grid with electrical energy storage (EES) equipments [4]. To date, different types of EES technologies have been developed for various applications, relied on their own merits (Figure 2.1) [4].

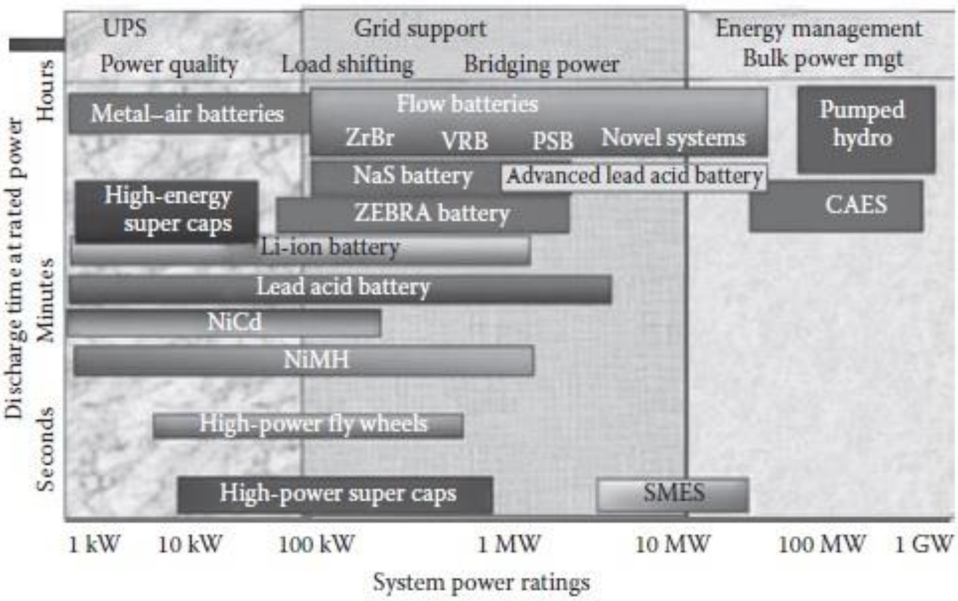

Figure 2.1 The fundamental characteristics of various electrical energy storage techniques [4]

As shown in Figure 2.1, batteries normally utilize different redox couples to meet different EES specific demands such as uninterrupted power supply (UPS), grid support and energy managements according to their range requirements of power rate, capacity and scale. For large scale energy storage systems (grid support), it can be seen that lead-acid batteries, Li-ion battery, NaS battery and Vanadium Redox Battery (VRB) are employed [4].

2.2 The Redox Flow Battery Technology From The Current Perspective

EES sytems can briefly be divided into three categories such as mechanical systems, electrical systems and chemical systems. Mechanical systems are low-energy, high power storage systems used for power management (e.g. frequency regulation)[25]. These technologies are not utilized in widespread area in tranmission owing to the materials limitations. Electrical systems are more suitable for grid energy and high power applications [25]. Battery storage technologies include lead-acid, lithium-ion, sodium-sulphur and redox flow batteries (RFBs) [25]. For large scale energy storage in the range of 10 kW-10 MW, RFBs have cost, mobility, flexibility, depth of discharge, rapid response and safety advantages over lithium ion and sodium sulphur batteries [13], [25].
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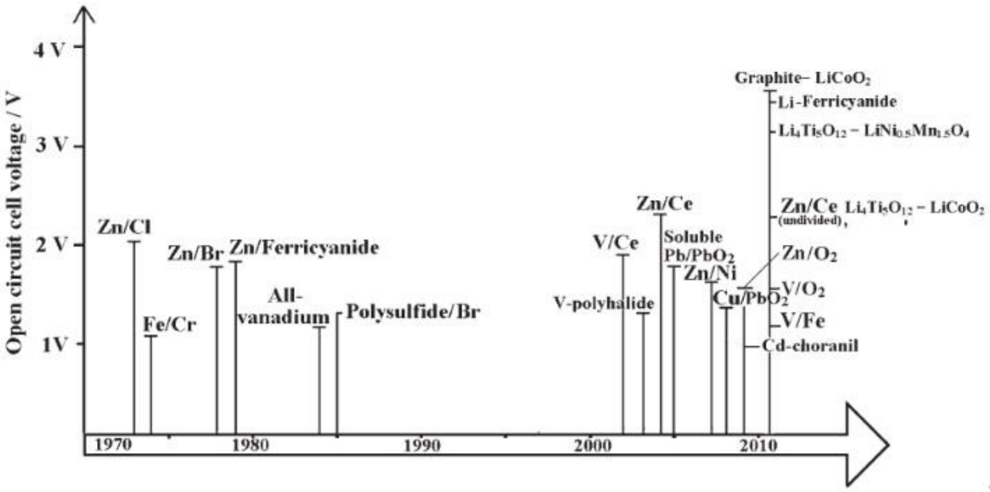

Figure 2.2 The timeline of the improvement of RFBs over the past 40 years [25]

The Figure 2.2 displays a brief history of RFBs which were varied from the first RFB, Fe/Cr that was designed and tested by NASA during 1970s, to lithium batteries [25]. After NASA improved and validated Fe/Cr system in many aspects, RFB system was further developed in Japan as a part of Moonlight Project whose prototypes were manufactured and tested in 10 kW and 60 kW between 1984-1989 [25]. Fe/Cr system is currently under development for wireless telecom applications by Deeya Energy® in Silicon Valley, USA [25]. In parallel, zinc- bromine and zinc-chloride RFBs were developed in USA in 1970s-1980s. Scale-up of 3, 10 and 20 kWh submodules were demonstrated in USA in 1983 and 1 MW /4MW system was installed in Japan. Currently, zinc-bromine is being developed by ZBB Energy Corporation, RedFlow Ltd., and Premium Power [25]. In 1977, V^{2+}/V^{+3} and V^{+4}/V^{+5} redox couples were evaluated as a potential by NASA [25]. Since 1985, many investigations and demonstations on VRFBs have been done and ascribed to Maria Skyllas-Kazacos at the Universit of South Wales, Australia [9], [25]. From 1993 to date, various VRB applications has been developed such as load-levelling, power quality control and renewable coupling. More than 20 large-scale plants has been established globally by manufacturers [9], [25]. The significant progress of VRB has been assisted by the developments of electrode and membrane materails [10], [11], [14], [17], [21], [25]. Besides, various groups subordinated at different universities or institutes, such as Central South University, Chinese Academy of Science or Dalian Institute of Chemical Physics, engaged in the research of VRB system and relative materials in China [8]. At Tsinghua University, a group prepared a poly (vinylidene fluoride)-graft-poly (styrene sulfuric acid) (PVDF-g-PSSA) membrane a solution-grafting method. In addition, Zhang and co-workers from Dalian Institute of Chemical Physics who had been devoted in the research of sodium multi-sulfide/Br_2 redox flow battery, directed their attentions to the VRB system last year [8]. It is reported that VRB has just commercialized in China. In September 1997, Kashima-Kita built a 200 kW x 4 h-rate battery interconnected to the company's power plant grid system for load levelling [8]. A Vanadium Energy Storage System (VEES) unifying a 250 kW/ 520 kW h VRB was installed in South Africa, which is crucial in that it is the first large-scale commercial trial of user-based applications for the VRB [8].

CHAPTER 3

VANADIUM REDOX FLOW BATTERIES

3.1 Principles of Vanadium Redox Flow Batteries

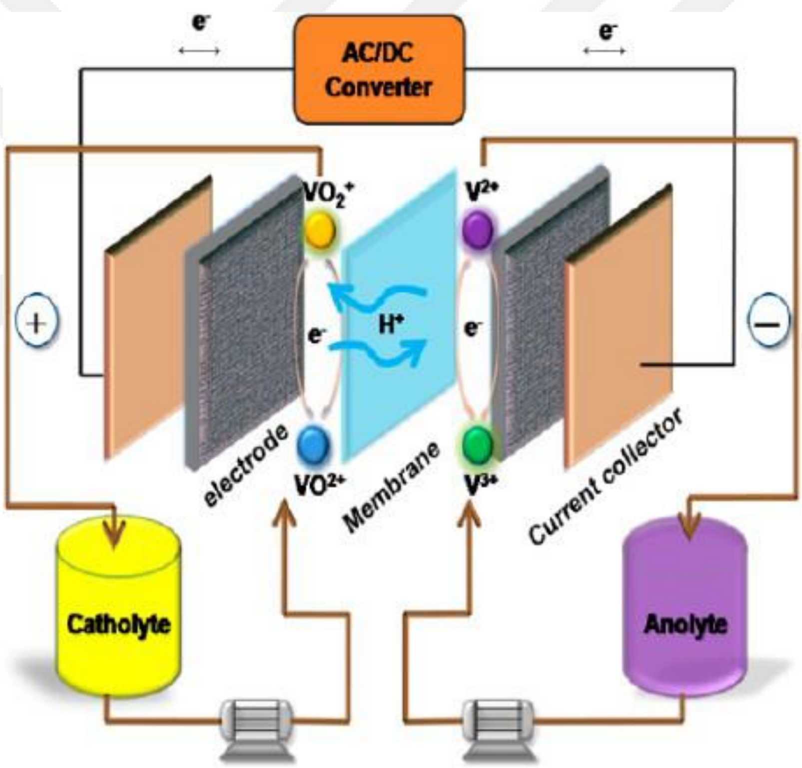

Figure 3.1 The basic schematic of a VRB single cell [27]

As shown in Figure 3.1, VRB employs different valence states of vanadium element (as positive side: VO^{2+}/ VO_2^+ and as negative side: V^{2+}/ V^{+3}) as redox-active species. A typical VRB stores or releases the energy according to charging or discharging process [4]. During charging, VO^{2+} is oxidized to VO_2^+ whereas V^{3+} is reduced to V^{2+} by taking the electron which is flown through the external power source and the reverse reaction is available during discharging [9].

Positive electrode reaction [27]:

$VO^{2+} + H_2O + e- \leftrightarrow VO_2^{+} + 2H^{+}$ $E° = 1.004$ V (3.1)

Negative electrode reaction:

$V^{3+} + e- \leftrightarrow V^{2+}$ $E° = -0.255$ V (3.2)

Overall electrochemical reaction of cell:

$VO^{2+} + H_2O + V^{3+} \leftrightarrow VO_2^{+} + 2H^{+} + V^{2+}$ $E = 1.259$ V (3.3)

During charging, by exposion of an external power source, the discharged form of the redox species is converted to the charged form. During discharge, electron flows between the redox species thus converting the chemical energy into electricity. As a result, the concentration of the redox species and electrolyte volume determine the energy capacity whereas the numbers of cells in the stack and the electrode area determine the power of the system [10]. All active species are generally dissolved in sulfuric acid solution that is in between 1-2 M or 1-3 M, respectively [4].

VRBs are normally configured by mounting several cells together in a series to form a battery stack as shown in Figure 3.2.

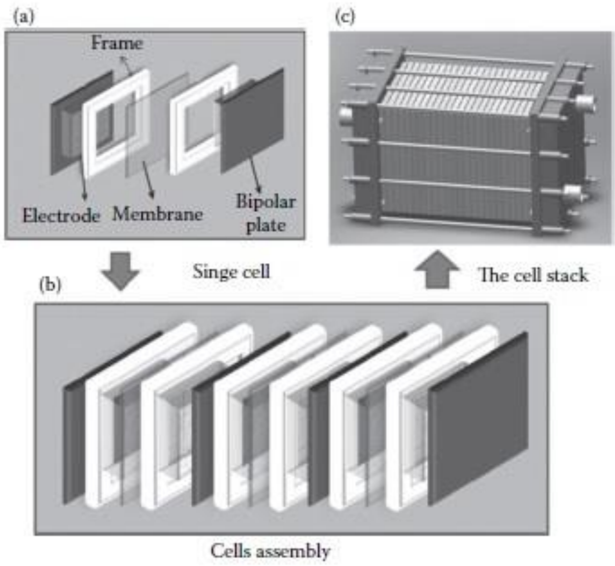

Figure 3.2 The mount of a) single cell, b) multiple cells and c) cell stack [11]

The membrane act to seperate each cell from each other (Figure 3.2 a) where the bipolar plate acts as the current-conducting medium between the negative electrode of one cell and the positive electrode of the next one (Figure 3.2 b). The cells in the battery are electrically assemblied in series and the electrolyte flows through the cells in paralell (Figure 3.2 c) [27]. The electrolytes are seperated via a membrane to maintain the volume of each electrolytes and not to lose the capacity of the VRB system.

The critical components in a VRB cell are the electrolyte, the carbon felt electrodes, the ion exchange membrane, bipolar plates, end frames, insulating frames and pumps [26]. Above mentioned, a basic assembly of all key components of a single VRB cell is shown in Figure 3.3. Each component will be discussed in the following sections.

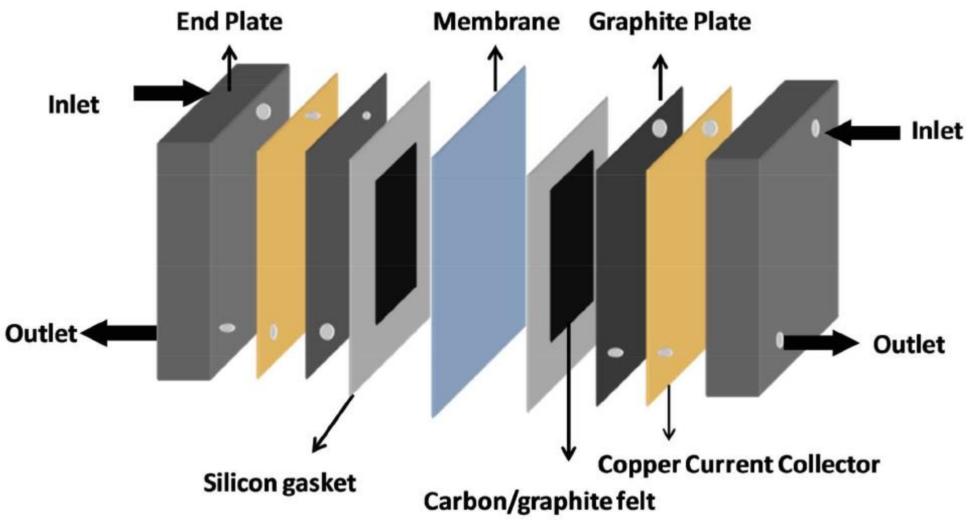

Figure 3.3 A basic schematic of all key components of a single VRB cell [26]

3.2 Advantages of The Vanadium Redox Flow Batteries

One of the major difficulties about the cross contamination of all redox flow batteries is denoted to utilize various types of redox couples in each half-cell in the literature [7]. On the other hand, VRB differs from the other redox flow batteries as employing same elements in each half cell that is one the most efficient approaches [26]. Having different valence states (V^{2+}, V^{3+}, V^{4+}, V^{5+}) of vanadium brought current VRB system concept about [26]. Apart from the richness in the oxidation states, the redox potential of V^{2+}/V^{3+} couple is well above the potential at which H_2 evolution occurs on carbonaceus electrodes, that is also very significant on sustainability of the anolyte form [26]. Besides, the wide span of redox active vanadium couples standard redox potential provide an advantage as well as the solubility of species in acidic solution (V^{2+}/V^{3+}= -0.26 V vs. a standard hydrogen electrode, SHE, and V^{+4}/ V^{+5} = 1 V vs. SHE). Utilizing vanadium redox couples give other salient facilities such as regenareting the electrolyte easily after a cross-diffusion and restoring the capacity simply, high energy efficiency and providing a commercial prospect since the vanadium is one the most abundant elements in the earth's crust [8], [26], [27].

It can be evaluated from Table 3.1 that VRB cycles are remarkably desirable when among all the chemical storage technologies are compared to each other. Besides, VRFB's operation and management (O&M) costs are the most feasible one. Although the best efficiency values belong to the Na-S storage system, its undesirable operation temperature (~300 ℃) seems to limits its utilizing in a wider area according to the Table 3.1.

When the voltage values are considered together, there are the battery couples which have on salient voltages such as lead (2,0 V) and zinc- cerium (2,3) redox couples. However, it can be claimed that their more harmful effects to the environment compared to the vanadium's toxic effect can be obstructed their preferabilities.

Table 3.1 Comparisons of various redox flow batteries on cost and operation[26]

Flow Cell	Efficiency Full Cycle (%)	Operation Temperature (° C)	Cycle Charge/ Discharge	Voltage (V)	Energy Related Cost ($ /kWh)	Operation& Management ($ /kWh)
Zn-Br	75	Room Temperature	2000	1,8	200-400	0,015
Zn-Ce	75	Room Temperature	-	2,3	750	-
PS-Br	60-75	Room Temperature	2000	1,5	175-190	0,020
Na-S	89-92	~300	2500+	2,0	~250	0,020
Lead	85	Room Temperature	500-800	2,1	175-250	0,020
VRFB	70-85	Room temperature	>200 000	1,4 (50% SOC[a]) 1,6 (100% SOC)	175-400	0,001

SOC [a] : State of charge

3.3 The Components of Vanadium Redox Flow Batteries

A typical VRB undamentally utilizes two soluble redox couples as it electrolytes, two electrodes as anode and cathode side, an ion exchange membrane to seperate the redox active species, bipolar plates as a current collector for the electron transfer, copper collectors for conducting electrons, end frames to close the cell, gasket materials for insulation for half-cell cavities and pumps for circulating the electrolytes [7].

3.3.1 Electrolyte

In a typical VRB set-up, the battery consists of two electrolyte reservoirs which are circulated through the cell by pumps [10]. In a VRB, the electrolyte is composed of active species of different valence states of vanadium ions and supporting electrolyte (e.g. sulphuric acid, hydrochloric acid, methane sulphonic acid and a mixed acid of above or organic electrolyte) to dissolve $VOSO_4$ and carry the ions [4]. The V^{2+}/V^{3+} couples are served as anolyte while V^{4+}/V^{5+} couples are acted catholyte [12]. The conversions between electrical energy and chemical energy (electrochemical) are realised via changes in vanadium valence states through electrode reactions, when the electrolytes are pumped from the tanks to the cell stack [4]. As the VRB employs soluble redox couples as active materials, the concentration of electrolytes will determine the system-specific energy density [4]. Therefore, as a high solubility of all redox active species are provided, the high energy density is possible theoretically [4], [28]. The electrolyte needs to possess a sufficient ionic conductivity to provide a decent rate capability. Viscosity is not normally created a problem in aqueous systems. However, one need to take into consideration pressure alteration owing to high viscosity when designing a non-aqueous system [4].

3.3.2 Electrode Material

VRB electrode materials can be classified into two main categories: a) metal and b)carbon materials. Pt, Pd, Au, platinised titanium (Pt-Ti) and iridium oxide are well known as dimensionally stable electrodes (DSAs) and employed as positive electrodes in VRBs [4]. Carbon –based electrodes are evaluated more ideal than metal electrodes for VRB applications [4], [26]. The materials which serve as electrodes in a cell construction should follow these properties: a) high electrical conductivity, b) high active surface area, c) optimum porosity (ε= 0.8 to 0.6), d) increased functionalization for good electrochemical activity, e) shape retention during compression to decrease the ohmic resistance f) good wettability or hydrophilicity, g) chemical stability, h) good oxidation resistance during overcharge, i) low cost [26].

Various types of carbon materials such as carbon felt, graphite felt, carbon paper and carbon powder have been sought as VRB electrodes up to date. Among them, carbon felt and graphite felt electrodes are more preferable options thanks to their three-dimensional network structure, providing the channels for electrolyte, large specific surface area, high conductivity and more decent chemical and electrochemical stability [4]. It is reported in the literature that polyacrylonitrile(PAN) and rayon-based carbon can be employed as porous electrodes akin to graphite felt (GF) [26]. While some materials possess good swelling property and electrochemical activity, some pre-treatment or surface modifications are denoted to impart suitable surface functional groups which expedite the reactions between redox couples [26].

3.3.3 Membranes

The ion exchange membrane (IEM) is a crucial component irrespective of electrolyte chemistry as it precludes the cross contamination of electrolytes and plays a critique role for preventing the loss of volume of the electrolytes while allowing the transfer of protons [17]. A prospective IEM for VRB applications should possess the following features:

a) High ion selectivity: the membrane must hinder the mixing of redox active species(e.g. V^{3+} or V^{4+}) which would result loss of system capacity while allowing the transferring of inactive redox species (e.g. protons, H^+, or sulfate, SO_4^{2-}, ions) which means to complete the circuit. An ideal membrane should exhibit low diffusion coefficients of active species to minimize self-discharge rate of the system and to gain higher coloumbic efficiencies and depending on this higher energy efficiencies [11].

b) Good ionic conductivity: one of the important roles of the membrane is to allow the transferring of protons or sulfates to complete the circuit. As a membrane possesses higher ionic conductivity , it indicates the minimized the ohmic losses in the cell to decrease the voltage and energy efficiency [26].

c) Good chemical stability: a membrane should display a good chemical stabiliy in highly acidic medium, VO_2^+ solution environment, to ensure both for a longer calendar life and cycle life [16].

3.3.4 Bipolar Plates

Bipolar plates show as a current collector feature for electron transfer reactions on the graphite felt (GF) electroactive material and seperate the mixing of electrolytes between cells while conducting current from one cell to the other inside the cell stack [26]. In addition to have chemical stability against highly corrosive vanadium electrolyte medium, bipolar plates must display decent electrical conductivity and resistivity to the oxidation during overcharge at the positive electrode surface. Moreover, bipolar plates should exhibit enough mechanical stability, too [26].

3.3.5 Copper Collectors

Copper collectors play a role of transferring electrons as a solid conductive material. While the cell construction is done, it should be paid attention to contact the bipolar plates and copper collectors directly. It can be encountered the resistance in case there is not a direct contact between bipolar plate and copper collector. Therefore, the electrons can not be transferred to the other side and the battery cannot be charged.

3.3.6 Flow Frames

Flow frames are used for fixing all of VRB components and provide a connection between pumps and the cell. Besides, they help to distribute the electrolyte across the cell. They should possess the following features: a) high acidic resistance, b)high durability, c) mechanical stability when compressed, d) ease of fabrication and low cost, e) recyclability [26].

3.3.7 Gasket Materials For Insulation

The insulating frames facilitate the half-cell cavity that accomodate the porous felt electrode material. The can be made from ethylene propylene diene monomer (EPDM) rubber or fluorocarbon caoutchouc (FKM) rubber materials. They should have the following features: a) high acidic resistance, b) flexibility with less weight, c) high durability, d) mechanical stability when compressed, e) ease of fabrication and low cost, d) recyclability [26].

3.3.8 Pumps

Pumps serve to circulate the electrolytes through the single cell or cell stack. Pumps act to provide a constant flow rate to the battery system. A pump should possess the following properties: a) providing a constant flow rate, b) chemically stable against acidic solutiouns, c) moderate cost. To provide a constant flow rate, peristaltic pumps are generallly preferred for vanadium redox flow batteries [5], [29].

CHAPTER 4

PRINCIPLES OF MEMBRANES

4.1 Basic Principles of Ion Exchange Membranes

Ion exchange membranes are basically relied on ion-exchange operation which means a reversible process in which one species replaces with the ionic species through exchanger functional group. Its main function in a VRB is to prevent the mixing of catholyte and anolyte while giving permission to transfer the non-redox species. Some of important features which should possess a membrane in RFBs are summarized in Figure 4.1.

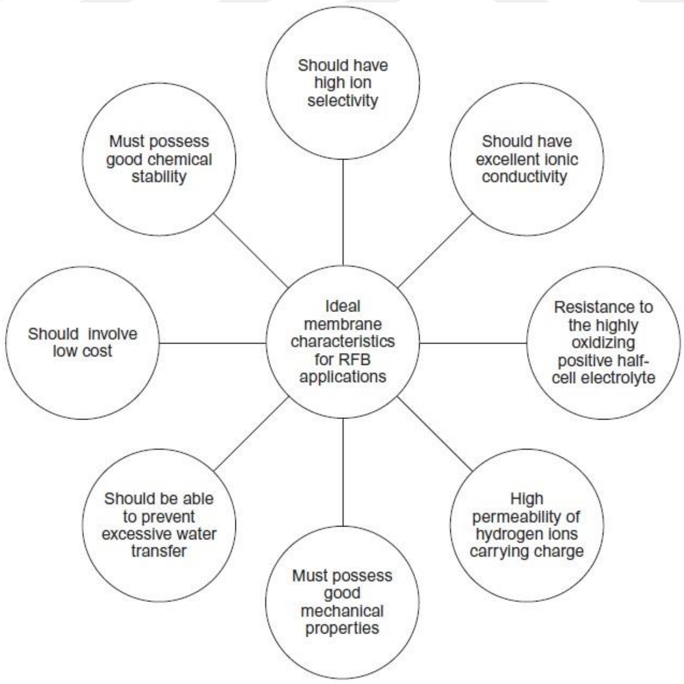

Figure 4.1 Prospect membranes' characteristics for a RFB [9]

As it can be evaluated in Figure 4.2 that the ionic functional groups are the exchange sites which have capability to constitute an electrostatic bond with an ion of opposite charge. The mobile counter ions are replaced by other ions from the solution with the same charge [9].

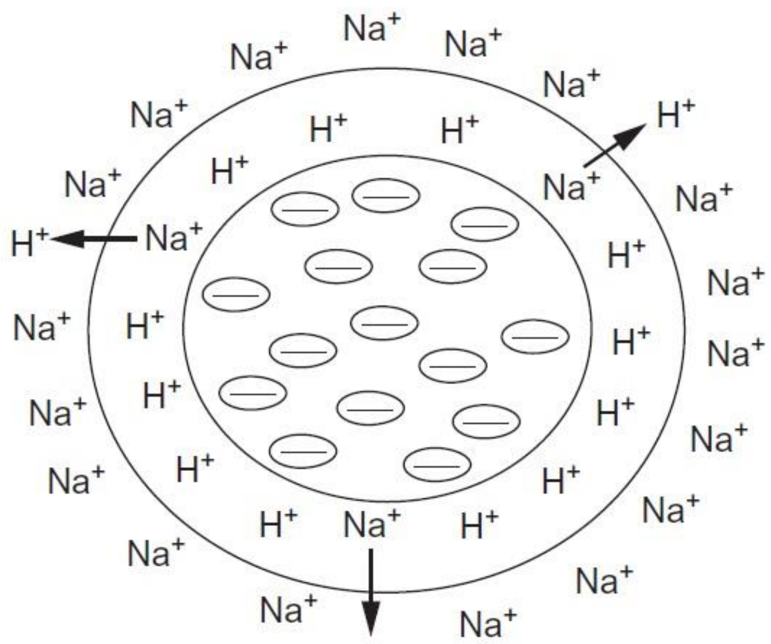

Figure 4.2 Ion exchange process [10]

Although the ion exchange resins are similar to the ion-exchange membranes, they are differed on mechanical requirements. Ion-exchange resins are normally well known on having unstability mechanically whereas ion-exchange membranes are not. The mechanical stability is provided thanks to the backing polymeric material which is necessary to gain strength to the membrane [9].

4.2 Types of Ion Exchange Membranes

Membranes are classified into the charged groups which are attached to the membrane structure. A general and a basic classification of ion exchange membranes are exhibited below in the Table 4.1.

Table 4.1 General classification of ion exchange membranes [9]

Classification Basis	Membrane Types
Relied on type of ion exchanged	Anion exchange membranes Cation exchange membranes Composite membranes
Relied on structure	Homogeneous Heterogeneous Interpolymeric Symmetric/asymmetric membranes
Relied on other physical properties	Nature of the material Morphology Pore size Driving force

Cation exchange membranes include negatively charged groups such as $–SO_3^-$, $-COO^-$, $-PO_3^{2-}$,$-PO_3H^-$, and $–C_6H_4O^-$ to admit the transfer of cations, such as Na^+ shown in Figure 4.2, through membrane while rejecting anions. In contrast, anion exchange membranes possess positively charged groups such as $–NH^{3+}$, $-NRH^{2+}$, $-NR_2H^+$, $-NR^{3+}$, and $–SR^{2+}$ to allow the passage of anions while refusing cations [9]. Both cation and anion functional groups can also be existed in a membrane, causing the amphoteric and bipolar exchange membranes. In an amphoteric exchange membrane (AIEM), both anion and cation exchange groups are adjusted throughout the membrane whereas bipolar exchange membrane will possess both a cation-exchange layer and anion-exchange layer, producing bilayer membranes [9]. Depending on charged groups' attaching to the polymer matrix, IEMs can be called as homogeneous or heterogenous. Homogeneous membranes are directly possessed the ionic groups which are attached to the base polymer structure. Heterogeneous membranes are produced by compressing a mixture of ion exchange resins and an elastic binder. These membranes are more durable than homogeneous membranes due to the binder support [9]. Interpolymeric membranes are fabricated by casting a film from a homogeneous solution of two polymers, one of which represents the polyelectrolyte and the other a water-soluble filmogenic material [9].

Porous membrane seperators are evaluated as alternative non-fluorinated membranes for RFBs thanks to their remarkably and relativley low cost . Porous seperators are well known to possess low selectivity [30]. They can seperate vanadium ions from protons based on pore size exclusion via Stokes radius difference. Besides, their performance can be arranged via adjusting the the morphology and by membrane modification [14]. Figure 4.3 displays various types of membranes which are employed in RFBs.

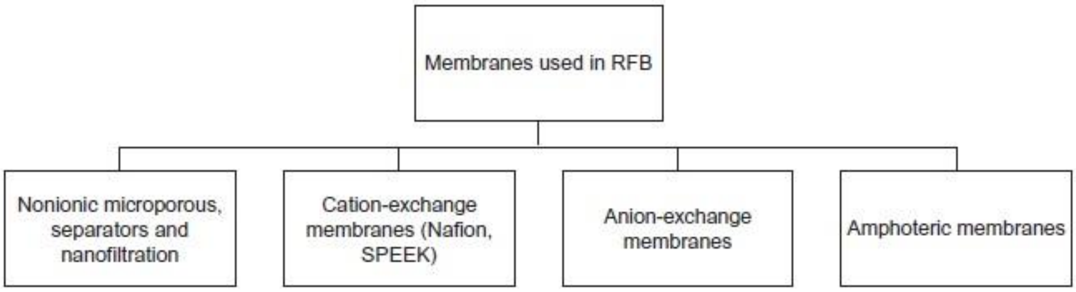

Figure 4.3 Membranes which are generally utilized in RFBs [9]

4.3 Preparation of Ion Exchange Membranes

The fabrication of membranes are a multistage process, beginning with the production of polymer followed by post-treatments to impart selectivity and mechanical stability to the membrane. Most polymer membranes are fabricated by melt, dry and extrusion process [10]. Melt and dry process are evaluated more inexpensive compared to wet extrusion process thanks to higher production rates.

Other membrane production methods are paste method and membrane casting method. The process begins with a paste of monomer with a functional group to attach an ion exchange group, divinylbenzene (DVB), a radical polymer initiator, and a finely powdered poly (vinylchloride) (PVC). Ion exchange membranes are produced by this method [9]. Membrane casting is method that ion exchange membranes are produced by imparting ion exchange functionality directly (such as sulphonic acid groups) to a base polymer material (such as polystyrene) [9]. Cation exchange membranes are taken their characteristic from the carboxylic acid groups or sulfonic acid groups which are attached to the base polymer. Anion exchange membranes are fabricated by two step process, chloromethylation followed by quaternary amination [31].

Microporous seperators are often produced from organic and inorganic materials. The simplest method of preparation involves the streching of a homogenous polymer film of a particular crystallinity. The streching leads to a partial fracture of the film and relatively uniform pores [10]. Selectivity across the membranes is obtained through the different transport rates of various ionic species [10].

CHAPTER 5

EXPERIMENTAL

5.1 General

This part of the master thesis respectively includes the materials and chemicals, the decision of porous membrane's modification technique, characterization of each membranes, battery performance tests of the membranes and the results.

5.2 Membrane Properties

FAP® 450 (FuMA-Tech, Germany) is an anion ion exchange membrane; Nafion ® 117 (DuPont, the USA) is a cation ion exchange membrane and Amer-Sil FF60 (Amer-Sil, Luxembourg) is a porous membrane. FAP ® 450 has a poly(ether-ether-ketone) (PEEK) backbone; Nafion® 117 has a polytetrafluoroethylene (PTFE) backbone and a sulhonic acid (SO_4^{2-}) functional group and Amer- Sil FF60 porous membrane has a polyvinylchloride (PVC) backbone and silica (Si) hydrophilic functional group.

5.3 Membrane Modification

5.3.1 The Properties of The Coating Solution

Nafion® (5,7%, wt) dispersion was utilized to modify the Amer-Sil FF60 porous membrane. The Nafion® (5,7%, wt) dispersion's main features were shown in the Table 5.1.

Table 5.1 The properties of Nafion® (5,7%, wt) dispersion

The dispersion's full name	**Basis**	**Polymer content (wt, %)**	**Water content (wt, %)**	**Volatile organic compound (VOC) (wt, %)**	**Viscosity (cP at 25℃)**
Nafion® polymer (D521 Alcohol based)	Alcohol based 1100 Equivalent weight(EW) 5% weight	5 (minimum) 5,4 (maximum)	45∓ 3	48∓3 (1-propanol) <4 (Ethanol) <1 (mixed ethers and other VOCs)	10-40

5.3.2 Coating Techniques

Dr. Blade and spraying technique techniques were selected as a start. Then, Energy Dispersive X-Ray Spectroscopy (EDX) (Oxford Insturments, Xmax, 50 mm^2, Germany) analyses were done in order to decide which coating technique was more efficient than the other one. It was decided according to the images of some characteristic elements as the proof of the homogenity of the coating. The main equipments for the membrane modification was shown in the Figure 5.1 a and Figure 5.1 b.

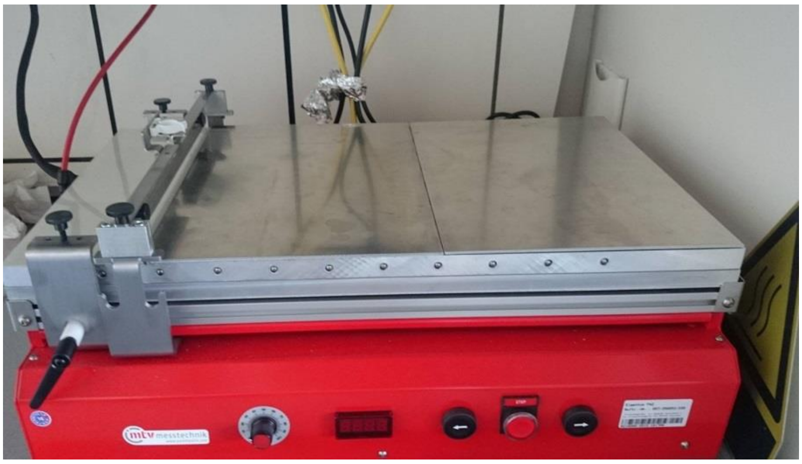

Figure 5.1 a) Dr. Blade for membrane coating

Figure 5.2 b) Spray gun's main components for spraying

Nafion® (5.7 %, wt) (DuPont, the USA) was employed for coating as it was one of the most widely studied membrane solutions for modifying.

5.3.3 Characterization of Coating

It was decided to analyse via EDX (Oxford instruments, XMAX, 50 mm^2). A sample having 6 cm^2 area coated with Nafion® (5.7 %, wt) was prepared with 5 ml volume which was described in the Figure 5.2. It was shown the coating ratio for the EDX analysis sample in the Table 5.2. A piece of sample having 1 cm^2 was cut for EDX analysis.

Table 5.2 The ratio of coating for the EDX analysis

Coating amount Nafion® (5.7 %, wt) (ml)	**Coating amount Et-OH (ml)**	**Coating ratio**
2,5	2,5	1:1

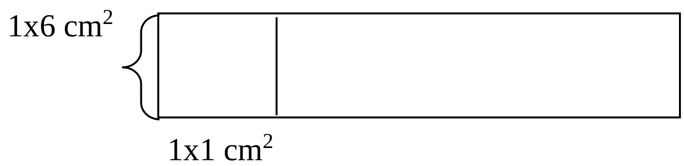

Figure 5.3 A sample of modified porous membrane for EDX analysis

5.4 Membrane Characterization

Membrane characterization tests were respectively experimented for each membranes, FAP 450, Nafion® 117, Amer-Sil FF60 (porous membrane), Amer-Sil FF60/Nafion® (5.7 %, wt) (0,5:1) and Amer-Sil FF60/ Nafion® (5.7 %, wt) (1:1) which were shown below from Figure 5.3 to Figure 5.7.

Figure 5.4 FAP 450 membrane

Figure 5.5 Nafion 117 membrane

Figure 5.6 Amer-Sil FF60 membrane

Figure 5.7 Amer-Sil FF60/ Nafion® (5.7 %, wt) (0,5:1) membrane

Figure 5.8 Amer-Sil FF60/ Nafion® (5.7 %, wt) (1:1) membrane

In the view of the membrane characterization for all vanadium redox flow batteries such as vanadium diffusion coefficient for permeability, ionic conductivity, water uptake, chemical stability , Nafion® (5.7 %, wt) stability as the modifying dispersion and cell performance tests were finalized. All the measurements except the samples for chemical stability test have been applied for one membrane. Additionally, the battery performances were carried out for three samples.

5.4.1 Vanadium Ion Permeability Tests

To determine the rate of the diffusion of the V(IV) ions across the membrane, it was configured a dynamic cell test set-up as shown Figure 5.8.

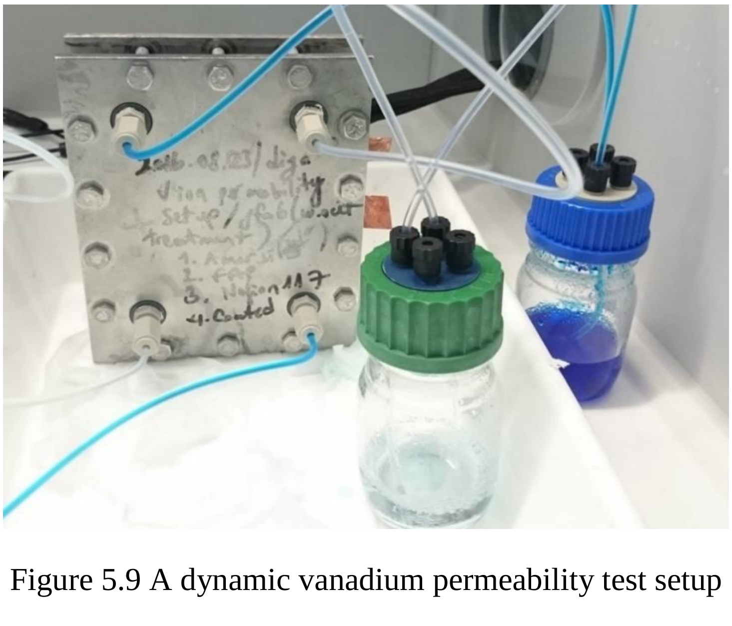

Figure 5.9 A dynamic vanadium permeability test setup

Respectively, FAP 450 (FuMA-Tech GmbH), Nafion 117 (DuPont, the USA), Amer-Sil FF60 (Amer-Sil , Luxembourg), Amer-Sil FF60/ Nafion® (5,7 %, wt) (0,5:1) and Amer-Sil FF60/ Nafion® (5,7 %, wt) (1:1) was placed two compartments of the cell. 1 M $VOSO_4 . 4,9H_2O$/ 2 M H_2SO_4 and 1 M $MgSO_4$ / 2 M H_2SO_4 stock solutions which were exhibited in Figure 5.9 for each compartment were prepared. One side was filled with 60 ml 1 M $MgSO_4$ / 2 M H_2SO_4 while the other side was filled 60 ml 1 M $VOSO_4$ / 2 M H_2SO_4 . $MgSO_4$ was added to the one side to equalize the ionic strengths and to avoid osmotic pressure differences [11]. The circulating of each solutions were provided by a pump (KnF, Switzerland). Samples from the $MgSO_4$ compartment were taken at different intervals. The time interval was varied for each membrane due to the different characteristics of the membranes (anion exchange, cation exchange and porous and modfied porous membrane). The samples including VO^{2+}, V (IV), ions from the $MgSO_4$ side were analyzed via UV-VIS Spectrophometer (UV-1650PC, Shimadzu, Japan) at 760 nm wavelenght [10]. 5 different V(IV) solutions (0,00 M- 0,04 M) were prepared to draw a calibration curve based on the association between absorption and concentration for the calculation of V(IV) concentration in $MgSO_4$ [29]. The effective membrane area was 40 cm^2.

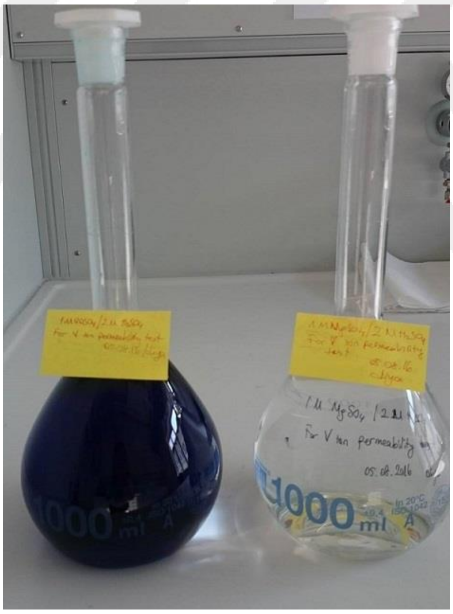

Figure 5.10 1 M VOSO4 / 2 M H2SO4 and 1 M MgSO4 / 2 M H2SO4 stock solutions

The diffusion coefficient of each membrane was calculated according to the Equation (5.3) combining of Beer's Law which was shown in the Equation (5.1) and Fick's Diffusion Law which was displayed in the Equation (5.2) [29].

Beer's Law ;

$$A= \varepsilon \times l \times C \tag{5.1}$$

Fick's Diffusion Law;

$$J = -D \times \frac{dC}{dX} \tag{5.2}$$

$$-Log_{e}\frac{(Co-Ct)}{Co} = \frac{(D\times a)}{(l\times v)} \times t \tag{5.3}$$

Where A is absorbance, ε molar absorptivity constant, l the thickness of the kuvette, mm, C is the concentration, mol/L; J the diffusion flux, 1 / m^2 s , dC/dX the concentration gradient, mol/m^4 , C_t the vanadium concentration in the $MgSO_4$ compartment in mol /L, C_o the inital concentration of the vanadium in the vanadium compartment in mol/L, D the diffusion coefficient in cm^2 /min, a the area of the membrane exposed to the solution in cm^2, l the thickness of the membrane in cm, v the volume of the solution on both sides in ml and t is the time in minute [29].

5.4.2 Ionic Conductivity Test

The ionic conductivity is one of the most significant criterion while evaluating RFB performance. The ionic conductivity means proton conductivity as another term. The ionic conductivity of the membranes is determined by electrochemical impedance spectroscopy. As illustrated and modelled in Figure 5.10, most of the losses come from imperfect contact between electrodes, current collectors, impurities in electrolyte and conductivity of membrane. All these resistances are measured via electrochemical impedance spectroscopy (Solartron analytical modulab ECS, UK) and proton conductivity of the membrane is gained [5], [18].

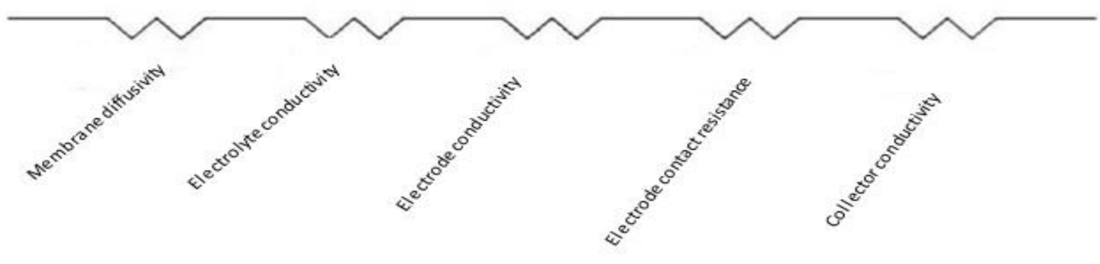

Figure 5.11 Factors contributing to the total increased ohmic resistance of a cell [5]

Proton conductivity (σ, S/ cm) of the membrane can be determined by the following Equation (5.4) [32]:

$$\sigma = \frac{L}{(A\times R)} \tag{5.4}$$

Conductivity measurements were carried out by electrochemical impedance spectroscopy (Solartron Analytical Modulab ECS) at ambient temperature. The cells with each membrane was configured and humidified with the electrolyte by pump (KnF, Switzerland). The impedance measurements were applied in the frequency region from 100 mHz to 100kHz. The probes were connected and the distance between working electrodes were measured as 0.4 cm. Where L is the membrane thickness, cm, A the lateral area of the membrane, cm^2, R the resistance from EIS, Ω and σ, the resistivity (cm/S). Proton conductivity was calculated as the reciprocal of the resistivity, $1/\sigma$.

5.4.3 Water Uptake

Water uptake of the membranes are determined by measuring dry and wet weight difference according to the below Equation (4.3) which was taken from a water uptake standard test [35]. According to the standard's procedure, 7,6 cmx 2,5 cm specimens were cut and conditioned in the Heraeus Vacutherm® Oven (Thermo Scientific, Germany) for 24 h at 50 °C. After the samples were taken from the oven, they were cooled in a desicator for 2 hours and immediately weighed. The contidioned specimens were dipped into the beaker filled with 150 ml distilled water (ELGA, UK). An illustration of water uptake test for three Amer-Sil FF60 (porous membrane) samples were described in Figure 5.11.

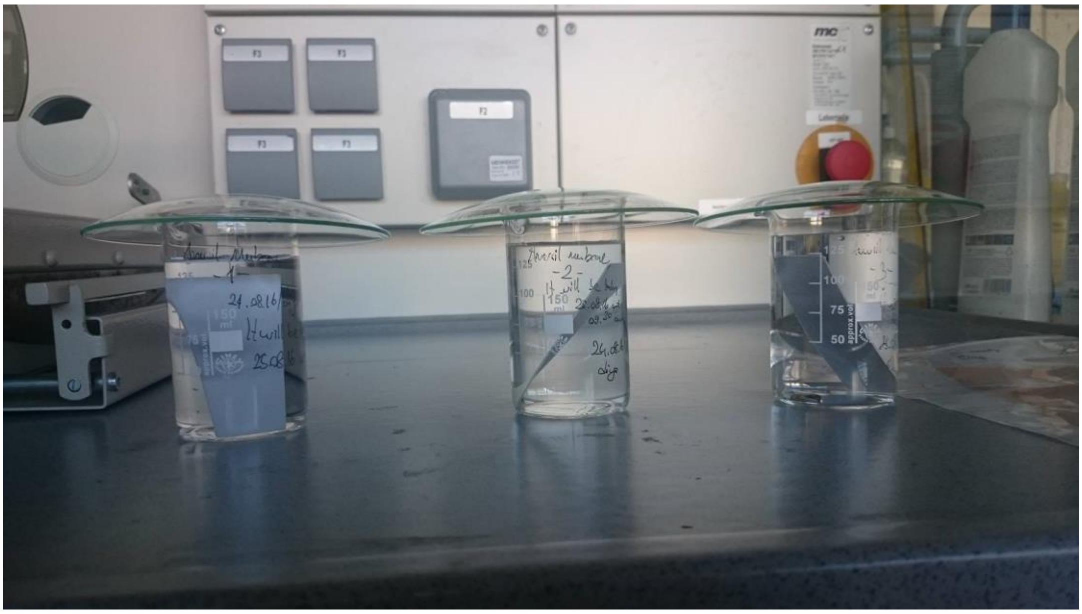

Figure 5.12 Water uptake tests for Amer-Sil FF60 porous membranes

After the specimens were swollen the distilled water for 24 hours, they were wiped off with a dry paper towel and then weighed. The swelling ratio was calculated for each membrane below following Equation (5.5).

$$Water\ Uptake\ (\%) = \frac{(Ws - Wd)}{Wd} \times 100 \qquad (5.5)$$

5.4.4 Chemical Stability

This test was only applied to Amer-Sil FF60 porous membrane since there was chemically no test for Amer-Sil FF60 porous membrane before. According to a relatively simple and standard method which was described in the literature, Amer-Sil FF60 membrane was firstly cut into nine specimens as 2x2 cm^2 [10]. Then, three samples of pre-weighted membranes are soaked in 1,6 M V(II) solution, three of them $V^{3,5+}$ as a mixing of 1,6 M V(IV) and 1,6 M V(III), and three of them 1,6 M V(V) solutions. One out of three samples was plainly put; one out of the rest was put with one notch and the last one was put with two notches. The goal of this test method was to check whether there was an alteration on its notches and control any deterioration on its shape of the notches. After the specimens were waited in the different vanadium solutions for two months, these operations were applied into them: a) they were analysed via optic microscope and b) their shore hardness were measured to check the toughness of the membrane.

5.4.5 Cell Performance Tests

After all the membranes were characterized as above mentioned, three cell tests were carried out for each membrane at least. As shown in Figure 5.12, all the components of a cell such as electrodes, bipolar plates, membrane, copper collectors, flow frames, insulating materials, bolts and nuts. Before the cell configuration, two GFA 6 felt electrodes (SGL Carbon, Germany) were activated by thermal treatment at 400 °C for 1 hour. After pre-treatment of the electrodes, their thickness were measured via digital thicknessmeter (Käfer, Germany) from nine different points and the average of GFA 6 felts were calculated. Bipolar plates, copper collectors, electrodes and membranes must directly be contacted to be capable of decreasing the resistance. Depending on the goal of the lowest resistance and "zero-gap" between all componets as much as possible, the average of electrodes were multiplied by the emptiness of 0,9 (90%) after the comppressed 10%. The emptiness due to flow of electrolyte was subtracted from the latter value. According to the last result, it was choosed the necessary insulating (Ristaro

Gummiprofil GmH, Germany). The bipolar plate which were directly in contact with copper collectors (Schlenk, Germany) was put on an flow frame. The electrode was put inside it and the insulating materials on it. The membrane (FAP 450, Nafion 117, Amer-Sil FF60, Amer-Sil FF60/ Nafion® (5,7 %, wt) (0,5:1), Amer-Sil FF60/ Nafion® (5,7 %, wt) (1:1) membranes, respectively) was placed and the other side components were situated in a mirror symmetry. All the assemblied components were compressed via torque wrench (Stahlwille, Germany) with 3 N force. After it was waited for 2 hours, it was fixed with same torque.

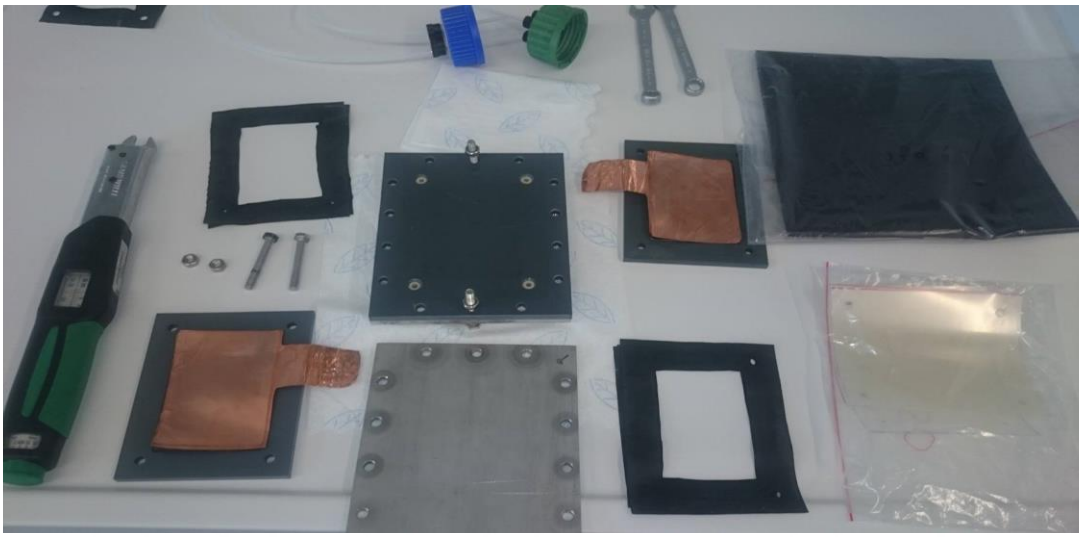

Figure 5.12 All the main components of a single cell

Then, the cell was operated as filling V(III) and V(IV) electrolyte (GfE Metalle and Materialien GmbH, Germany) vessel 60 ml via an automatic Ceramus® dispenser (Hirschmann, Germany) for each side as shown in Figure 5.13.

For the negative side, it was adjusted the nitrogen gas amount and connected into the vessel which was for the negative side to avoid from the toxic effects of V(II) species. It was used a battery test program equipped with data analysis software (BaSyTec GmbH, Germany).

Figure 5.13 An image of a running single cell

For each membrane sample, the same charge and discharge properties were applied. The software was arranged to collect time (s), voltage (V), current (A), charge (C) and power (W) values automatically. According to this values, current density (mA/ cm^2) (CD), coloumbic efficiency (%) (CE), energy efficiency (%) (EE) and discharge power density (mW /cm^2) (DPD) were calculated by utilizing all the collected data. Efficiency calculation formulas can be seen in the Equation (5.6), (5.7) and (5.8) [11]:

$$CE = \frac{Qdis}{Qch} \times 100 \tag{5.6}$$

$$\left.\begin{aligned} &Voltage\ Efficiency = \frac{Vdis}{Vch} \times 100 \\ &EE = CE \times EE \end{aligned}\right\} \tag{5.7}$$

$$\left.\begin{aligned} &W = I \times V \\ &DPD = \frac{\int_0^t I \times V dt}{t} \end{aligned}\right\} \tag{5.8}$$

5.4.6 Nafion Stability Test

Nafion stability test was carried out to determine if the Nafion® (5,7 %) dispersion was stable on the membrane’s surface after cell test or not. After all the Amer-Sil FF60/

Nafion® (5,7 %) tests were completed, modified Amer-Sil FF60/ Nafion® (5,7 %) (0,5:1) membrane was investigated in terms of Nafion® (5,7 %)'s stability via EDX. It was sought that how much Nafion® (5,7 %) amount was remained on the Amer-Sil FF60 membrane surface.

CHAPTER 6

RESULTS AND DISCUSSION

From the Figure 6.1 to Figure 6.4 show that the distribution of the characteristic elements of silica (Si) from porous membranes' functional group (Si) and fluorine (F) from Nafion® (5.7 %, wt) dispersion's characteristic functional group of polytetrafluoroethylene (PTFE) with both techniques, Dr.Blade and spraying, as mentioned before in the experimental part. All the EDX images were taken with the same magnification and same energy values.

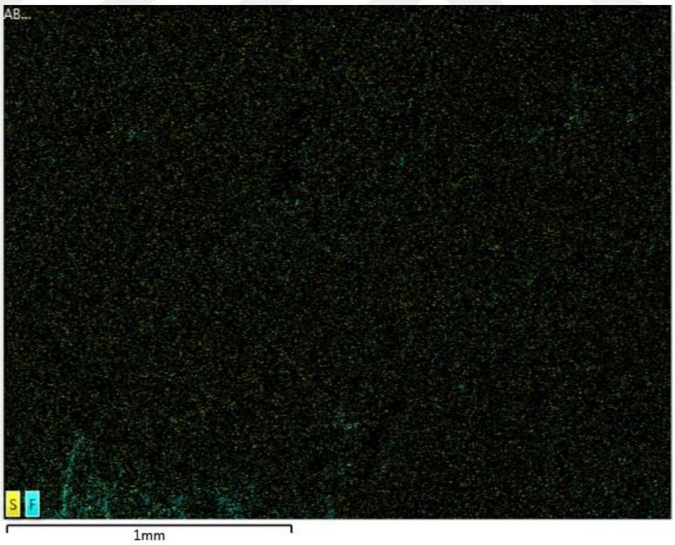

Figure 6.1 Si, F elements of Amer-Sil FF60/ Nafion® (5.7 %,wt), Dr.Blade, 100X,20 KV

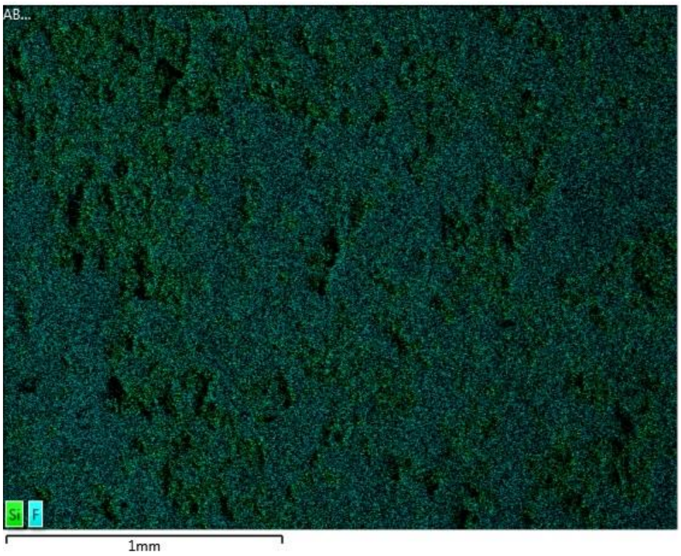

Figure 6.2 Si, F elements of Amer-Sil FF60/ Nafion® (5.7 %,wt), Spraying, 100X,20 KV

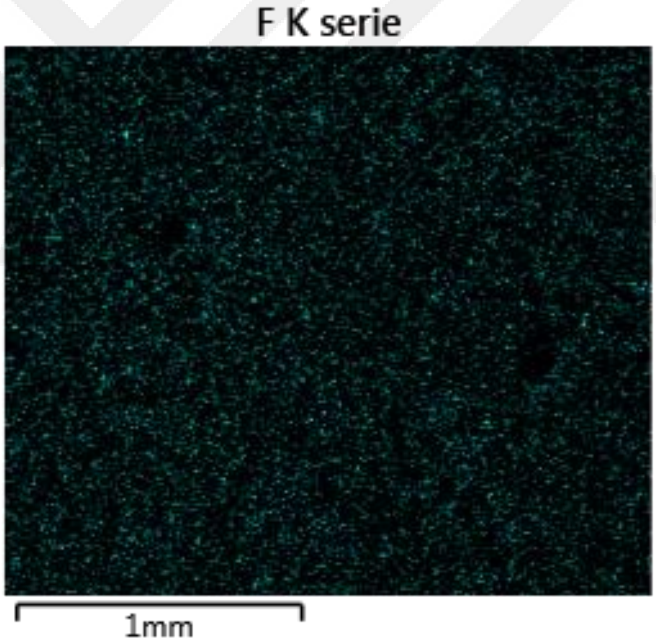

Figure 6.3 F element of Amer-Sil FF60/ Nafion® (5.7 %, wt), Dr.Blade, 100X, 20 KV

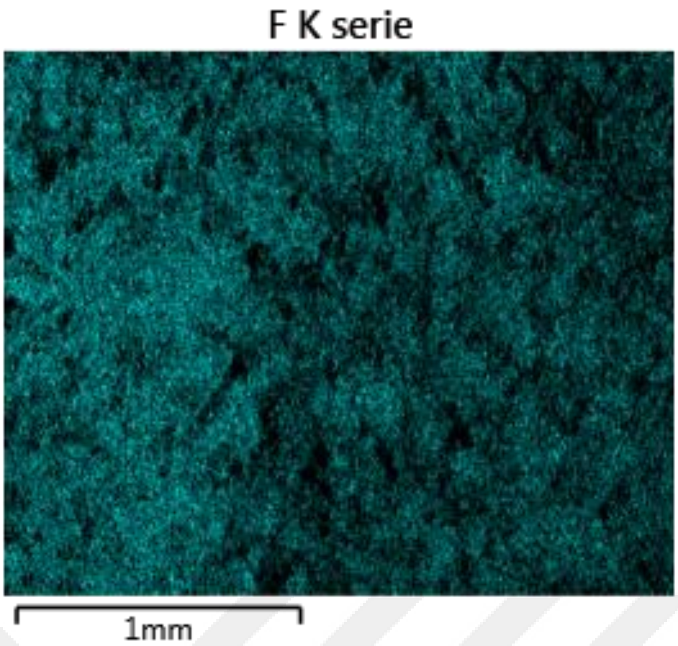

Figure 6.4 F element of Amer-Sil FF60/ Nafion® (5.7 %, wt), Spraying, 100X, 20 KV

According to the morphological and elemental distribution analyses, it was decided to modify the porous membrane via spraying technique. It was prepared two different coating amount solution with Nafion® (5,7 %, wt) as 20 ml Nafion (5,7 %, wt) : 40 ml Ethanol (Et-OH) (Carl Roth GmbH, Germany) (0,5: 1) and Nafion® (5,7 %, wt) as 40 ml Nafion (5,7 %, wt) : 40 ml Ethanol (Et-OH) (1: 1) for spraying. Different weight ratios of coating amount solution were prepared as shown in Table 6.1.

Table 6.1 Different modifying proportions of porous membrane

Coating amount Nafion® (5,7 %, wt) (ml)	**Coating amount Et-OH (ml)**	**Coating ratio**
20	40	0,5:1
40	40	1:1

The porous membranes were cut into 13x13 cm^2 area and were measured before and after coating with Nafion® (5,7 %, wt) via scale (Mettler Toledo, Switzerland). They were fixed to a 10x10 mold as shown in Figure 6.5.

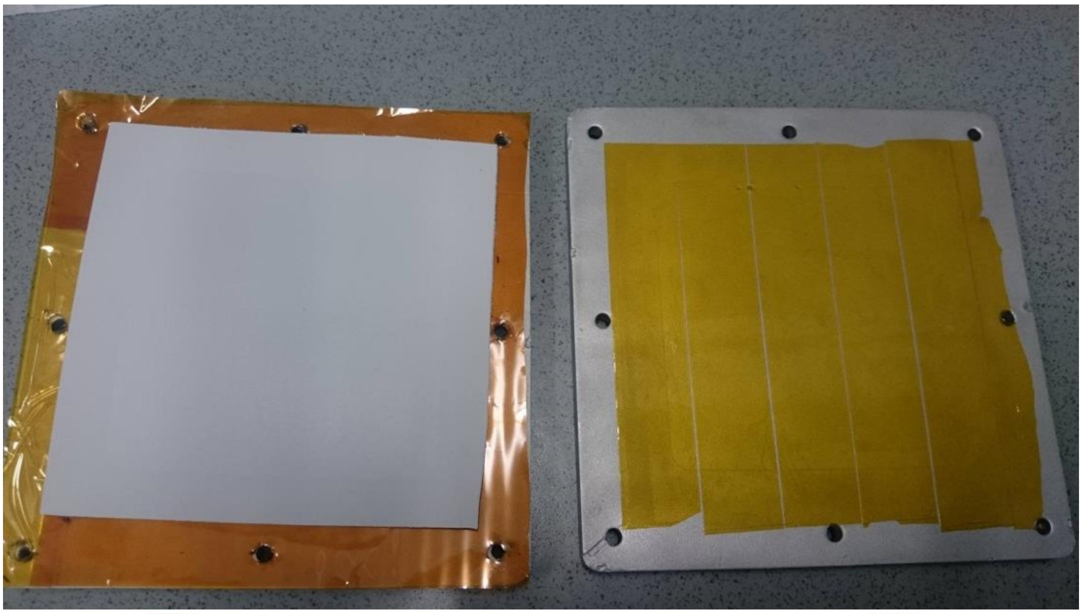

Figure 6.5 A 10x10 cm^2 mold and porous membrane on it for spraying

According to the previous explanations and experiments, the membrane characterization properties such as V^{4+} diffusion coefficients (cm^2 /min), ionic conductivity (S/cm), water uptake results are listed in the Table 6.2.

Table 6.2 The characterization values of all membranes

Membrane name	**V^{4+}diffusion coefficients (cm^2 /min)**	**Ionic conductivity (S/cm)**	**Water uptake (%)**
FAP 450	$45x10^{-7}$	0,167	6,86
Nafion 117	$133,35x10^{-7}$	0,320	18,29
Amer-Sil FF60(porous membrane)	$499x10^{-7}$	0,345	105,32
Amer-Sil FF60/ Nafion® (5,7 %) (0,5:1)	$96x10^{-7}$	0,123	87,90
Amer-Sil FF60/ Nafion® (5,7 %) (1:1)	$19,2 x10^{-7}$	0,073	74,89

The Amer-Sil FF60 membrane had the one of the most permeable values owing to the fact that it was a porous membrane. FAP 450 membrane exhibited the lowest diffusion coefficient compared to the Nafion® 117 and Amer-Sil FF60 porous membrane and modified ones since it was an anion exchange membrane. With upon the addition of Nafion® (5,7%) dispersion, Amer-Sil FF60 porous membrane's relatively undesired permeability values could be decreased. While it could be decreased the permeability values for modified porous membranes, their ionic conductivities were declined as an undesired property, too.

It is reported in the literature that there is an antogonistic relationship between diffusivity and ionic conductivity [33]. However, it is also reported that swelling behavior and ionic conductivity has a parallel association [33]. When it is evaluated in itself, the results can be interpreted relevant with each other. Amer-Sil FF60 porous membrane's swelling behavior which could be attributed to the silica (Si) functional inorganic group was quiet the highest among all membranes and also it had the best ionic conductivity although it was incapable of precluding the cross-over of redox species. It can also be ascribed to the some air traps or some water molecules which couldn't be removed during spraying process. Higher degree of swelling would raise the permeation of different ions and increase the ionic conductivity as a result. With the addition of PTFE, which was ascribed to the Nafion® (5,7 %) dispersion, the water uptake was reasonably supressed and correspondingly to this situation, the ionic conductivity decreased. Considering the hydrophobic nature and the different crystallinities of different backbone polymers (FAP 450 membrane's hydrophobic backbone polymer is poly (ether ether ketone) (PEEK) ; Nafion 117 membrane has polytetrafluoroetylene (PTFE) ; Amer-Sil FF60 porous membrane has polyvinyl chloride (PVC)), it is highlighted that the swelling behavior and mechanical stability are closely related to each other. These different polymers are brought about different water absorptions and mechanical stabilities [33].

<u>Chemical stability test;</u>

According to some optic microscope images as shown in Figure 6.6 and Figure 6.7, it was observed that Amer-Sil FF60 porous membrane was seemed durable against highly corrosive and acidic vanadium medium. Besides, it was shown in the Table 6.3 that how much amount Amer-Sil FF60 membrane was absorped the electrolyte and increased its weight.

Table 6.3 The membrane weight alteration after to the exposion of vanadium electrolyte for two months

Membrane before soaking into the vanadium electrolyte (g)	**Membrane after soaking into the vanadium electrolyte (g)**	**The change (%, wt)**
0,138	0,25590	85,43
0,1373	0,25570	87,69
0,1358	0,25400	87,04
0,1498	0,26410	76,30
0,1244	0,21790	75,16
0,15	0,23460	56,40
0,14	0,23490	67,79
0,1328	0,22900	72,44

Figure 6.6 A miscroscopic image of Amer-Sil FF60 sample before test

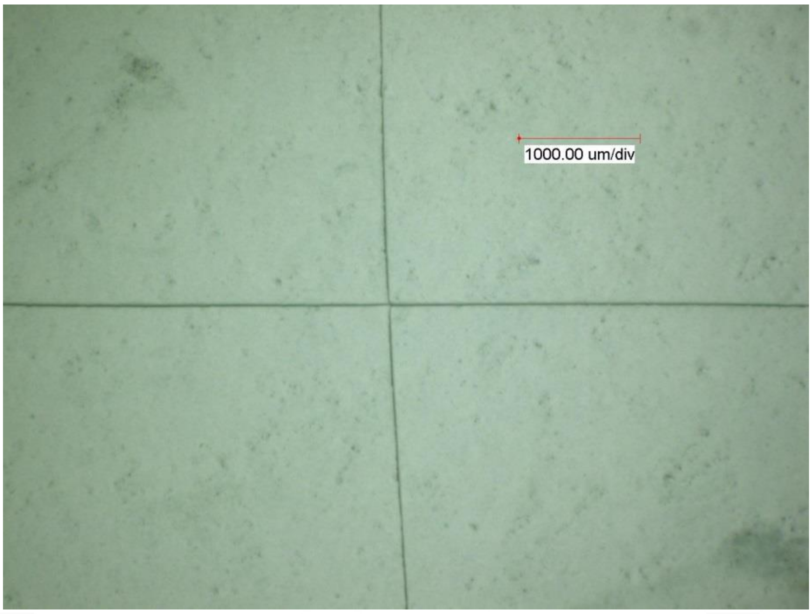

Figure 6.7 A microscopic image of Amer-Sil FF60 sample after test

It can obviously be observed that there was almost no difference after the exposion to the chemical environment. Additionally, the shore hardness test could not be applied since the Amer-Sil FF60 porous membrane was relatively thin $(\cong 0{,}64\ mm)$ $(< 1\ mm)$. It can be claimed that Amer-Sil FF60 is probably stable in the vanadium electrolyte. It is necessary to make long-term stability tests in order to check the stability of the membrane for four months or one year. However, it couldn't be carried out for this thesis due to the time limitation.

<u>Cell test results;</u>

Single vanadium redox flow battery cell was constructed as mentioned before in the experimental part. All the experiments were repeated at least three times for each membrane and the values were displayed with their mean and the standard deviation values. As shown in Figure 6.8, FAP 450 exhibited the best performance in terms of capability of preventing the loss of capacity. Correspondingly, its coloumbic efficiency was the highest whereas the Amer-Sil FF60 porous membrane's performance was the worst due to possessing the higher diffusion coefficient than FAP 450 membrane. However, Nafion®117 membrane's coloumbic efficiency and correspondingly energy effficiency performance was better than Amer-Sil FF60 porous membrane despite its relatively higher diffusion coefficient than Amer-Sil FF60 membrane. It should not be evaluated that diffusion coeffients are not plausible by oneself. The can be evaluated with ion exchange capacity and ionic conductivity. It can be claimed that Amer-Sil FF60 /Nafion (5,7%, wt) (0,5:1) and Amer-Sil FF60 /Nafion (5,7%, wt) (1:1) modifications hindered the cross-over problem of redox species and consequently, they exhibited not only better performance than Amer-Sil FF60 unmodified one but also their capacity performance were close to the Nafion 117 membrane which was commonly studied in the literature [11], [32], [33]. The relatively high standard deviations on the second cycle and the last cycle of the Nafion® 117 membrane were due to the pumps. Pumps stopped by itself at an unclear time for a while and after they were run again, the cycles were normally operated.

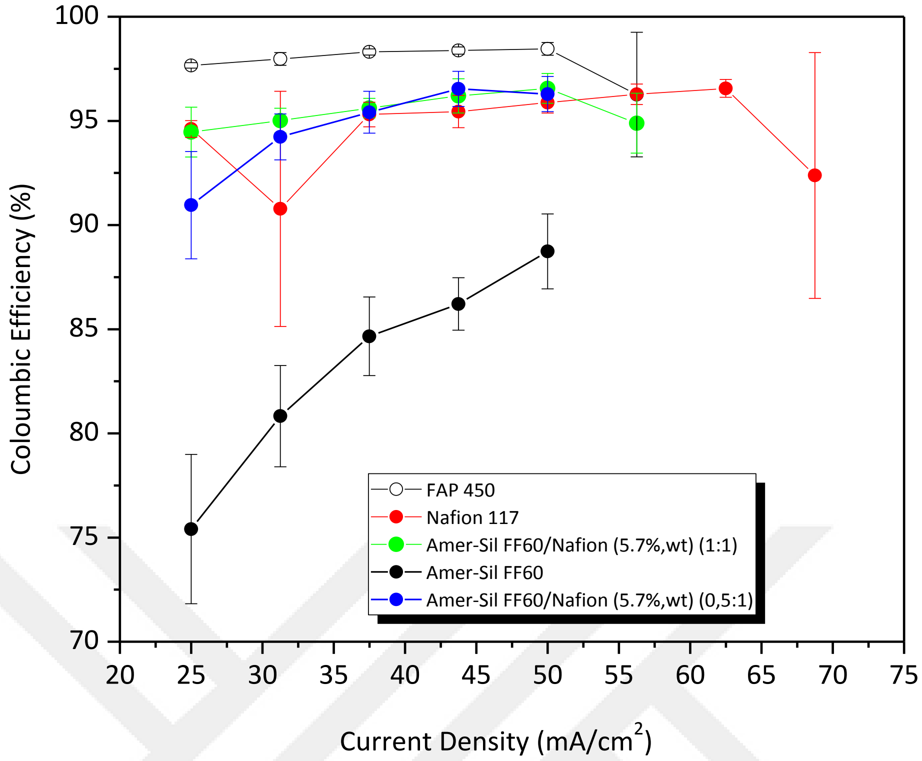

Figure 6.8 Coloumbic efficiency (%) performances of all membranes

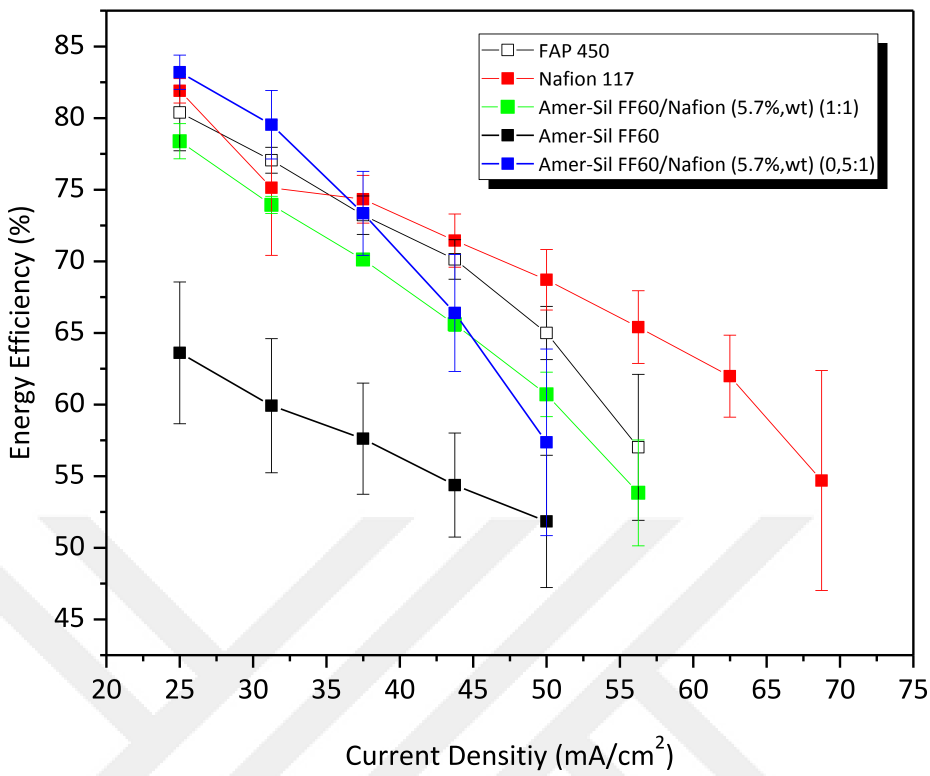

Figure 6.9 The energy efficiency (%) performances of all membranes

Enery efficiencies of all membranes were correspondingly akin the coloumbic efficiencies as expected since the energy efficiencies are a function of coloumbic efficiencies. As a preferable result, the modification of Amer-Sil FF60 /Nafion (5,7%, wt) (0,5:1) was displayed close values to the Nafion 117 and FAP 450. Energy efficiency depends on coloumbic efficiency and voltage efficiency notions as mentioned before in Equation (5.7). Akin to coloumbic efficiencies, Amer-Sil FF60 /Nafion (5,7%, wt) (1:1) membrane's cycles were longer than Amer-Sil FF60 /Nafion (5,7%, wt) (0,5:1) membrane.

Discharge power densities as a power scale of the system were compared below in the Figure 6.10 The worst performance belonged to the Amer-Sil FF60 /Nafion (5,7%, wt) (1:1) modified membrane that it could be ascribed to the probable tortousity rise and pore size decrease much more than to be intended [20] . In the literature, it is well known that as tortousity gets higher, more complex ways which mean to create the difficulty on transferring of ions are constituted [36]. Amer-Sil FF60 porous membrane was differed with its porosity feature which meant the transport of all species were simple relatively to the others. Therefore, Amer-Sil FF60 porous membrane had the second desirable result which could be attributed to the possessing relatively lower tortousity for the transfer of counter and co-ions. In this experiment, it has not been experimented tortousity and porosity alteration. As the discharge power density values are higher, more reactions could be carried out. As a result of this, Amer-Sil / Nafion® (5,7%, wt) (0,5:1) membrane's much more electrode area could be reacted.

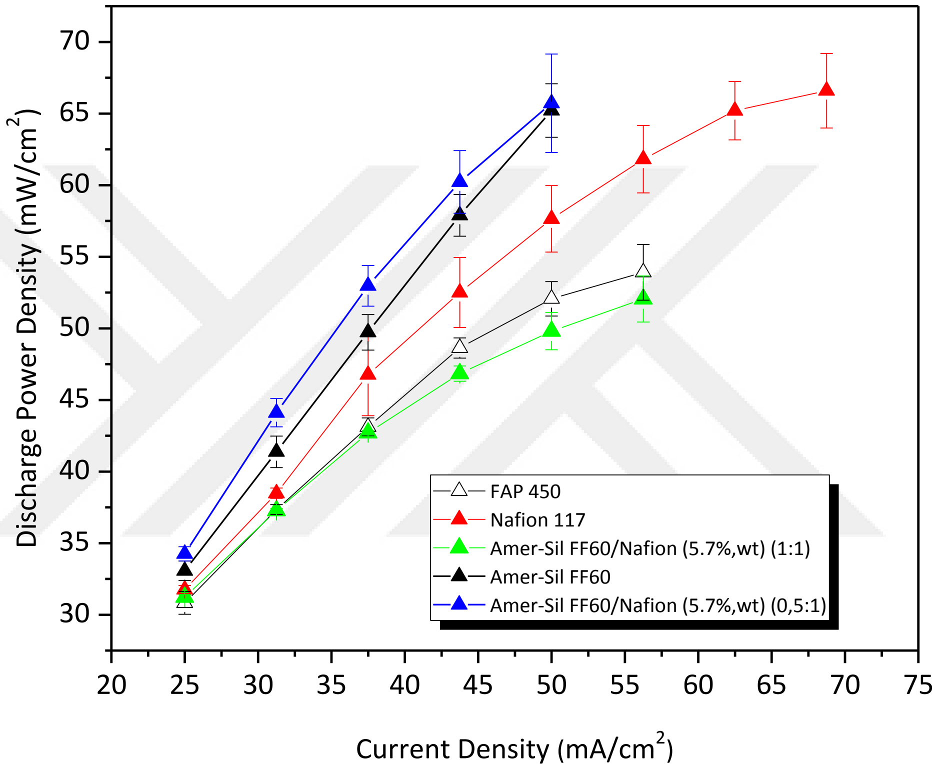

Figure 6.10 The discharge power density (mW/cm2) performances of all membranes

Nafion stability test;

Nafion stability tests were carried out to determine whether the Nafion® (5,7 %, wt) dispersion was stable on the membrane surface after the cell tests. It was taken some images from two different points before and after cell test via EDX. It could be seen a few of them below and can be evaluated to decide if Nafion (5,7 %, wt) was stable or not on the surface. It can clearly be observed that Nafion® (5,7 %, wt) dispersion was not stable after cell test as it can be seen in from Figure 6.11 to Figure 6.14. All the images from Nafion® (5,7 %, wt) test were at the same magnification values and same energy figures (100X and 20 KV). It can be seen below how Nafion ® (5,7 %, wt) dispersion amount was distributed homogeneously in the Figure 6.11 and Figure 6.12.

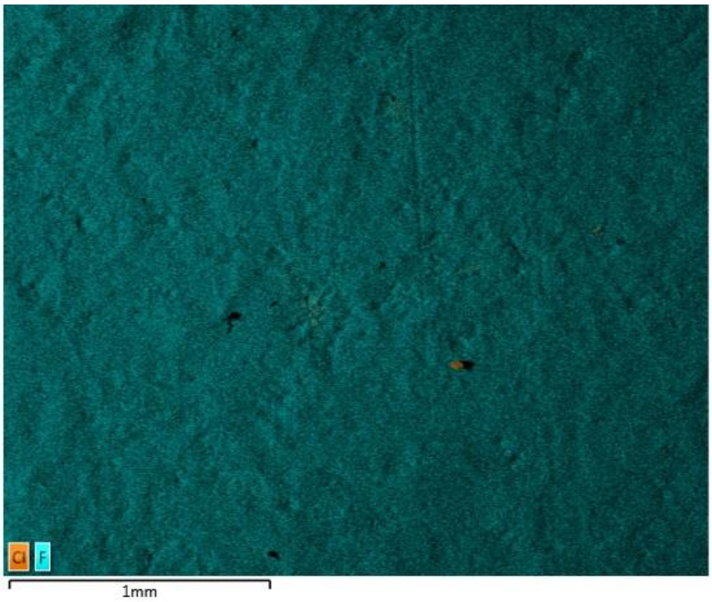

Figure 6.11 Cl and F distribution of Nafion (5.7 %,wt) dispersion on Amer-Sil FF60 porous membrane's surface before cell test, 100X, 20 KV

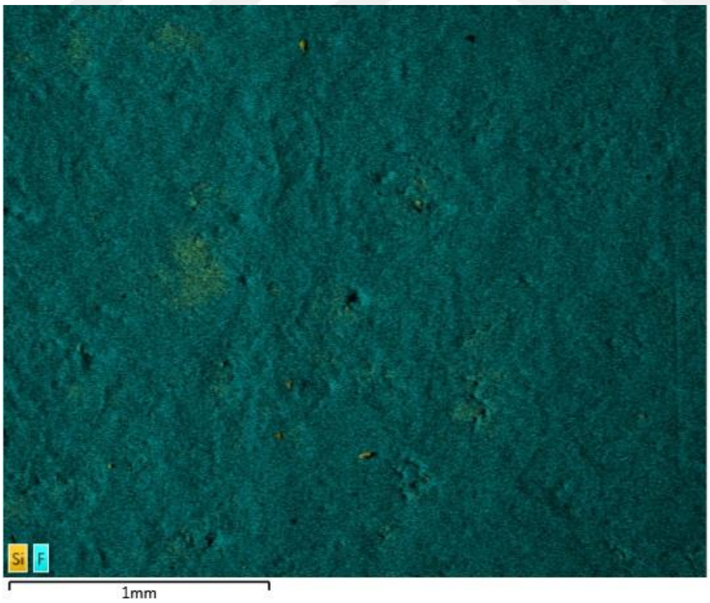

Figure 6.12 Si and F distribution of Nafion (5.7 %,wt) dispersion on Amer-Sil FF60 porous membrane's surface before cell test, 100X, 20 KV

As it can be seen from the Figure 6.13 and Figure 6.14 that Nafion® (5,7 %, wt) distribution was quiet different after cell test compared to the before cell test images. It can be followed the characteristic fluor (F) element on the membrane surface from below two figures. Cl element indicates Amer-Sil FF60 porous membrane's PVC backbone and F element indicates PTFE from Nafion® (5,7 %,wt) dispersion.

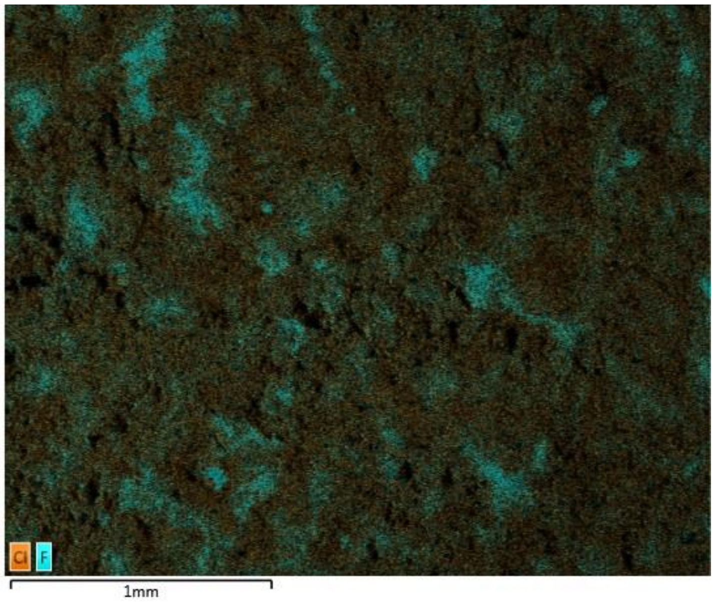

Figure 6.13 Cl and F distribution of Nafion (5.7 %,wt) dispersion on Amer-Sil FF60 porous membrane's surface after cell test, 100X, 20 KV

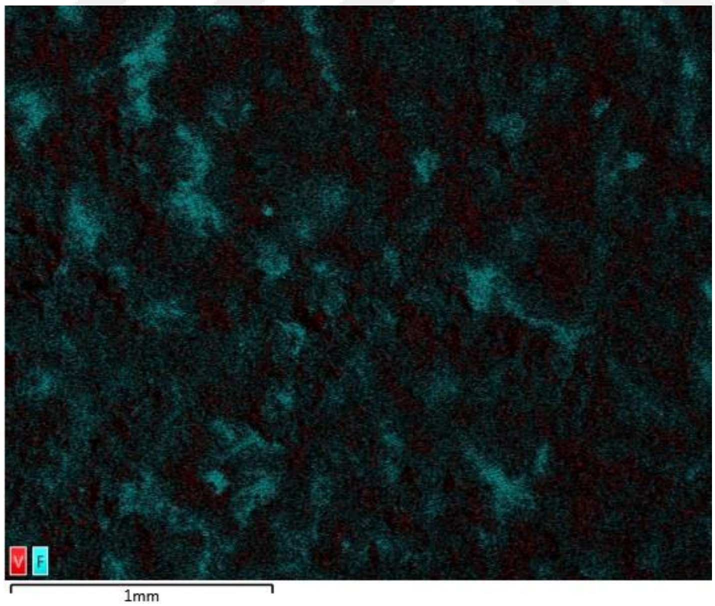

Figure 6.14 V and F distribution of Nafion (5.7 %,wt) dispersion on Amer-Sil FF60 porous membrane's surface after cell test, 100X, 20 KV

It can be claimed that Nafion (5,7 %, wt) dispersion on Amer-Sil FF60 porous membrane's surface after cell test was not remained homogeneously. It can be attributed to the extremely strong acidic environment. During spraying process, there was a limitation to fix the Nafion (5,7 %, wt) dispersion onto the membrane surface through temperature due to the membrane's sensibility against the temperature. The temperature could be limited between $60\ °C \leq x \leq 80°C$. Correspondingly to this limitation, it can be claimed that Nafion (5,7 %, wt) dispersion could not be fixed properly. Consequently, it might be interpreted that the Nafion (5,7 %, wt) dispersion might be swept out of the surface by vanadium electrolyte.

CHAPTER 7

CONCLUSIONS

In this work, it was focused on improving low cost microporous ion exchange membrane's, Amer-Sil FF60, main problem which induces the cross-mixing of redox active species and causing the loss of system capacity. It was experimented by two different techniques to decide which coating method, Dr.Blade and spraying, was more efficient. According to the EDX results, it was observed that Nafion® (5,7%, wt) distribution was more homogeneous via spraying technique. Its surface was successfully modified with Nafion® (5,7 %, wt) dispersion by a simple surface method, spraying. After FAP 450, Nafion 117, Amer-Sil FF60 and modified Amer-Sil FF60 which was coated with two different proportions were characterized, it was accomplished decreasing the Amer-Sil FF60's diffusion coefficient compared to the pristine Amer-Sil FF60 porous membrane. Although Amer-Sil FF60 / Nafion® (5,7 %, wt) (0,5:1) membrane's diffusion coefficient was higher than Amer-Sil FF60 / Nafion® (5,7 %, wt) (1:1) membrane, its energy efficiency was better than Amer-Sil FF60 / Nafion® (5,7 %, wt) (1:1) one. This can be attributed to their different ionic conductivities. It is suggested that diffusion coefficients shouldn't not only be evaluated in itself but also should be evaluated with ionic conductivity. Besides, ion exchange capacity and ionic conductivity show a close relationship according to the literature [29]. Ion exchange capacity (IEC) represents the total of active site or functional groups of the ion-exchange membrane. This parameter is measured by acid-base titration. Meanwhile, proton conductivity shows the conductivity of membrane to transport proton. The property of conductivity is provided by the active site of the membrane and other conductive part of membrane such as interstitial solution (water adsorbed by membrane in its swollen state). There is a relationship between IEC and conductivity. Higher IEC leads to higher conductivity since more active site which can be used to transport ion [10], [11]. The ionic conductivity values were reasonable in itself when they were evaluated with the water uptake results together. The proton conductivity and water uptake behaviour are generally tended to show similar behaviours as reported in the literature. Pristine Amer-Sil FF60's conductivity had the best value which could be attributed to the silica (Si) inorganic group that was also employed for increasing hydrophilicity in the membranes. It can be evaluated that the wettability of the Amer-Sil FF60 decreased upon the addition of PTFE which is indicated Nafion®(5,7%, wt)'s characteristic backbone polymer. Considering the hydrophobic nature and relatively high crystallinity of different polymers, PEEK which characterized the FAP membrane as reinforcing its mechanical properties and PTFE which characterized the Nafion 117 membrane and Nafion® (5,7 %, wt) dispersion as their backbone polymer, controlled the membrane's swelling behavior. With upon their different crystallinity, the crytalline region of the membrane would extend and probably suppress their water absorption. It is well known that swelling behavior is closely associated with mechanical stability of the membranes. With upon the addition of PTFE, Amer-Sil FF60's water absorption decreased as to be expected. However, its mechanical durability did not increase due to the sensibility of PVC polymer, which was characteristic backbone of Amer-Sil FF60 , against exposing a constant temperature more than one hour. Additionally, it could not be maintained the ionic conductivity as same as possible after modification. It might be achieved to decrease permeability of Amer-Sil FF60 one third of pure Amer-Sil FF60. When it is evaluated this relationship between vanadium ion permeability values and proton conductivity, the results are plausible. In terms of chemical stability, it can be evaluated that Amer-Sil FF60 membrane is pretty stable in highly acidic environment. As a proof, it can be shown that there was no shape or dimension alteration on the scratches of Amer-Sil FF60 samples. This result was also compatible with the Amer-sil FF60's main usage area that was noted for lead-acid battery applications.

When it comes to one of most crucial performance evaluation tests, cell tests, different ratios for coating were utilized as Nafion (0,5:1) and Nafion (1:1) and it was observed that a remarkable performance increase in terms of coloumbic energy efficiencies and discharge power densities belong to the coating with the least amount of Nafion compared to the pristine Amer-Sil FF60. Significant performance developments were obtained with Amer-Sil FF60 /Nafion (5,7%, wt) (0,5:1) and Amer-Sil FF60/Nafion (5,7%, wt) (1:1) modified membranes when they were compared to the both pristine Amer-Sil FF60 porous membrane. Moreover, Amer-Sil FF60/Nafion (5,7%, wt) (0,5:1) modified membrane's coloumbic, energy efficiencies were pretty close to the Nafion 117 which is relatively one of most expensive and widely studied membrane. Furthermore, new Amer-Sil FF60 /Nafion (5,7%, wt) (0,5:1) membrane's discharge power density results were better than FAP membrane which is well known more sophisticated and shown more decent coloumbic and energy efficiency as an anion exchange membrane. As a result, it can be claimed that the modification of the porous membrane could be an alternative to the the one of most expensive and studied membrane Nafion 117. Coloumbic efficiency and energy efficiency performances are not only relied on diffusion coefficients but also ion exchange capacity and ionic conductivity values. In this work, it wasn't experimented the ionic exchange capacity tests. However, Nafion 117 membrane's ionic conductivity (0, 320 S/cm) was close to the best value which belonged to the Amer-Sil FF60 porous membrane(0,345 S/cm). Although it could additionally be decreased the diffusion coefficients of modified Amer-Sil FF60 membranes as one of the lowest ones, their coloumbic efficiency and energy efficiency performances were not expectable when their the lowest diffusion coefficients were considered. This unexpectable result could be attributed to their relatively the lowest ionic conductivity values. Briefly, it could be claimed that the single diffusion coeffients should not be evaluated in themselves without ionic exchange capacity and ionic conductivity.

It was observed during spraying process that Amer-Sil had some mechanical problems against exposing around or more PVC's glass temperature, 60° C, constantly. For a better modification, this detail may be taken into consideration in order to minimize the temperature effect.

As a brief result, it could be accomplished the goal of developing the most feasible membrane among our experimented membranes, Amer-Sil FF60, in terms of decreasing permeability of the redox active ions and increasing the performance of the battery such as coloumbic, energy efficiency and discharge power densities preventing the loss of capacity. It could relatively be gained good results as being close to the commonly studied membrane Nafion 117. However, it couldn't be achieved the goal of maintaining the ionic conductivity as same as possbile. This is also reported in the literature as one of main conflicts between the permeability and the conductivity.

CHAPTER 8

FUTURE WORK

According to the results, it seems that Amer-Sil FF60's coating with the least amount may be possessed a desirable result. To improve this coating for further studies, the spraying technique may be changed with a more sophisticated method which includes the minimized exposing to the temperature effect such as a phase inversion or an interpolymerization method. Besides, the spraying technique may not be encountered a standard and independent from human factor. Based on this claim, the method can be standardized removing usage differences due to human factor.

It can be claimed that Amer-Sil FF60 may also be needed to be experimented as mechanical stability test, too. It seems to be possessed a sensibility against exposing to the temperature perpetually. Besides, it can be applied an ion exchange capacity (IEC) characterization test for Amer-Sil FF60 porous membrane to evaluate the diffusion coefficients and swelling behavior more scientifically.

It can be analysed of Nafion coating economically and correspondingly to this analysis and can be experimented the modification in terms of different volumes and different solutions.

In this study, Amer-Sil FF60 was coated with Nafion® (5,7 %, wt) including an anionic functional group dispersion. For a future work, it can be considered that it may be modified with a solution including a cationic functional group.

In this work, it was not known and characterized how much the amount of pore size change was accomplished and how the tortousity was amended. Depending on these details, Amer-Sil FF60 may also be needed to be characterized in terms of pore size and tortousity change.

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Undergraduate	Chemistry	Ankara University	2007
	Chemical Engineering	Osmangazi University	2012
High School	Science	Buldan Akın High School (Super High School)	2002

WORK EXPERIENCE

Year	**Corporation/Institute**	**Enrollment**
2015-2016	Fraunhofer Chemical Technology Institute (ICT)	Research Assistant
2014-2015	MİR R&D/Dizayn Group	R&D Engineer
2012-2013	Menderes Textile Plant	Sample Printing Department Engineer

PUBLISHMENTS

Conference Papers

1. International Conference on Battery and Fuel Cell Technology December 8-9, 2016 in Dubai, UAE (Poster Presentation).

AWARDS

1. Best Poster Award on ‘’The Development and the application of porous membrane via surface modification for all-vanadium redox flow batteries, International Conference On Battery and Fuel Cell Technology, December 8-9, 2016 in Dubai, UAE.