

Membrane processes and membrane modification for redox flow battery applications

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# MEMBRANE PROCESSES AND MEMBRANE MODIFICATION FOR REDOX FLOW BATTERY APPLICATIONS.

A thesis submitted as part of the requirements for the degree of

Doctor of Philosophy (Ph.D.)

by

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March, 1993

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of a university or other institute of higher learning, except where due acknowledgment is made in the text.

## SIE CHUNG CHIENG

## PUBLICATIONS ARISING FROM THIS STUDY

- S.C. Chieng, H. Chau and M. Skyllas-Kazacos, "Evaluation of modified membrane for the Vanadium redox cell", CHEMECA 91, the Nineteenth Australasian Chemical Engineering Conference, Newcastle, Australia.
- S.C. Chieng, H. Chau and M. Skyllas-Kazacos, "Composite membrane for the Redox Battery Application", Paper presented as poster at the Conference organised by Royal Australian Chemical Institute Electrochemistry Division (EDRACI), Newcastle, 1991.
- S.C. Chieng, M. Kazacos and M. Skyllas-Kazacos, "Permeation Selective Separator for use in a Redox Battery and Process for making such a Separator", Australian Patent (applied).
- S.C. Chieng, M. Kazacos and M. Skyllas-Kazacos, Preparation and Evaluation of Composite Membrane for Vanadium Redox Battery Applications, J. Power Sources, 39 (1992) 11-19.
- S.C. Chieng, M. Kazacos and M. Skyllas-Kazacos, Modification of Daramic<sup>\*</sup>, Microporous Separator, for Redox Flow Battery Applications, J.Mem.Sci., 75 (1992) 81-91.
- 6) S.C. Chieng, M. Skyllas-Kazacos, Evaluation and Characterization of modified Daramic<sup>\*</sup>, Microporous Separator, for Redox Flow Battery Applications, Paper presented at the International Membrane Science Technology Conference (IMSTEC'92), Sydney, Australia, Nov., 1992.
- S.C. Chieng and M. Skyllas-Kazacos, "Transport studies of membrane for vanadium redox battery", in preparation.
- 8) S.C. Chieng and M. Skyllas-Kazacos, "Factor affecting volumetric transfer of electrolytes across membrane in vanadium redox battery", in preparation.

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### ABSTRACT

Evaluation of commercial membranes for the vanadium redox battery applications was conducted for three different classes of membranes. These included anionexchange membranes: Selemion\*-AMV, DMV, ASS, DSV and RAI-R1010, R4010 and K142. Cation-exchange membranes evaluated were: Selemion\*-CMV and CMS. PTFE-based membranes tested were: Nafion\*-117 and 324, Flemion\* and DOW\* XUS1 3204.10. Anion-exchange membranes had slightly higher resistance than the cation-exchange and PTFE-based membranes however these type of membranes possess higher selectivity. Most of these membranes evaluated were unstable in the V(V) solution with the exception of PTFE-based membranes and the 'New' Selemion\* membrane recently developed by Asahi Glass Co. (Japan). Overall energy efficiencies above 85 % had been achieved with the earlier Selemion\* membranes but the performance deteriorated rapidly due degradation caused by the oxidizing nature of the V(V) solution.

Nafion<sup>\*</sup> 117 offers the highest overall performance in terms of membrane life and efficiency in the charge/discharge cycling tests although the 'New' Selemion<sup>\*</sup> membrane from Asahi Glass Co. (Japan) which is comprised of a PVC substrate and active layer of polysulfone also exhibited excellence performance with energy efficiencies above 90 % and excellent long-term stability reported by Japanese workers.

Methods of incorporating ion-selective capability to improve the selectivity of the microporous separator, Daramic<sup>\*</sup> were also investigated with the aim of developing a low cost alternative for larger scale energy storage application. The adsorption of the polyelectrolyte/ion-exchange resin on the Daramic<sup>\*</sup> separator greatly reduced its hydraulic permeability ( $K_h$ ) but only a slight decrease in the diffusivity of the membrane was observed. The treated Daramic<sup>\*</sup> with the lowest diffusivity and area resistance of less than 3  $\Omega$ .cm<sup>2</sup>, was obtained by treatment with Amberlite CG400 and further cross-linking using divinyl benzene (DVB). A coulombic efficiency of greater than 90% was achieved during charge/discharge cycling of a vanadium redox test cell using this membrane, compared with about 77% for the original material. This membrane has been tested for over 8000 hours or 1650 cycles in a vanadium redox cell with no sign of deterioration. Long term exposure to the V(V) solution has also confirmed the excellent stability of the treated membrane for this application.

Transport studies were conducted to investigate the phenomena occurring in the vanadium redox cell during charge/discharge cycling. The transport of vanadium, sulphate and hydrogen ions as well as water across the membrane is due to the combined effects of diffusion, electro-migration and convection. Anion-exchange membranes investigated were more selective compared with the cation-exchange and PTFE-based membranes as indicated by their lower diffusivity values. Both cation and anion-exchange membranes possess low water ( $T^*<0.5$ ) transport compared to PTFE-based membranes which have a value of about 1. For the cation-exchange and PTFE-based membranes, the hydrogen ions were the major current carrying ions whereas for the anion-exchange membrane, a significant portion of the current was

carried by the sulphate ions. Self-discharge current for the vanadium redox battery was at a maximum when it was fully charged, the more selective membranes having a lower self-discharge current.

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## LIST OF SYMBOLS

Definition	

Symbol

## <u>Units</u>

Α	Area	$cm^2 \text{ or } m^2$
С	Conductivity of membrane	mS
C,	Concentration of species i	mol.L <sup>-1</sup>
D <sub>1</sub>	Diffusivity of ion i	cm <sup>2</sup> .S <sup>-1</sup>
E	Electrolyte uptake of membrane	%
E°oc	Standard electrode potential	V
E <sub>oc</sub>	Electrode potential	V
EMF	Electromotive force	V
EW	Equivalent weight	g
F <sub>sf</sub>	Stoichiometric flowrate	cm <sup>3</sup> .S <sup>-1</sup>
Н	Water uptake of membrane	%
H <sub>f*</sub> , H <sub>fo</sub>	Heat of fusion of the sample	J.mol <sup>-1</sup>
Ι	Current	Α
IEC	Ion-exchange capacity (expressed in	
	milliequilvalent per dry gram of membrane)	meq/dg
i <sub>ch</sub>	Charging current density	mA.cm <sup>-2</sup>
i <sub>dıs</sub>	Discharging current	mA.cm <sup>-2</sup>
i <sub>sd</sub>	Self-discharge current density	mA.cm <sup>-2</sup>
$(J_i)_{con}$	Convectional flux of ion i	mol.cm <sup>-2</sup> .S <sup>-1</sup>
$(J_i)_{diff}$	Diffusional flux of ion i	mol.cm <sup>-2</sup> .S <sup>-1</sup>
$(J_{\nu})_{elec}$	Electromigration flux of ion i	mol.cm <sup>-2</sup> .S <sup>-1</sup>
K,	Equilibrium constant of reaction i	-
K <sub>h</sub>	Hydraulic permeability	cm <sup>3</sup> /s/(kPa/cm <sup>2</sup> )
K <sub>s</sub>	Membrane diffusivity	cm.min <sup>-1</sup>
M.W	Molecular weight	g
Ν	Electrolytes capacity	A.min.cm <sup>-3</sup>
n	Number of electrons transferred	-
OCV	Open circuit voltage	V
Р	Pressure	kPa

Р	Power	kW
Q	Solution flowrate	cm <sup>3</sup> .s <sup>-1</sup>
Q <sub>T</sub>	Theoretical capacity	Ahr
R	Area resistance/ resistance	$\Omega.cm^2$
R	Average pore radius	μm
SCE	Saturated calomel electrode	-
SOC	State-of-charge	%
Т	Temperature	°C or K
Т	Increase in weight of membrane after treatment	%
T <sub>H2O</sub>	Water transport number	-
$T^*_{H2O}$	Transport of water	
T,	Transport number of species i	-
T <sub>m</sub>	Melting point of the sample	°C
t,	Transference number of species i	-
U,	Mobility of ion i	cm.s <sup>-1</sup>
v	Volume	cm <sup>3</sup>
v	Rate of motion relative to the centre of gravity	m.s <sup>-1</sup>
$V_{ch}$	Discharging voltage	V
V <sub>dis</sub>	Charging voltage	V
W	Initial weight of membrane	g
Z	Charge of ion i	-
η	Solution viscosity	g cm <sup>-1</sup> s <sup>-1</sup>
$\eta_{\rm A}$	Anodic polarization	mV
$\eta_c$	Cathodic polarization	mV
	Coulombic efficiency	%
$\eta_{\rm E}$	Energy efficiency	%
$\eta_v$	Voltage efficiency	%
θι	Coupling coefficient of ion i	-
λ	Wavelength	nm
П	Osmotic pressure	Pa
<b>CONSTAN</b>		
F	Faraday constant (96487)	coulombs.mol <sup>-1</sup>

### LIST OF REGISTERED TRADEMARK

Daramic<sup>\*</sup> is a registered trademark of W.R. Grace, U.S.A.. Selemion<sup>\*</sup> is a registered trademark of Asahi Glass Co., Japan. Flemion<sup>\*</sup> is a registered trademark of Asahi Glass Co., Japan. Nafion<sup>\*</sup> is a registered trademark of E.I. Du Pont, U.S.A.. Teflon<sup>\*</sup> is a registered trademark of E.I. Du Pont, U.S.A.. Celgard<sup>\*</sup> is a registered trademark of Celanese Plastics, U.S.A. Dow<sup>\*</sup> is a registered trademark of Dow Chemical Co., U.S.A.

### **CHAPTER 1**

## **INTRODUCTION**

During the oil shortages in the mid 1970s, world attention was focussed on alternative energy sources to reduce the total dependency on fossil fuels. More recently, general public concerns over the damage done on our environment associated with the use of fossil fuels, has led to a strong push from all sectors to seriously look, once more, at renewable energy systems.

Renewable energy systems based on photovoltaic arrays or wind turbine generators, require a means of storing energy so that supply can better suit demand. Electrical storage (such as battery) is much preferred over other kinds of energy storage systems such as pump hydro or compressed air, since it offers greater potential in sizing, siting flexibility and very rapid response to load changes.

A study on battery energy storage system (BESS) was initiated in the United States in 1974, jointly conducted by EPRI and the Department of Energy (DOE) [1]. Initially, a lead acid battery storage system was evaluated. The study concluded that, for lead acid batteries, even with the technological improvements, this system would still not be cost effective especially for longterm and longer discharge. In a later phase of this study, efforts were directed to development of advanced batteries such as: Sodium-Sulphur, Zinc-Bromine and the Redox Flow battery. Also in Japan, the New Energy and Industrial Technology Development Organisation (NEDO) has been actively conducting the Advanced Battery Electric Energy Storage System Project since 1980, as a part of the "Moonlight Project" of the Agency of Industrial Science and Technology (AIST), MITI. Advanced storage batteries developed under this project include: Sodium-Sulphur, Zinc-Chlorine, Zinc-Bromine and the Fe/Cr Redox Flow battery [2].

Among the various contenders for electrical energy storage systems, the redox flow battery possesses considerable advantages over the other systems.

These include:

- a) the use of fully soluble redox couples as reactants;
- b) the absence of plating/deplating reactions which lead to shedding or shorting in conventional batteries;
- c) independent sizing of power and storage capacity;
- d) the ability to be fully discharged without harm;
- e) the advantages of low maintenance, inexpensive and long life.

Extensive research work on the development of the Fe-Cr redox flow battery during the 1970s and early 1980s was independently conducted at the NASA Lewis Research Centre and the Electrochemical Laboratory, Japan. Despite extensive research on this system, two major problems still exist, these being poisoning of the electrocatalyst electrode by impurities and the cross-contamination of electrolytes, which results in serious limitation to cell-life and storage capacity. A 60 kW Fe-Cr redox battery stack has been successfully tested by Mitsui as part of the Moonlight project, however, further scale-up and testing was abandoned due to the problems of cross-contamination of the electrolytes and the low energy densities of this system The vanadium redox flow battery developed by the University of New South Wales, was proposed to overcome the deficiencies of the Fe-Cr as well as other energy storage systems. The vanadium redox battery employs V(II)/V(III) and V(IV)/V(V) redox couples in the negative and the positive half-cell electrolytes respectively [5-8]. The use of a single metal system for both the negative and the positive halves of the cell eliminates the problem of cross-contamination so that the electrolytes should theoretically have an indefinite life. Various potential applications of the vanadium redox battery as an energy storage system are: load levelling; large scale photovoltaic and wind energy systems; remote area power storage system (RAPSS); emergency power backup and traction.

In the vanadium redox battery, or any other redox flow battery, a separator/membrane is required to separate the positive and the negative half-cell electrolytes whilst still permitting the transport of charge-balancing ions of the supporting electrolyte. Ideally, the separator should exhibit very low resistivity and high selectivity, but the two properties are mutually exclusive; therefore, it is highly improbable to achieve both properties in the developed membranes. A compromise in the requirements for the separator must generally be made to optimize the battery's cost, life and efficiency. However, with the use of redox couples of the same element as the electrolytes, the problem of cross-contamination is eliminated, and this invariably, permits the use of less selective membranes. The lower coulombic efficiency that is achieved can easily be compensated by the lower resistance exhibited by a less selective membrane, thus still maintaining the overall energy efficiency. Development efforts in producing a new membrane are not essential however, since a whole range of commercial membranes with varying properties are available. This system also offers more flexibility in membrane selection for optimizing its performance for the various potential applications listed before.

Some of the commercially available ion-exchange membranes, PTFE-based membranes and microporous separators have been tested for their suitability in the vanadium redox cell applications [9,10]. With the exception of Nafion<sup>\*</sup> membranes, other ion-exchange membranes tested earlier have been found to be chemically unstable in the V(V) solution, whilst microporous separators have unacceptable selectivity.

Generally, the following membrane properties should be consider when selecting the appropriate membrane to be used in the battery for a particular application [10]:

- Selectivity membrane with high selectivity will result in a higher coulombic efficiency of the battery.
- Area resistivity electrical resistance must be low to reduce ohmic losses across the membrane with a subsequent decrease in voltage efficiency.
- Chemical stability the life of the membrane must be at least 5 years or more, without effecting the performance of the battery.
- 4) Mechanical and dimensional stability over a wide temperature range and adequate strength to resist any damage due to hydraulic pressure variation

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across the membrane in the battery.

5) Homogeneous to ensure good current efficiency and uniform current density distribution.

To date, few commercial membranes are available which satisfy all of these requirements, and those which do, are usually prohibitive in cost, rendering them uneconomical for commercial use. However, with this system or any redox flow battery, the availability of a separator with good selectivity, low cost and good chemical stability in the respective electrolytes is crucial for its successful commercialization.

The aims of this project are :

- a) To screen a variety of commercially available membranes and to identify suitable membranes to be used in the vanadium redox battery with respect to their specific application. The more costly membranes could be justified for the niche markets, in military and hospital use, where reliability of the battery system could over ride the cost consideration.
- b) To develop a technique to modify the properties of the microporous separator, Daramic<sup>\*</sup> (W.R. Grace), thereby improving its selectivity as well as producing a low cost membrane. The availability of a low cost membrane could reduce the battery cost significantly, and hence, increase the marketability of the system.

- c) To study the transport phenomena associated with the membrane/separator used in the vanadium redox cell. Transport properties of different types of membranes are evaluated to provide an understanding of the different processes occurring.
- e) To optimize the performance of vanadium redox cell. In the vanadium redox battery, net transfer of electrolyte across the membrane, from one half-cell to the other, is observed during charge/discharge cycling. This net transfer of electrolyte causes gradual loss in capacity of the system and in serious cases, flooding of the reservoir. Various techniques to reduce the capacity loss such as: using anion and cation-exchange membranes arranged alternatively in the battery stack and equalising the ionic strength of the positive and negative half-cell solutions using  $H_2SO_4$  are investigated.

## **CHAPTER 2**

## LITERATURE REVIEW

## 2.1 Status on Battery Energy Storage (BES) plant.

The Battery Energy Storage plant is a new but proven technology. In the late 1970s and 1980s, considerable effort has been put into the development of advanced batteries for large scale electrical energy storage. The BES plant has come about as the result of technological improvements in the lead acid battery. The potential benefits from incorporating battery storage capacity to a utility's generation mix includes: load levelling, increase operating flexibility and environmental trends [11,12]. However, these potential benefits are yet to be realised, since only three large BES plants using lead acid battery have been put into commercial operation to date [12-14]. These are:

Bewag (West Berlin) 17 MW / 14 MWh

Vaal Reefs (South Africa) 4 MW / 7.4 MWh

Chino (California) 10 MW / 40 MWh

Recent development and testing of prototype 1 MW advanced batteries such as: Sodium-Sulphur (Na/S) and Zinc-Bromine ( $Zn/Br_2$ ), in BES plant have shown promising results [15-18].

## 2.1.1 Status on the development of advanced batteries.

Research studies conducted by EPRI concluded that, for the lead acid battery, even
with technology improvements (although it is generally accepted that only limited opportunities exist for further improvement), it is still not cost effective for long-term and longer discharge for BES plant application. Due to the constraints imposed on the lead acid battery, attention has turned to the development of the advanced batteries - Zinc-Chloride (Zn/Cl<sub>2</sub>), Na/S, Zn/Br<sub>2</sub> and Redox Flow systems.

The development of advanced batteries was initiated in the United States in 1974, jointly by EPRI and DOE. Most of the research and development was carried out by NASA (National Aeronautics and Space Administration) since 1973, at the Lewis Research Centre, U.S.A.. Their objective is to demonstrate and test a 10 MW-4Hr advanced battery plant by 2000 [1].

In Japan, since 1978, NEDO under the sponsorship of AIST has promoted research and development of advanced batteries as part of the "Moonlight Project". Promising results achieved by the 60 kW battery modules for the Na/S and Zn/Br<sub>2</sub> systems have led to the construction of 1 MW-class pilot plants [2]. For the Fe/Cr redox flow battery, further scale-up and testing beyond the 60 kW stacks was abandoned due to the problems of cross-contamination of the electrolytes and the low energy densities and efficiencies of this system compared with the Na/S and Zn/Br<sub>2</sub> batteries.

Construction of the 1 MW Na/S Battery pilot plant was undertaken by Yuasa Battery Co. Ltd., NGK Spark Plug, Toshiba Corp. and Kansai Electric Power Co. Inc.. The battery system consists of 20 modules, rated at 50 kW/400 kWh, with each module consisting of 1,344 cells having a nominal capacity of 300 Ahr per cell. An energy

efficiency of 87 % in the battery charge/discharge is expected with approximately 76 % expected on the AC/AC basis [15,16].

Kyushu Electric Power Co. Inc. and Meidensha Corporation have undertaken the construction of the 1 MW Zn/Br<sub>2</sub> Battery pilot plant system. This system consists of 24 submodules arranged in series, with each module consisting of 24 stacks in parallel arrangement. Each battery stacks consists of 30 cells in serial arrangement, giving a total of 17280 cells for the whole system. The output capacity of the system is 4000 kWh with AC 6600 V and 87.5 A [17,18].

### 2.2 Development of the Redox Flow Battery.

Preliminary work on the redox flow cell was first published by Kangro et.al [19] in the early 1960s and the first patent for a redox fuel cell was issued to Jan Boeke in 1970 [20]. The redox flow system is based on the use of two fully soluble redox couples that are electrochemically oxidised and reduced at inert electrodes, which are separated by a selective membrane. The two half-cell electrolytes stored in separate tanks outside the cells stack, are circulated through the stack by the use of pumps. The schematic setup of a redox flow cell system is illustrated in Figure 2.1.



Figure 2.1 Schematic diagram showing the setup of a redox flow cell system.

Extensive research work on the development of a practical redox flow battery was started in 1973 by NASA at the Lewis Research Centre. Giner et.al. under NASA's contract undertook a systematic screening of several redox couples such as:  $Fe^{2+}/Fe^{3+}$ ,  $Ti^{3+}/TiO^{2+}$ ,  $Cr^{2+}/Cr^{3+}$ ,  $Sn^{2+}/Sn^{4+}$ ,  $Br^{-}/Br_{3}^{-}$ ,  $Sb^{3+}/Sb^{5+}$ ,  $Cu(NH_3)_2^{+}/Cu(NH_3)_4^{2+}$  and

 $Cr(CN)_6^4/Cr(CN)_6^{3-}$  [21]. Based on their conductivity, viscosity, exchange current densities at a rotating disk electrode and solubility in the supporting electrolyte,  $Fe^{2+}/Fe^{3+}$  and  $Br'/Br_3^-$  couples were found to be suitable for the positive half-cell whereas  $Cr^{2+}/Cr^{3+}$  and  $Cu(NH_3)_2^{+}/Cu(NH_3)_4^{2+}$  were chosen as the negative half-cell couples. NASA also conducted screening of redox couples at carbon, graphite and  $B_4C$  electrodes employing cyclic voltammetry for  $Fe^{2+}/Fe^{3+}$ ,  $Cr^{2+}/Cr^{3+}$ ,  $V^{2+}/V^{3+}$ ,  $VO^{2+}/VO_2^+$  and  $Fe(O)_3^{-3}/Fe(O)_3^{-4}$  [22]. From their studies,  $Fe^{2+}/Fe^{3+}$  and  $Cr^{2+}/Cr^{3+}$  couples were finally selected as the positive and negative half-cell respectively, for a redox flow cell.

In 1975, an electrically rechargeable redox flow cell based on the redox couples,  $Fe^{2+}/Fe^{3+}$  and  $Cr^{2+}/Cr^{3+}$ , was described by L.H. Thaller from the Lewis Research Centre [23,24]. Initial development efforts were directed towards the unmixed system, employing 1 M FeCl<sub>3</sub> in 2 M HCl and 1 M CrCl<sub>2</sub> in 2 M HCl for the positive and negative half-cell electrolytes respectively. However, the later stage of their development concentrated on the mixed electrolytes system, due mainly to the non availability of a membrane which could provide effective separation of the two half-cell solutions.

Other flow batteries which have received considerable attention are the  $Zn/Cl_2$ ,  $Zn/Br_2$  and Fe/Ti [25-27] and Zn/ferricyanide [28]. Since all these systems (including Fe/Cr) consist of more than one redox species, several problems such as electrolyte contamination and loss in battery capacity, caused by leakage of active species across the separator are also encountered.

Efforts to establish a common redox species battery system were pursued by other investigators. System such as:  $Fe^{3+}/Fe^{2+}/Fe^{0}$ ,  $Cr^{6+}/Cr^{3+}//Cr^{2+}$  [29],  $Mo^{2+}/Mo^{4+}/Mo^{5+}$  [30] and  $V^{2+}/V^{3+}//VO^{2+}/VO_2^{+}$  [5,6] were studied. With the exception of the vanadium system, no practical cell employing a common element has been reported as yet.

### 2.2.1 Fe/Cr redox flow battery

Development of the Fe/Cr redox flow cell was undertaken by NASA at the Lewis Research Centre in 1979 with the objective of applying this technology to utility generation and stand alone applications [31-41]. The initial unmixed reactant system employed 1 M FeCl<sub>3</sub> and 1 M CrCl<sub>2</sub> in 2 M HCl for the positive and the negative half-cell respectively. The electrode used is carbon felt. The formal potential of the  $Cr^{2+}/Cr^{3+}$  redox couple lies below that of the H<sub>2</sub> evolution overpotential, which is also produced during charging. Despite extensive research, two problems remain unsolved. First, the irreversibility of the  $Cr^{2+}/Cr^{3+}$  gave poor energy efficiency and the electrocatalyst used to improve the kinetics of the Cr half-cell reaction was difficult to prepare and was subject to poisoning by impurities. The second problem is the crosscontamination of electrolytes resulting in serious capacity limitation of the system. The later phase of their research efforts was devoted to a mixed reactant Fe/Cr redox flow cell. This system did solve the problems of cross-contamination, but the reactant cost was doubled and the OCV of the cell was also reduced by 50 to 70 mV. For the mixed reactant system, both half-cells solutions consist of 1 M FeCl<sub>2</sub> and 1 M CrCl<sub>3</sub> in 2-3 M HCl in the discharge state, while in the charged state, the solutions consist of 1 M FeCl<sub>3</sub> and 1 M CrCl<sub>3</sub> in the positive half-cell and 1 M FeCl<sub>2</sub> and 1 M CrCl<sub>2</sub> in the negative half-cell. The battery has to be operated at an elevated temperature of 65 °C to overcome the kinetic limitations of the Cr redox couple.

In 1980, a 1 kW / 13 kWh redox flow cell system was assembled and later combined with a photovoltaic array to simulate a remote area application [42]. The 1 kW redox flow cell demonstrates that the basic concept of the Fe/Cr cell is plausible, however, the system fails to meet the technical and cost requirements for industrial application. By 1984, NASA licensed their technology to the Standard Oil of Ohio company to evaluate the technology and undertake further development if warranted with a subsequent commercialization goal.

In 1978, AIST and NEDO, Japan, began funding research and development of the Fe/Cr redox flow battery, initially undertaken by ETL Laboratories and later by the Mitsui Engineering and Shipbuilding Co. Ltd., as part of the 'Moonlight' project. Initial development efforts were based on the unmixed reactants system, however, similar problems associated with cross-contamination has also led them to adopt the mixed reactants system [43-47]. These initiatives resulted in the construction and testing of a prototype 60 kW class Fe/Cr redox flow battery in 1989 [3]. The system consists of 2 modules arranged in parallel, with each module consisting of 300 cells (15 cells x 20 stacks) in series. Initial test results of this system showed that energy efficiencies of 83 to 84 % could be achieved. However, further development and scale up have been abandoned due to the inherent problems of this system.

### 2.2.2 Vanadium redox flow battery

The development of the vanadium redox battery at the University of New South Wales began in 1985 [5,6,48,49]. Research into the all vanadium redox cell was initiated to overcome the deficiencies of Fe/Cr as well as other energy storage systems. The NASA Lewis Centre conducted an initial screening of a number of redox couples including the  $V^{2+}/V^{3+}$  and  $VO^{2+}/VO_2^{+}$  couples, however, further study was not continued on the basis of cost consideration of the VOSO<sub>4</sub> [38].

Studies of the electrochemical behaviour of  $V^{2+}/V^{3+}$ ,  $V^{3+}/VO^{2+}$  and  $VO^{2+}/VO_2^+$ couples at glassy carbon, gold and platinum electrodes in H<sub>2</sub>SO<sub>4</sub>, HCl and NaOH solution using cyclic voltammetry and rotating disc voltammetry were conducted by Sum and Skyllas-Kazacos [5,6]. H<sub>2</sub>SO<sub>4</sub> was selected as the supporting electrolyte with  $V^{2+}/V^{3+}$  and  $VO^{2+}/VO_2^+$  as redox couples for the vanadium redox cell. The formal potential of  $VO^{2+}/VO_2^+$  in H<sub>2</sub>SO<sub>4</sub> is about 0.85 V vs. SCE, making it suitable for the positive half-cell and 0.6 V vs. SCE for the  $V^{2+}/V^{3+}$  redox couple. An open circuit voltage (OCV) of 1.6 V for a fully charged vanadium redox cell employing 2M V(II)/V(III) in 2.5 M H<sub>2</sub>SO<sub>4</sub> and 2M V(IV)/V(V) in 3.5 M H<sub>2</sub>SO<sub>4</sub> is achievable.

During 1989 and 1990, three 1-3 kW prototype batteries differing in design were constructed and tested [4,50]. These batteries had an electrode area was  $1500 \text{ cm}^2$  per cell, with 10 or 12 cells arranged in series. The end electrodes used consisted of a 6 mm thick graphite felt bonded to a graphite impregnated polyethylene sheet (0.26 mm) and a 0.02 mm copper foil bonded to the other sides acting as current collector.

The bipolar electrodes employed graphite felt bonded on both sides of the conducting plastic sheet. Two different types of membranes were used in the construction of the three 1 kW prototype batteries, these being Selemion<sup>\*</sup> CMV and Selemion<sup>\*</sup> AMV (Asahi Glass Co., Japan). The selectivity of the AMV membrane was marginally higher than the CMV membrane but the area resistance of the former is higher by about 1  $\Omega$  cm<sup>2</sup>. Energy efficiencies as high as 90 % have been achieved in the 1 kW prototype battery employing the CMV membrane.

Recent evaluations of the vanadium redox battery by a Japanese group comprising scientists from ETL Laboratories and Ebara Corporation have led to confirmation that the vanadium redox battery is superior to the Fe/Cr redox battery, with recommendations that further development should be undertaken. In spite of an over-estimate of the electrolyte cost (based on an isolated peak in  $V_2O_5$  prices), the vanadium redox battery was still shown by these investigators to be economically competitive with lead-acid and Fe/Cr batteries for short to medium term storage. Moreover, a recently disclosed process for the production of vanadium electrolytes from oil waste, described by K. Kaneko et.al [51] makes this system even more attractive for large scale energy storage.

### 2.3 Membranes and separators in electrochemical processes.

Membranes and separators are widely used in electrochemical processes such as the chloro-alkali process, batteries and fuel cells, in electro-dialysis and desalination, as well as in many other industrial applications. More and more novel electrochemical processes are being developed which required a membrane or separator to play an integral function in the whole process [52]. The requirements and the function of a membranes/separators for each process may vary and there are available commercially a large variety of membrane/separator with varying properties. However, it is not the intention of this chapter to summarize all the commercially available membrane/separator or the methods of synthesising membranes or separators but to describe some of the more promising membranes or separators with implications for redox flow cell applications.

A wide variety of separators/membranes are used in batteries, and these include ionexchange membranes, microporous separators and supported-liquid membranes. For batteries and electrochemical power systems, the following properties are well recognised requirements of a membrane/separator [53,54]:

- 1. Chemical resistance to degradation by electrolytes, impurities, and electrode reactants and products.
- 2. Mechanical and dimensional stability over a wide temperature range.
- 3. Minimal electrolytic resistance.
- 4. Electronically insulating.
- 5. Mechanical shock-resistance, particularly in solid state battery.
- 6. Sufficient flexibility to be wrapped around the electrodes.
- 7. Sufficient physical strength to allow easy handling.
- 8. Readily wetted by the electrolyte.
- 9. High permeability to gas molecules to provide overcharge protection in sealed

batteries, but low permeability for redox and fuel cells.

- 10. Homogeneous to ensure good current efficiency and uniform current density distribution.
- 11. High permselectivity especially for redox flow cell system.
- 12. Leak-free, especially when the electrolytes are toxic.
- 13. Low cost and continuous supply.

Generally, the properties required are to some extent mutually exclusive. Various compromises have evolved in selecting the appropriate membrane for a particular application. Multi-layer separators are often used, with each layer conferring a different set of properties [54]. However, the usual course taken in the selection, is to apply empirical screening tests for the more important properties required by the process; and then, subject the most promising separators to evaluation trials in the actual system.

Membranes/separators which may find potential application in the vanadium redox flow battery are either microporous separators which have been modified with ion selective capability imparted to them or ion-exchange membranes. Modified microporous separators are particularly attractive due to their low cost and ionexchange membranes are sought for their high selectivity. In selecting the type of separator to be used, energy efficiency of the system with the particular separator, cost and life, have to be taken into consideration.

### 2.3.1 Microporous separators

Microporous separators are chemically inert materials within which the mobilities and concentrations of the current carrying ion species are identical to those in the external bulk solution. Transport of molecules through them generally occurs by hydrodynamic flow and they are not able, to any significant extent, to discriminate between specific species that pass through. The degree of selectivity that is obtained with these separators is due to the different transport rates of the various ionic species in the separator [53].

Water transport in microporous separators arises from many factors, such as pressure, temperature, concentration gradients and the presence of an electric field across the separator. The electroosmotic flow of water through the separator is the algebraic sum of water transported by electro-convention and water contained in the solvation shells of counter and co-ions. The transport number varies with the electrolyte concentration, current density and the nature of the separator [55].

The microporous separators generally contain pores that are >0.05 to 0.10  $\mu$ m [53,56]. The porous structure of the separator does not provide an effective barrier to prevent the growth of dendrites into and through the separator, as could occur in certain secondary batteries. By reducing the average pore size, however the extend of dendrites growth could be minimized. The literature also mentions a type of separator that exhibits properties that bridge those of the microporous separator and ion-exchange membrane called the membrane separator (semipermeable membrane) [57].

Generally, there is no clear distinction between this type and the microporous separator. These membranes contain smaller pore (about 0.05  $\mu$ m) and possess high tortuosity to selectively restrict the passage of certain ionic species. In some cases, an interaction exists between the permeating species and the membrane, hence providing some characteristics of an ion-exchange membrane. The reduction in average pore size of the separator is generally accompanied by an increase in electrolytic resistivity and decrease in water permeability [57]. The porosity of these separator could, in part, also affect their ionic selectivity. Studies by Hernandez et. al. show that ionic selectivity increases linearly with porosity [58].

Depending on the pH and the ionic strength of the electrolyte passing through, microporous separator could be charged [59] and hence, this may affect the adsorption affinity of certain ions and the electroosmotic flow rate. Lee et.al details a technique to determine the charge characteristic of the microporous separator or membrane separator based on their electroosmotic flowrate [59].

Thermoplastic polymers such as PVC, polyethylene and polypropylene are commonly used in the manufacture of these microporous separators. However, they all have a low softening temperature which leads to deformation of the separator under service conditions. Various methods of preparing microporous are reviewed by Lee et.al [54]. Porous thermoplastic sheets are obtained by heating powdered thermoplastic under carefully controlled conditions and sintering of the particles results in a porous matrix. These type of separators are inherently brittle although the brittleness has been overcome to some extent by the addition of plasticisers. Microporous films are also made by preparing a dough of polymer with suitable solvent and a powdered filler. The mass is extruded to the desired shape and dried. Porosity may be imparted to the film by the porous nature of the filler or by leaching the latter from the film. Alternatively, a filler may be incorporated into the existing porous film altering its pore characteristics. Films consisting of very small uniform pores of 10 nm were produced using this technique by Weininger et.al. [60]. A microporous polypropylene film, trade name Celgard\* (Celanese Plastics), is made by stretching an extruded film. This generates porosity in the crystalline structure with an average pore size of 0.1  $\mu$ m.

Table 2.1 presents some of the commercially available microporous separator and their related properties [54].

Types of separator							
Classification	Polymer	Manufacturer	Trade name	Porosity $(1 - V_p)$	Typical thickness <sup>a</sup> (cm)	Mean effective pore diameter (µm)	
Fabric of non-woven fibres	Polyamide or poly- propylene	Freudenberg (Germany) Pellon (USA) Bondina (GB)		0.65-0.80	0.02	3050	
	Copolymer of acrylonitrile and vinyl chloride	Kendall (USA)	Dynel	0.50-0.70	0.01	10-40	
	Cotton	Kendall (USA)	Webril	0.85	0.14	4050	
Sintered film	Polyvinyl chloride	Electric Power Storage (GB)	Porvic 2	0.42	0.06	10-25	
	Polyvinyl chloride	J. Lucas (GB)	KG4, KG5		0.05, 0.04	18,12	
	Polyethylene			0.47		50	
	Polytetrafluoro- ethylene			0.250.90		0.15-2.0	
Filler incorporated at some stage of preparation	Polyvinvl cnioride	Electric Power Storage (GB)	Porvic 1	0.86	0.05	13	
	Polyvinyl chloride	J. Lucas (GB)	KG2, KG3		0.08, 0.07	2530	
	Polyethylene	W.R Grace (USA)	Daramie	0.65	0.07	0.03	
	Polyethylene, polypropylene			0.53	0.01-0.02	0.004-0.012	
Resin on a fibrous web	Resin impregnated non-woven cellulose	W.R. Grace (Germany)	Darak ArmoribAR- 60	0.7	0.06	20	
	Resin impregnated non-woven cellulose	Catalin (GB)		0.65	0.05	20	
	Resin plus polyester fibres	W.R. Grace (Germany)	Darak 2000	0.55	0.06	0.4-0.8	
	Resin plus polyester fibres	W.R. Grace (Germany)	Darak 5000	0.5	0.05	1	

## Table 2.1Commercially available separators for the battery system.

\* Not including ribs where present.

Methods of producing improved separators were also reported by several investigators [57,61-63]. Yankov et.al [57] reported the preparation of phenolic resinbased microporous separator materials with improved high temperature, acid and oxidation resistance. The effects of the degree of polycondensation of the resin, the quantity of modifying resin, the duration of modification, the ageing time of phenolic resin, the quantity of catalyst, and the pre-curing temperature of the resin upon the properties of the separator material, were also studied. Separators prepared from polyvinyl alcohol (PVA) cross-linked chemically with aldehyde reagents have shown to demonstrate oxidation resistance, dimensional stability, low ionic resistivity and high selectivity [61,62]. Several types of microporous separators which showed improved properties over the then state-of-art nylon or polypropylene separator were also reported by Lim et.al [63]. These separators include: polypropylene felt coated with a wettable polymer - polybenzimidazole (PBI), polypropylene felt coated with zirconia emulsion to make the felt wettable, zircar cloth reinforced for its mechanical strength with PBI, Zircar cloth reinforced with polysulfone, zircar cloth reinforced with Teflon<sup>\*</sup> emulsion, and zircar fiber-polymer composite felt.

### 2.3.2 Ion-exchange membranes

Ion-exchange membranes can be classified as homogeneous and heterogeneous membranes [54]. Their differences arise from their preparation and hence, they possess different characteristics. They are generally fabricated from polymeric materials which contain pores with diameter less than 2 nm and thickness ranging from 0.1 mm to 0.6 mm [53]. General characterization of ion-exchange membranes is

usually based on their ion-exchange capacity, conductance and swelling.

Homogeneous membranes are coherent ion-exchange gels. Their structure is that of the usual ion-exchange resins. The fixed ionised sites are incorporated into the polymer matrix and cross-linking agents are generally used to provide the mechanical strength. But, they are homogeneous only in dimensions which are large as compared to the mesh width of the matrix. Heterogeneous membranes consist of colloidal ionexchange particles embedded in an inert binder (usually thermoplastic). This type of membrane usually has superior mechanical stability, but their electrochemical properties such as conductivity and barrier action, are not as good compared with homogeneous membranes. With the recent syntheses of homogeneous or 'almost' homogeneous membranes with greatly improved mechanical strength, heterogeneous membranes have lost much of their appeal. It should be noted that the majority of the commercially available ion-exchange membranes have structures more complex than ideal homogeneous gels.

Factors which determined the properties of the ion-exchange membranes are: the chemical nature (hydrophilic or hydrophobic, chain flexibility and crystallinity) of the polymeric matrix, and the functional or ionic group covalently bound to the polymeric material [64-66]. The functional groups can be cationic or anionic and even amphoteric, where both cationic and anionic groups are present. Strong cationic groups like  $SO_3H$  can fully dissociate even in very low pH's, whereas for weak ionic groups like COOH, the degree of dissociation is pH dependent. The counter ion of the fixed ionic group, the hydrogen ion, can be exchanged with other kinds of

cations. Strong anionic groups like  $NH_3^+$  (or tertiary and secondary amines) can also dissociate easily. The concentration of these fixed ionic groups is generally referred to as the ion-exchange capacity (IEC). For commercially available membranes, the IEC usually ranges from 1 to 4 meq/g-dry membrane.

The presence of the fixed ionic group in the ion-exchange membranes confers its permselectivity, that is the ability of the membrane to selectivity inhibit or reject the permeability of ionic species (Donnan exclusion) [66,p134]. In essence, counter ions are admitted to the membrane and thus, have little difficulty in passing through from one solution to the other. And co-ions are efficiently excluded from the membrane and find it difficult to pass through. The permselectivity is reflected not only in differences in permeability; but also, in the electric potential difference which arises between the two solutions (membrane potential). The extent of Donnan exclusion is governed by the concentration of the fixed ionic groups (ion-exchange capacity) and the concentration of the external solution. With the increase in solution concentration or ionic strength of solution, the fixed groups are effectively shielded, and this invariably reduces the membrane permselectivity due to diminishing Donnan exclusion effects. Other factors which also determine the permselectivity of ionexchange membranes are the polymer backbone, morphologies and cross-linking level.

### 2.3.3 Preparation methods for ion-exchange membranes.

Commercially available ion-exchange membranes are all formed from synthetic

polymeric and ion-exchange materials, with high ion-exchange capacity and high ionic mobilities. The polymeric materials are usually composed of derivatives of styrene-divinylbenzene copolymer, chloromethylstyrene-divinylbenzene copolymer or vinylpyridines-divinylbenzene copolymer. These membranes are mostly reinforced with backing material and chemically cross-linked to provide the mechanical strength. The new class of PTFE-based ionomer is becoming increasingly important due to its inertness in harsh oxidative environments. Conventional ion-exchange membranes are usually produced by direct introduction of fixed ionic groups to the polymeric material which can be achieved by: radiation grafting [67-73], sulfonation [74-77] and chloromethylation-quaternization with tertiary amine [78,79]. In contrast, ionomers are thermoplastic polymers (generally classified as Interpenetrating Polymeric Network, IPN) which consist of carbon backbone with pendent acid groups such as carboxylic and sulfonic moieties [80-82]. Their mechanical strength is attributed to the presence of physical cross-linking. The majority of these ionomers consist of hydrocarbon backbones, the exception being Nafion\*, with its fluorocarbon parent chain.

### 2.3.3.1 Radiation grafting

Radiation grafting is a versatile process for the manufacture of ion-exchange membranes. Different combinations of polymeric materials and monomers, can produce unlimited types of ion-exchange membranes, and this is well documented in the literature. Hence, in this section, only those grafting processes which have direct implication on battery applications, will be discussed. General properties sought of

the grafted films are: hydrophilicity, low electrical resistivity and high selectivity.

There are usually three components in the grafting process: the polymeric substance, the active monomer and the radiation source. By proper choice of substrate and by changing the functional groups in the active monomer, ion-exchange membranes with specific properties can be produced [68]. The films used are usually polyethylene, polypropylene and polytetrafluoroethylene (PTFE). Acrylic and methacrylic acids are the monomers usually used to produce ion-exchange membranes, whilst for non-ionic polymeric material, other type of monomers (e.g styrene) are used.

In radiation grafting [68], high energy gamma rays produce cleavage of a carbonhydrogen bond on the polyethylene to give a highly reactive free radical. The mechanism and the kinetics of radiation grafting are essentially the same as for standard polymerization reactions. With PTFE, the carbon-fluorine bond would be similarly cleaved to produce a free radical site. If no monomer is present, the radical undergoes cross-linking or scission. Cross-linking produces a three dimensional structure while scission leads to molecular cleavage and polymer degradation. For polyethylene, cross-linking predominates while in the case of PTFE, scission occurs. During the grafting process, the use of small radiation doses prevent excessive crosslinking or scission from taking place. To effect cross-linking, the polymer is usually exposed to large doses of high energy electron radiation prior to the grafting process.

Using radiation grafting, a whole variety of ion-exchange membranes can be produced as illustrated in Figure 2.2 [68].



Figure 2.2 Different types of radiation grafted ion-exchange membranes.

The use of acrylic results in the formation of a weak cation-exchange membrane on either a polyethylene or a perfluorinated base polymer. The grafting of styrene with subsequent sulfonation and hydrolysis gives a strong cation-exchange membrane. Vinylbenzylchloride is grafted and then quaternized to give a strong anion-exchange membrane, while grafting of pyridine follow by conversion with sulphuric acid yields a weak anion-exchange membrane. The ion-exchange capacity and/or the electrical resistance of each type of membrane produced is a function of the percent of graft yield- which is usually expressed as a percentage increase in the weight of the membrane after grafting.

Radiation grafting applied to the following types of polymers has been extensively studied by Pall RAI Inc [68]. These include: high and low density polyethylene, polypropylene, TFE and FEP (Du pont Teflon<sup>\*</sup>), polyvinylidene-fluoride, Aclar (Allied Chemical), polyvinyl chloride and silicones. Developmental ion-exchange membranes based on radiation grafting produced by RAI have undergone extensive testing for redox battery applications. The following redox battery systems have been tested with RAI membranes: Fe/Fe and Fe/Zn (Gel Corp.), Fe/Cr (NASA-LEWIS) and Zn/Ferrocyanide (Lockheed Corp.). Further details of these systems will be discussed in the relevant sections later in this chapter.

The most commonly used monomers in the grafting process are methacrylic [70-73] and acrylic acids [83,84]. Acrylonitrile [85-87], acrylamide [88], styrene [89-91] and a host of other monomers are frequently used to obtain ion-exchange membranes with different properties. Preparation and properties of cation-exchange membranes obtained by radiation grafting of methacrylic onto polyethylene [71,72], polypropylene [73] and polytetrafluoroethylene (PTFE) [70] have been studied by many. Grafting of acrylic acid on substrates such as PE, PP and PTFE has also been extensively studied [83,84]. The most commonly used radiation source is cobalt-60 gamma ray. The grafting process is conducted in both air and under vacuum. The degree of grafting obtained in the two processes does vary slightly and, is influenced by the type of substrate and solvents (methanol, ethanol, DMF, water, sulphuric acid etc.) used. During the grafting process, homopolymers which are also formed, not

only effect the grafting yield but are also unwanted side reactions. Inhibitors like ammonium ferrous sulphate (Mohr's salt) and  $FeCl_3$  are extensively used to prevent homopolymerization from occurring. Their effectiveness is dependent upon the grafting type. The irradiation dose also has a great influence on the grafting yield.

Grafting of PE with styrene has also been studied [89-90], however, the grafted film does not possess ion-exchange capacity until a further sulfonation process. The typical sulfonation technique used for the polyethylene-g-styrene copolymer films is soaking them in concentrate sulphuric containing 1 % silver sulphate at 50 °C for 24 hours.

# 2.3.3.2 Direct introduction of ion-exchange groups into conventional polymers.

Most of the conventional ion-exchange membranes based on styrene-divinylbenzene polymeric material are obtained by sulfonation or choromethylation/amination, to give cationic and anionic exchange membranes respectively. Direct introduction of cation or anion-exchange groups into polymeric materials such as polysulfone [74,77,91], polyethersulfone [92], polyphenylene oxide [93] and polyvinylidene flouride [94,95] has also studied by many. In this section, some of the techniques frequently used to achieve sulfonation and chloromethylation/amination to produce ion-exchange membranes will be described.

Table 2.2 shows the properties of some commercially available ion-exchange membranes [96].

The most common commercially available ion-exchange membrane is made of a copolymer of styrene and divinylbenzene on a fabric support. The cation-exchange group is introduced into the copolymer by sulfonation with concentrated  $H_2SO_4$  at 60-90 °C. The anion-exchange group is introduced into the polymer by chloromethylation and amination with a triamine (such as  $(CH_3)_3N$ ). The chemical reactions involved in the process are given as follows [96]:



## Table 2.2 Properties of some commercially available ion-exchange membranes.

Manufacturer	Name of membranes	Membrane	Thickness (mm)	Capacity (meq/gm)	Electrical resistance (Ω cm <sup>2</sup> in 0.1 N NaCl)	Reinforcemen
lonac Chemical Co.	lonac	MC-3142	0.15	1.06	9.1	Yes
New Jersey		MC-3470	0.35	1.05	10.5	Yes
-		MA-3148	0.17	0.93	10,1	Yes
		MA-3475	0.40	1.13	23	Yes
		IM-12	0.13		4	Yes
American Machine and	A.M.F.	C-60	0.30	1.5	6	No
Foundry Connecticut		A-60	0.30	1.6	5	No
lonics Inc.	Nepton	CR61 AZL 183	0.60	2.7	9	Yes
Massachusetts		AR 111 BZL 183	0.60	1.8	14	Yes
Asahi Glass Co. Ltd.	Selemion	CMV	0.15	1.4	6,1	Yes
Tokyo, Japan		AMY	0.14		4.0	Yes
Tokuyama Soda Ltd.	Neosepta	CL 25 T	0.16	1.8-2.0	3 5	Yes
Tokyo, Japan		AV 4 T	0.15	1.5-2.0	4.0	Yes
Asahi Chemical Industry	A.C.I. or	DK I	0.23	2.6	6.5	Yes
Co. Ltd. Tokyo, Japan	Aciplex	DA 1	0.21	1.5	4.5	Yes
Ben-Gurion University of	Neginst	NEGINST-HD	0.35	0.8	12	Yes
the Negev, Research &	-	NEGINST-HD	0.35	0.8	10	Yes
Development Authority		NEGINST-HC	0.2	1.6	6	No
Beersheva, Israel		NEGINST-HC	0.2	1.7	8	No

**Properties of Commercially Produced Membranes** 

Preparation of sulfonated polysulfone membranes is described in [74,77]. The polysulfone was sulfonated at room temperature in 1,2-dichloroethane solution using 2:1 sulfur trioxide/triethyl phosphate complex as sulfonating agents. The resulting polysulfone sulfonic acid was neutralised with sodium methoxide to produce the sodium salt and membrane sheets were obtained by casting the sulfonated polysulfone dissolved in dimethylformamide. Sugaya et.al. [91] described the preparation of both cationic and anionic exchange membranes from a block copolymer containing a polysulfone unit. The block copolymer containing polysulfone unit was synthesized by a 2 step condensation polymerization. A anionexchange polymer was synthesized by chloromethylation using methyl chloro methyl ether in the presence of SnCl<sub>4</sub>, as a catalyst and, subsequently quaternized using aqueous solution of triethylamine  $(CH_3)_3N$ . A cation-exchange polymer was obtained by sulfonation, similar to that described in [77]. Preparation of ion-exchange membranes based on aromatic polyethersulfone is described in [92]. Both cation and anion-exchange membranes are produced after sulfonation and chloromethylation respectively, with the methods described before.

The synthesis of sulfonated polyphenylene oxide was reported in [93]. The polyphenylene oxide was synthesized through oxidative coupling from 2,6-dimethylphenol with copper (I) chloride-pyridine catalyst. Sulfonation of the polymer was carried out in a chloroform solvent system at ambient conditions using chlorosulfonic acid as the sulfonating agent. The membrane sheet was cast from ion-exchange polymeric material dissolved in methanol. A cation-exchange membrane prepared from polystyrene sulfonic acid and polyvinylidene fluoride was reported by [94,95]. A cross-linker, an expoxy-novolak (DEN-438, Dow Chemical) was used to effect cross-linking. The interpolymeric material was sulfonated using concentrated sulphuric acid at 98 °C, and silver sulfate is used as the catalyst.

A composite membrane based on the polyethylene substrate and styrenedivinylbenzene copolymer were studied [76,78,79]. Low density polyethylene was heated in toluene at 55 °C and, was transferred to a mixture consisting of 95:5 vol.% styrene and divinyl benzene with benzoyl peroxide added as initiator. Polymerization was achieved at 80 to 95 °C after a few hours. A cation-exchange membrane was prepared via sulfonation, using 30:70 vol.% of chlorosulfonic acid and carbon tetrachloride and the chlorosulfonic groups were hydrolysed with aqueous solution of sodium hydroxide [76]. An anion-exchange membrane was obtained by chloromethylation using methyl chloro methyl ether in the presence of  $SnCl_4$  catalyst, and subsequent amination with diethylamine [78,79].

## 2.3.3.3 Ionomer based on thermoplastic interpenetrating polymeric networks (IPNs).

Ionomers are thermoplastic IPNs in which the chemical cross-linking is replaced by physical cross-linking. The principal types of physical cross-linking are: the hard blocks in blocks copolymers, the ionic portions of ionomers and the crystalline portions of semicrystalline polymers. The physical cross-link makes the material behave as a thermoset at the service temperature but softens and permits the material to flow at some elevated temperature [80-82].

Since thermoplastic IPNs cover a wide spectrum of polymeric materials, only some of the PTFE-based ionomers which have found extensive applications in electrochemical processes are described here [97,98]. In particular, the Nafion<sup>\*</sup> class of membranes has been subjected to extensive testing in the Fe/Cr, Zn/Ferrocyanide and All-Vanadium redox flow batteries as a separator. Excellent performance in all the different types of batteries mentioned above was achieved, indicating the versatility of this class of membrane in different types of applications.

The transport processes or the diffusion properties observed in the PTFE-based ionomer are quite different to those of the conventional ion-exchange membranes. In conventional ion-exchange membranes, the ion-exchange capacity affects the rate of diffusion whereas in a PTFE-based ionomer, the fixed charge density has a minor effect on its diffusional properties. In PTFE-based ionomers, their microstructure can be described as a microphase separated system in which a matrix of low ion content (due to multiplets) is interspersed with ion-rich domains (clusters). Multiplets are small aggregates consisting of a few ion pairs while clusters are referred to as large aggregates comprising of non-ionic backbone material as well as many ion pairs. The transport properties of these types of membranes are dependent on the cluster size and the percentage of ions present in the clusters and in the channels [99-102].

Nafion<sup>\*</sup> membranes developed by Du Pont have the following structure [99]:

$$\begin{array}{c} -[(CF_2 - CF_2)_m - CF_2 - CF_2]_n - \\ & | \\ & \\ \begin{pmatrix} O \\ \\ \\ \\ CF_2 \\ \\ \\ \\ CF_2 - CF_2 \\ \\ \\ \\ \\ \\ O - CF_2 - CF_2 SO_3 H \end{array} \right) \qquad p \\ \end{array}$$

(m = 5 - 13.5, n = -1000, p = 1,2,3...)

In polymer preparation, tetrafluoroethylene reacts with  $SO_3$  to form a cyclic sultone. After rearrangement, the sultone can then be reacted with hexafluoropropylene epoxide to produce sulfonyl fluoride adducts. When these adducts are heated with sodium carbonate, a sulfonyl fluoride vinyl ether is formed. The vinyl ether is then copolymerized to form the resin which upon hydrolysis is converted into Nafion<sup>\*</sup> perfluorosulfonate polymer.

A perfluorocarboxylate membrane named Flemion<sup>\*</sup> was developed by Asahi Glass Co. [103]. Perfluorocarboxylate polymers were prepared by copolymerization of tetrafluoroethylene and carboxylated perfluorovinyl ether, which is carried out either in solution, bulk or emulsion system with a radical initiator. The general formula of the copolymers is shown as follows:

$$\begin{array}{c} -(CF_2 - CF_2)_x - (CF_2 - CF_2)_y - \\ | \\ (OCF_2 CF)_m - O(CF_2)_n - C - O - R \\ | \\ CF_3 \\ O \end{array}$$

(m = 0 or 1, n = 1-5, R = alkyl)

Neosepta-F membrane developed by Tokuyama Soda Co. has the chemical structure as follows [104]:



where, 1/(m+n) = 6-8, m/n = 5-20 and p,q = 1,2

The membrane material is prepared by hydrolysis of a copolymer of tetrafluorothylene and perfluoro(3,6-dioxa-4-methyl-7-octene-sulfonyl fluoride) in aqueous solution of dimethyl sulfoxide and potassium hydroxide.

A series of fluorinated carboxylic acid membranes is produced by Asahi Chemical Industrial [105]. The are hydrolysed copolymers of tetrafluoroethylene and perfluoro vinyl ether containing ion-exchange groups or its precursor with the general formulas:

$$CF_2 = CFO - (CF_2CFO)_m - (CF_2)_n - X$$

$$|$$

$$CF_3$$

where, m = 0 or 1, n = 2-12,  $X = SO_2F$ , SR,  $SO_2R$ , COOR, COF or CN

### 2.4 Modification of ion-exchange membranes.

Post treatment of commercially available membranes is being increasingly used to modify or enhance certain properties (such as selectivity, chemical stability and fouling resistance), so as to improve performance. Moreover, the processes involved are versatile and relatively simple to apply. With the treatment process, there is generally a trade off in the selectivity and the electrical resistivity of the resulting membrane. Polyelectrolytes are the most commonly used chemicals to effect the transport properties of the membrane. Other types of treatments which have been reported include: lamination of a thin condensation-type cation-exchange membrane having a high degree of cross-linking on the surface of the low cross-linked cationexchange membrane [106,107]; formation of a thin neutral layer having low electrical conductivity on the surface of the cation-exchange membrane [108], amphoteric ionexchange membrane [109], or cation-exchange membrane having phosphoric groups as the ion-exchange groups [110]; formation of a thin cationic condensation-type polymer layer on the surface of the polymerization-type anion-exchange membrane [111,112], or bipolar ion-exchange membrane [113]; and formation of a thin oxidized layer on the surface of the strongly basic polymerization-type anion-exchange membrane [114]. The mechanisms of permselectivity achieved by the treatment are usually mechanical sieving effects, and the interaction of a particular ion with a particular ion-exchange group in the membrane. Some of the modification techniques which could be applied to the membranes for redox flow battery applications are discussed here.

### 2.4.1 Modification of ion-exchange membrane using polyelectrolytes.

Extensive studies on the influence of the characteristics of polyelectrolytes on the properties of ion-exchange membrane was initially investigated by Caplan and Sollner [115-117]. Ionic membranes were prepared by sorption of polyelectrolytes (polystyrene sulfonic acid and polyacrylic acid) from aqueous solution into highly porous membranes made of an inert matrix material, such as collodion. The loading of polyelectrolytes on the porous matrix is dependent on its charge and contractility in the impregnating solution. The functional electrochemical and hydraulic properties of the resulting polyelectrolyte-activated membrane depends primarily on its pore size and pore size distribution, the number and the nature of the ionizable groups of the polyelectrolytes, and the distribution of the polyelectrolytes within the membrane [118-120]. Under usage, the polyelectrolytes in the pores of the membrane can also undergo configurational changes, and the different degree of absorption and desorption depends on the ionic strength and the pH of the medium.

Sata et.al studied the effects on the transport properties of cation-exchange membranes modified by adsorption of various cationic polyelectrolytes [121,122]. The resulting membrane showed increase in permselectivity of monovalent ions over divalent ions and further, the permeation of cations with larger hydrated diameter  $(K^+)$  was higher than those with the smaller hydrated diameter  $(Na^+)$ . The change in the permselectivity by the cationic charge layer on the membrane surface is due to the difference in the strength of the electrostatic repulsion between two cations against the cationic charge layer. The in-situ treatment of a cation-exchange

membrane in electrodialysis of sea water by the cationic polyelectrolyte, 'Nonisold' (Daiichi Kogyo Pharmaceautical Co. Ltd.), was reported [123]. Nonisold is an organic polyelectrolyte with many quaternary ammonium groups. The reagent when added to the electrodialysis cell dissociates to form polycations, which would migrate to the surface of the cation-exchange membrane and combine with the sulfonated exchange groups. The charged quaternary ammonium groups packed closely together on the membrane surface, creates a potential barrier, and thus selectively permits certain cations to pass through.

### 2.4.2 Other methods of modification of ion-exchange membranes.

Improvement in the permselectivity of the cation-exchange membrane by the formation of a thin surface layer of sulfonamide groupings has been studied by many [124-126]. It was shown that the sulfonamide groupings on the surface of the cation-exchange membrane conferred stable monovalent cation permselectivity in electrodialysis. The sulfonamide groups on the membrane's surface are prepared by soaking in chlorosulfonic acid, dichloroethane and dioxane mixture to effect sulfochlorination. The membrane into which the -SO<sub>2</sub>Cl groups have been introduced is then immediately immersed in an aqueous solution of amino compounds to form sulfonamide groups. Different conditions of preparation, solvents and amino compounds used, are reported by the various investigators [124-126].

Enhancement of proton selectivity of cation-exchange membranes (in particular Nafion<sup>\*</sup> type) by plasma modification was reported by Ogumi et.al [127,128]. The

permselectivity of the membrane was enhanced by depositing a thin anionic exchange layer on its surface. The anionic layer was prepared by plasma polymerization of 4vinylpyridine followed by quaternization with 1-bromopropane in propylene carbonate. The influence of the plasma parameters - polymerization pressure, on the deposition rate, membrane resistivity and transport properties, was also investigated.

Preparation of photoinduced polymerization of 4-vinylpyridine and divinylbenzene on both sides of the cation-exchange membrane, Selemion<sup>\*</sup> CMV, was reported by Ohya et.al [129]. The preparation of the surface layer involved coating the membrane with mixed monomers consisting of; 4-vinylpyridine, divinylbenzene, nitril-rubber, benzoyl peroxide added as initiator, and benzoin isobutyl ether as photosensitizer, and photopolymerization was carried out under high pressure mercury lamp. Improvement in the selectivity of the resulting membrane was achieved, when employed in the Fe/Cr battery. Ohya et.al [129] also prepared a series of modified membranes using Selemion<sup>\*</sup> CMV by direct quaternary amination on both sides of the membrane. The procedures involved were similar to the usual preparation of anion-exchange membranes, involving chloromethylation and amination.

Preparation of an ionic membrane by impregnation of Nafion<sup>\*</sup> polymer on the PTFE film (Gore-tex) was reported [130-131]. Dissolution of Nafion<sup>\*</sup> 117 membrane was achieved in an ethanol/water mixture under high pressure and temperature. The treatment method involved sorption of the dissolved 'Nafion<sup>\*</sup> solution' onto the porous PTFE substrate. The treated membrane shown improvements in hydrophilicity and, hence, conductivity [132].

### 2.5 Membrane development for redox flow battery applications.

The primary function of the membrane/separator in the redox flow cell is to provide a barrier to the electrical short circuit of the positive and negative electrodes, and the undesirable mixing of the anolyte and the catholyte, while at the same time allowing rapid transport of ionic charge carriers to complete the circuit during the passage of current. Ideally, the membranes should exhibit very low resistivity and high selectivity to the charge balancing ions, from the standpoint of redox cell performance. However, other membrane characteristics unrelated to cell performance, which require equal emphasis are operational life, mechanical strength, amenability to scale-up, ease of manufacture and cost. Depending on the redox flow battery application, emphasis on the requirements in membrane available. For instance, as emergency power backup, a highly selective membrane is sought, whereas for mobile application, the power output is a more important factor and, thus requires a membrane with low resistivity.

### 2.5.1 Fe/Cr redox flow battery membrane.

Initially, screening of commercially available anion-exchange membranes were conducted by NASA for the unmixed Fe/Cr redox flow battery system, envisaged for solar photovoltaic and electric utility applications. The membranes were either chemically incompatible or failed to meet the resistivity and the selectivity requirements. The requirements in selectivity and resistivity for the two applications

are presented in Table 2.3 [133].

 Table 2.3
 Requirements of the membranes for the applications listed.

Application	$\begin{array}{c} \text{Resistivity} \\ \Omega \ \text{cm}^2 \end{array}$	Selectivity µg/h/cm²/mol/l
Solar Photovoltaic	3	20-25
Electric Utility	1.0-1.5	5

The more severe requirements on the resistivity and selectivity for electric utility, compared to solar photovoltaic application, are due to the expected higher current densities on charge and discharge and the lower reactant solution volume to membrane area ratio, respectively.

Ionics Inc. was contracted to develop specific membranes for the unmixed system ( refer Section 2.2.1) [134-136]. Several novel membrane systems (a copolymer of vinylbenzylchloride and dimethylamionethylmethacrylate and copolymer of vinylbenzylchloride and either 2 or 4 vinylpyridine) were developed, which employed monomers that contained ion-exchange sites on both the backbone and cross-link portions of the copolymer. The ion-exchange resins that were fabricated as thin sheets, were reinforced by a layer of woven fabric (Dynel cloth). Anion-exchange membranes with thickness up to 0.6 mm were produced, and they represented a significant improvement over the commercially available membranes tested previously. Routine testing of resistivity and selectivity as well as longterm stability testing for the membranes produced by Ionics, were also evaluated by NASA in their in-house efforts [22]. Stable area resistivities were not found in all the membranes

tested, some showing an increase in resistivity before reaching a steady value, while others registered a prolonged and steady increase. The increase in the resistivity of the membranes was found to be caused by reversible fouling, since the fouled membranes, when equilibrated in the HCl solutions, reverted back to their initial values [137].

Attempts by Ionics [22] to produce even thinner membranes of 0.1 mm thickness by depositing a skin of active material onto a porous supportive substrate such as PTFE, polypropylene and modacrylic fabrics, succeeded in reducing the resistivity by a factor of 3, but the selectivity was severely taxed. Only modacrylic fabrics, when used as the substrate produced promising results. The decrease in the resistivity is attributed by the more porous nature of the membranes produced with the new substrate.

Further studies by Ionics [22], led to the development of the CD1L series of membrane. The CD1L membranes were a formulation based on a copolymer of vinylbenzylchloride (VBC) as the backbone and dimethylamionethyl methacrylate (DMAEMA) as the cross-linker, on a modacrylic fabrics. Membrane samples were fabricated by incorporating variations in the membranes parameters such as: cross-linking type and density, catalyst level, nonpolymerizable fraction, functional group addition and reduction of total membrane thickness, in an attempt to produce a membrane more resistant to fouling without sacrificing in its selectivity and conductivity. The resulting membrane produced coded CD1L-AA5-0.0625, was considered to be the most suitable one at that time [39,138]. Considerable efforts
followed to optimize the CD1L fabrication process. The resulting membrane was designated CD1L-AA5-LC (NP 27.5), and was used as the standard membrane at Lewis Research Labs [40]. Performance characteristics of this membrane are resistivities of 4.2  $\Omega$  cm<sup>2</sup> in 0.1 M HCl and 2.6  $\Omega$  cm<sup>2</sup> in the Fe/Cr redox test cell, and a selectivity of about 20 µg Fe<sup>3+</sup>/(h/cm<sup>2</sup>)/(mol/l). Longterm charge/discharge testing of this membrane employed in the Fe/Cr test cell had been achieved for over 3000 hours with no significant change in it properties.

Several approaches were also evaluated for the reduction of membrane resistivity [41]. The one that received major emphasis was a composite membrane with heterogeneous structure consisting of two bonded layers: one a highly porous, fabric-supported low resistance substrate to provide strength, and the other is a much thinner, tighter and more highly charged film to provide selectivity. The substrates were given a porous character by a non polymerize (NP) content ranging from 50 to 70 % in the resins composition. The resins used for the substrate contained chloride, amine or oxirane functional groups to provide compatibility with the films. Although some of the composite membranes produced had a resistivity as low as 3.4  $\Omega$  cm<sup>2</sup>, this represented an insignificant improvement over the standard CD1L membrane.

In 1982, NASA decided to operate the unmixed Fe/Cr system at 55 to 65 °C (previously the operating temperature was 25 °C) in order to avoid kinetic difficulties with the chromium redox reaction [41,139]. Operation at the elevated temperature of 65 °C reduced the resistivity of the membrane by a factor of 2 to 3 but resulted in worsening of the selectivity by up to 10 fold. A membrane with resistivity as low as

1.5  $\Omega$  cm<sup>2</sup> was required to achieved acceptable energy efficiency, since coulombic efficiency decreased with the decrease in selectivity at the elevated temperature. The standard CD1L membrane with a resistivity of 2.6  $\Omega$  cm<sup>2</sup> was unsatisfactory in this respect.

Efforts were made to improve the resistivity and selectivity of the standard CD1L using a non-woven backing, but these yielded no substantial improvement [41,140]. A number of cation-exchange membranes with a resistivity less than 1  $\Omega$  cm<sup>2</sup> were also developed [141]. This class of membrane was mechanically weak and imperfections such as pinholes were present. Several types of composite membranes were also prepared using: dimethylaminoethyl methacrylate (DMAEMA) and ethylene glycol monoethylether (EGDM); vinylbenzylchloride (VBC) and DMEMA; and, GMA and EGDM, on woven and non woven substrates. However, after exhaustive efforts, Ionics concluded that it is highly improbable though not impossible, to produce a membrane that could fulfil the requirements of the unmixed Fe/Cr redox battery operating at 65 °C.

In 1982, NASA adopted a mixed Fe/Cr redox system [142] to eliminated the problem of cross contamination of the two half-cell electrolytes, which also permitted less severe requirements on the selectivity of the membrane. It was observed that, in the mixed reactant system, although a high coulombic efficiency was sacrificed using a less selective membrane, an improved voltage efficiency was obtained. Therefore, the overall energy efficiency of the system was maintained. In order to keep the mixed reactant system at a comparable cost to the unmixed reactant system, it had to

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operate at higher current densities in the range of 50 to 75 mA/cm<sup>2</sup>. This was made possible by the use of the less selective and lower resistivity membrane. Developmental membranes including both cation and anion-exchange type, acquired from Ionics Inc., RAI Research Corporation and Asahi Glass Co., were also screened for the mixed reactant system operating at elevated temperatures [142]. However, attention was soon focused on the cationic type due to their excellent resistance stability, ease of fabrication, durability and reduced cost. Membranes from Ionics were films produced from polyacetate with sulphonic (CPS) and weakly basic polyalkyl amine hydrochlorides (VCTP) ion-exchange groups for the cation and anion-exchange types respectively. The membrane acquired from RAI was a radiation grafted polyethylene, while the composition of the membrane from Asahi Glass was unknown. An energy efficiency of about 80 % at a current density of 80 mA/cm<sup>2</sup> was achieved with the test cell employing the RAI-cation-exchange membrane for up to 160 hours without deterioration in performance.

Development of the Fe/Cr redox battery was also conducted at ETL Laboratories. For the unmixed reactant system, a 1 kW demonstration battery was constructed employing a cation-exchange membrane [44]. Much of the effort on the membrane development was concentrated on modification of the existing commercially available cation-exchange membrane - Selemion<sup>\*</sup> CMV, to improve its selectivity [143,144]. Although, a significant improvement in the selectivity over the original material was reported, no scale up testing in the prototype battery was carried out. In a later phase of the development, efforts were also concentrated on the mixed reactant system. Each of the membranes, Selemion<sup>\*</sup> CMV by Asahi Glass (a polystyrene sulphonic membrane) and Nafion<sup>\*</sup> (E.I. du Pont), had been successfully demonstrated in the test cell and a coulombic efficiency of about 92 %, and an overall energy efficiency of 75 % was achieved by both membranes [46]. The use of cation-exchange membranes has enabled the highly mobile H<sup>+</sup> ions to be the major current carrying ions, thereby lowering the cell resistance significantly. This also enabled the mixed reactant system battery to operate at a much higher current density. For the anion-exchange membrane, the Cl<sup>-</sup> ions are believed to be the charge balancing ions to attain electroneutrality of the two half-cell electrolytes during charge/discharge. However, the high cost of Nafion<sup>\*</sup> had lead to the use of CMV membrane in the construction of prototype 10 kW and 60 kW batteries [3,46,47].

#### 2.5.2 Vanadium redox flow battery membranes.

### 2.5.2.1 Screening of commercial available membrane.

Considerably less effort was placed on the development of a new membrane for the vanadium redox battery as compared to the Fe/Cr redox system. The use of commonions in the two half-cell electrolytes have eliminated the problem of cross contamination, therefore, less stringent requirements are placed on the selectivity of the membranes used in this system. This also open up the possibility of using a less selective and low cost microporous separator. Most of the commercially available membranes have acceptable selectivity (to ensure high coulombic efficiency) and resistivity less than 2  $\Omega$  cm<sup>2</sup>. However, the main requirements for the membrane to be suitable for the vanadium redox battery application are its chemical stability in the vanadium electrolytes and cost. The majority of the commercially available membranes failed to satisfy either one of these criteria.

Initial screening of a variety of microporous separators and ion-exchange membranes for the vanadium redox cell application was conducted by Grossmith et.al. [9]. The microporous separators included: PVC separator and ultramicroporous filter membranes from Durapore GMV, while the ion-exchange membranes tested were: Selemion<sup>\*</sup> CMV, RAI-P2241 30/16, Nafion<sup>\*</sup> 432 and 324, Aquapore and Gellman NFWA. Based on the area resistance and the diffusion coefficient measured in the VOSO<sub>4</sub> solution, only Selemion<sup>\*</sup> CMV and Nafion<sup>\*</sup> 324 membranes were considered suitable. Charge/discharge tests employing Selemion\* CMV and Nafion\* 324 in the vanadium redox test cell gave coulombic and energy efficiencies of 90 and 73 % for Selemion\* CMV and, 99 and 65 % for Nafion\* 324 membranes, respectively. The low energy efficiency achieved was partly due to the higher resistance of the electrodes used, which were Le Carbonne graphite felt on graphite plate collectors. Development of a more suitable electrode material has led to the successful use of graphite felt bonded to conducting plastic substrates as electrodes in 1 kW vanadium battery prototypes, with overall energy efficiencies up to 90 % for the CMV membrane.

Studies of the membrane diffusivities of various vanadium species were conducted with Selemion<sup>\*</sup> CMV and AMV, which are cation and anion-exchange membrane, respectively [9]. The different vanadium species exhibit different membrane diffusivities and, hence, different rates of diffusion across the same membrane. For

the CMV membrane, the V(III) ions exhibited the highest diffusivity while the V(IV) species has the lowest, while similar values were obtained with the V(II) and V(V) species. With the AMV membrane, the V(IV) species has the lowest diffusivity value while all the other species have similar values. The notable differences between the two membranes is that, the diffusivities of all vanadium species were of an order of magnitude lower for the AMV membrane, however, the AMV membrane has a higher resistivity value compared with the CMV membrane.

Oei [145] also investigated the permeation of V(IV) and V(V) species across the Nafion<sup>\*</sup> 125 and Selemion<sup>\*</sup> - CMV, DMV and AMV membranes and consistent findings with Grossmith et.al. [9], for the diffusivities of V(IV) and V(V) species were reported. It was also shown that the permeation of V(IV) and V((V) species across the membrane increased with increasing temperature. Measurement by Oei of both the resistivity and the diffusivity values of the above membrane indicated that DMV has the most desirable properties of high selectivity and low resistivity.

The diffusivity and resistivity of CMV and DMV membranes as well as several microporous separator in V(IV) solutions were also measured by Hoong [10]. CMV and DMV membranes have a similar area resistance of about 1.2  $\Omega$  cm<sup>2</sup> but the later has diffusivity value which is a factor of 4 lower. The microporous separators, Daramic<sup>\*</sup> (W.R. Grace) and polypropylene, have resistivity values of less than 0.5  $\Omega$  cm<sup>2</sup>, but the selectivity of these membranes was found to be relatively poor. Charge/discharge experiments conducted with the 25 cm<sup>2</sup> (electrode area) test cell employing CMV membrane and FMI graphite felt electrodes gave; coulombic,

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voltage and energy efficiencies of 96, 87 and 85 %, respectively. For comparison, the test cell using the microporous separator, Daramic<sup>\*</sup>, produced a coulombic efficiency of 81 % and overall energy efficiency of 65 %. It was found that different batches of separator supplied in by the manufacturer gave poor reproducibility in performance and efficiency of the battery.

To date, both AMV, DMV and CMV membranes have been tested in the prototype 1 kW battery. The CMV membrane produced the most promising results, with an energy efficiency above 90 % being achieved [50]. However, longterm charge/discharge cycling has shown poor stability of the membrane with a life of only around 6 months in the vanadium redox battery.

Since 1989, research on the vanadium redox flow cell system has also been undertaken at ETL laboratories in Japan and an energy efficiency of 87 % was reported with the test cell employing CMV membrane [146]. Improvements in the electrode and the use of a new anion-exchange membrane, based on polysulfone material on a PVC substrate (Asahi Glass Co.), gave an energy efficiency of 87 % at a current density of 80 mA/cm<sup>2</sup> in the test cell [147]. Moreover, it is claimed that membrane is claimed to exhibits remarkable stability in the V(V) electrolyte during longterm cycling.

## 2.5.2.2 Modification of microporous separator

Hoong [10] attempted modification of the microporous separator, Daramic<sup>\*</sup>, to enhance its selectivity for improved performance in the vanadium redox battery. Three different methods were tried. The first method was based on the use of polyelectrolytes- sulfonated polystyrene similar to that reported by Grimes et.al [148]. No significant improvement in the efficiency of the vanadium redox cell was achieved with the treated separator.

The other two methods were based on the formation of interpenetrating polymeric networks in the porous substrate of Daramic<sup>\*</sup> [149]. In the first case, the separator was soaked in divinyl benzene and methanol mixture for a period of time, and later polymerized using sodium persulphate as the initiator. Various formulations and different soaking times were investigated. An improvement in coulombic efficiency of 5 to 10 % was reported for the vanadium redox cell employing the modified membranes, however, overall energy efficiency of less than 60 % was achieved. In the other method used, the separator was soaked in a mixture consisting of divinyl benzene, ether, freon and boron trifluoride etherate. The resulting membrane was subsequently chloromethylated. Once again, however, only a slight improvement in the coulombic efficiency of the battery was observed with this treated separator.

Studies of radiation grafting using acrylonitrile and acrylic acid monomers on the microporous separator, Daramic<sup>\*</sup>, was conducted by Cheok [150]. The grafting behaviour of both monomers was studied under ultraviolet light and gamma ray

radiation. Inhibition of homopolymerization with the introduction of additives such as sulphuric acid, cupric sulphate and Mohr's salt, were investigated. The percentage of grafting as high as 25 % was achieved with the proper selection in the ratio of the additives and the monomers. It was observed that extensive homopolymerization also occurred during the grafting process. The modified Daramic<sup>\*</sup> showed a decrease in pore size uniformly across the whole piece. But no tests were performed with this membrane to evaluate its properties in the vanadium redox battery system.

## 2.5.3 Membrane for other flow battery systems.

Although the Zinc-Bromine and Zinc-Ferricyanide (Zinc/redox battery) batteries do not come under the definition of redox flow cells, there are a large number of similarities between the two systems such as in the cell design, configuration, material development and requirements of the membrane separator. A brief description of the membranes or separators used for these systems are thus presented here.

## 2.5.3.1 Separators for Zn/Br battery

For the Zn/Br battery, microporous separator, Daramic<sup>\*</sup> (W.R. Grace) is the one most widely used [151-153]. The choice is based on its low cost, mechanical robustness and proven durability. The separator functions are to permit the transport of  $Zn^{2+}$  ions while restricting the migration of  $Br_3^-$  species from the cathode to the anode and furthermore, it acts as an insulator to prevent short-circuiting of the electrodes.

Problems that have been encountered with the use of this separator are the loss of coulombic efficiency due to its low selectivity to the bromide ions, and the dendrite growth through the separator.

A method of improving the selectivity of the Daramic<sup>\*</sup> separator using in-situ treatment with polyelectrolyte was reported by Grimes et.al. [148]. With this method, the polyelectrolyte materials which is disposed in the cell fluid, migrates to the membrane surface under the influence of an electric field. Whether the polyelectrolyte actually penetrates the porous structure or only substantially coats the surface is still not fully understood. However, it has been demonstrated that the polyelectrolyte would form a barrier to the unwanted ions and prevents their migration through the separator. The treatment effectively increases the selectivity of the microporous separator. Tests conducted with the Zn/Br cell showed an increase in coulombic efficiency from 70 to 85 %. Longterm charge/discharge cycling test indicated good stability of the barrier layer, with coulombic efficiency remaining essentially constant during the testing period.

Another treatment method to enhance the selectivity of the microporous separator, Daramic<sup>\*</sup> for the Zn/Br battery application was disclosed by Arnold and Assink [154,155]. Daramic<sup>\*</sup> was impregnated and/or coated with small quantity of cationic polyelectrolyte. The ideal polyelectrolytes used should be stable and insoluble in the battery electrolyte, but soluble in a solvent that does not attack the separator. Sulfonated polysulfone resins were found to satisfy these requirements. Impregnation of the separator with polyelectrolytes was achieved by either soaking them in the

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polyelectrolytes solution under vacuum or without. The treated separator showed a modest increase in its resistivity value while a significant improvement in the selectivity was also achieved.

### 2.5.3.2 Membrane for Zinc/Ferricyanide battery

The Zinc/redox battery is a flow battery system in which the electrolytes, sodium zincate and sodium ferrocyanide, are stored in external reservoirs and pumped through the cell like the conventional redox flow cell [156]. During charging, Zinc is plated on the Zinc electrode while ferrocyanide is oxidized to ferricyanide. The requirement of the membrane is to provide a barrier to the cross mixing of the two half-cell electrolytes, especially the permeation of ferrocyanide and ferricyanide ions to the positive half-cell.

During the battery's initial development, Nafion<sup>\*</sup> 114 and Nafion<sup>\*</sup> 117 membranes were used extensively in the studies and have shown excellent performance [157]. An energy efficiency of about 80 % was obtained with these membranes. In an attempt to find a low cost replacement for Nafion<sup>\*</sup>, numerous commercially available membranes such as grafted membranes based on polyolefinic supports and several homogeneous sulfonated polystyrene membranes, were evaluated [157]. However, all these membranes were shown to be chemically unstable due to the oxidative nature of the ferricyanide solution. These membranes failed in less than 10 cycles under charge/discharge cycling in the Zinc/redox battery. It was hypothesised that the instability of these membranes was attributed to the presence of tertiary hydrogens which are known to be susceptible to oxidative attack [158]. Assink et.al. [158] synthesized model compounds to study the effect of tertiary hydrogens on the stability of membranes used in oxidative aggressive environments. The compound, sulfonated isopropylbenzene, which contains a tertiary hydrogen yielded substantial amounts of degradation products when exposed to a strong oxidizing solution. The sulfonated t-butylbenzene, which is identical to sulfonated isopropylbenzene, except the tertiary hydrogen is replaced by a methyl group, yielded only minute amounts of degradation products when exposed to the same oxidizing solution.

Further developmental work on the membrane was concentrated on the synthesis and screening of developmental membranes in which tertiary hydrogens are not present in the membranes, membranes which contain only aromatic hydrogens and membranes in which all the hydrogens have been replaced by fluorines [159]. Various developmental membranes as shown in Table 2.2 were obtained from suppliers for evaluation [160].

Supplier and type	Base film	Membrane structure
Atomic energy, Japan MT-P-8-AF-4 (1) MTEF-130 (2)	PFA Teflon <sup>*</sup> -	Poly(trifluoroacrylic acid) Co-poly(trifluoroacrylic acid- tetrafluoroethylene)
RAI R-1010 (1) P-1080 (1)	PTFE PTFE	Cross-linked sulfonated polystyrene Poly(methacrylic acid)
Ionics 61-CZL-386 (2) 61-AZL-386 (2)	Modacrylic cloth	Cross-linled sulfonated polystyrene Cross-linked sulfonated polystyrene

Table 2.4Developmental membranes evaluated for the Zn/redox cell.

(1) radiation grafted, (2) homogeneous

The membranes obtained from the Atomic Energy Laboratory, Japan, were perfluorocarboxylates based. The membrane coded MT-P-8-AF-4 was made by a radiation grafting procedure during which the methyl  $\alpha,\beta,\beta$ -trifluoroacrylate was incorporated into a poly(tetrafluoroethylene) substrate, and the ester group was later hydrolysed. The MTEF-130 membrane was prepared by copolymerizing methyl- $\alpha,\beta,\beta$ -trifluoroacrylate and tetrafluoroethylene followed by hydrolysis. These membranes were shown to be stable in the accelerated life test in which they were soaked in ferricyanide solution. Charge/discharge cycling tests were not carried up due to the non availability of sufficient sample.

Membrane R-1010 obtained from RAI was prepared by radiation grafting of styrene onto a fluorocarbon film followed by sulfonation, and the membrane R-1080 was made from grafting methyl methacrylate acid onto a fluorocarbon substrate. The membranes obtained from Ionics, 61-CZL-386 and 61-AZL-386, were cross-linked

sulfonated polystyrene fabricated by casting a homogeneous gel on the modacrylic cloth. Excellent stability and performance was demonstrated by the membranes obtained from RAI.

The most promising developmental membrane obtained from RAI was a  $\alpha$ methylstyrene radiatively grafted onto PTFE film and subsequently sulfonated to form a cation-exchange membrane [158]. The membrane produced by this method does not contain tertiary hydrogens on the polymeric backbone, and was envisaged to display excellent chemical stability in the electrolytes. The energy efficiency obtained with this membrane in the Zn/redox cell was 83 % for more than 700 cycles, and did not show any sign of deterioration [160].

Synthesis of sulfonated polysulfone membrane for the Zn/redox battery application was investigated by Assink and Arnold [74]. Sulfonated polysulfone contains no tertiary hydrogens and should have excellent stability in the Zn/redox battery electrolytes. Three different methods of preparing these membranes were reported. These include: casting from dimethylformamide solutions, impregnation of films with solutions microporous PTFE of sulfonated polysulfone in dimethylformamide and the phase inversion technique. However, with the exception of the casting technique, no practical membranes were successfully produced. The sulfonated polysulfone membranes obtained from the casting technique demonstrated an energy efficiency of 78 % in the Zn/redox cell initially, but in the extended cycle testing for over 520 cycles, the energy efficiency decreased slightly.

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#### CHAPTER 3

#### THEORETICAL BACKGROUND

### 3.1 Vanadium Redox Flow Cell.

The first practical redox flow cell which employed common metal ions for both of the half-cells was demonstrated by Skyllas-Kazacos and coworkers [4-8]. Research and development of the vanadium redox battery at the University of New South Wales has now reach the commercialization stage. The redox couples used are V(II)/V(III) and V(IV)/V(V) for the negative and the positive half-cells, respectively. Both of the redox couples employ  $H_2SO_4$  as the supporting electrolyte. The V(III)/V(II) couple in the sulphuric acid media has a standard reduction potential of -0.255 V. Its half-cell reaction is represented by:

$$V^{3+}(aq) + e \rightarrow V^{2+}(aq)$$

For the V(IV)/V(V) couple, the standard reduction potentials are 0.9996 V and 1.0120 V in HCl and  $H_2SO_4$  respectively and the corresponding half-cell reaction is:

$$VO_2^+ + 2H^+ + e \rightarrow VO^{2+} + H_2O$$

The overall theoretical open circuit voltage (OCV) of these redox couples is 1.27 V. But in the operating prototype vanadium redox battery, employing 2 M vanadium in  $H_2SO_4$ , an OCV of 1.6 V per cell at 25 °C is observed when it is fully charged and 1.35 V per cell at 50 % SOC.

The state of charge (SOC) of this system can be easily monitored by measuring the OCV, and is described according to the Nernst Equation as [161]:

$$E_{o.c} = E_{o.c}^{o} + \frac{RT}{nF} \log \frac{[VO_2^+][V^{2+}]}{[VO^{2+}][V^{3+}]} \qquad 3.1$$

$$\Delta E_{o.c} = \Delta E_{o.c}^{o} + \frac{RT}{nF} \log \frac{[VO_2^+][V^{2+}]}{[VO^{2+}][V^{3+}]} \qquad 3.2$$

where 
$$[VO_2^+] = [V^{2+}]$$
 and  $[VO^{2+}] = [V^{3+}]$   
and  $[VO_2^+] \propto SOC$  and  $[VO^{2+}] \propto 1 - SOC$ 

Therefore at 25 °C,

$$\Delta E_{o.c} = \Delta E_{o.c}^{o} + \frac{RT}{nF} \log \frac{[SOC]^2}{[1-SOC]^2} \qquad 3.3$$

$$\Delta E_{o.c} = 1.35 + 0.118 \log \frac{[SOC]}{[1-SOC]}$$
 3.4

The relationship between the OCV and the SOC is represent in Figure 3.1.



Figure 3.1 Graph showing OCV of the cell at different SOC at 25 °C.

Another method which has been developed to monitor the SOC of the battery is by measuring the conductivity of the two half-cell solutions, and comparing the conductivity with the calibration graph obtained from experimental measurements [161]. The conductivity of the vanadium solutions at various temperatures is presented in Figure 3.2. However, this technique is quite cumbersome and is subject to error since the concentration of the solutions can fluctuate during charge/discharge cycling.



Figure 3.2 Conductivity of vanadium cell electrolyte (2 M V in 3 M  $H_2SO_4$ ) as a function of SOC: a) negative half-cell, b) positive half-cell.

A qualitative judgement of the battery SOC, especially when it has attained 0 % or 100 % S.O.C., is also easily indicated by the solution colour. The vanadium ions at different oxidation states display distinctive colours which are indicated by:  $V^{2+}$  (violet)  $\rightarrow V^{3+}$  (green) and  $VO^{2+}$  (blue)  $\rightarrow VO_2^+$  (yellow/orange) Under normal operating conditions, however, the battery is seldom allowed to fully charge or discharge. Hence, monitoring the battery S.O.C. from the colour of the electrolytes other than at the fully charged or discharged state, is inaccurate.

#### 3.1.1 Chemistry of vanadium in aqueous systems.

The chemistry of vanadium in aqueous media has already been reviewed by several authors [10,161,162]. However, complex formation of vanadium species in  $H_2SO_4$  is still poorly understood and furthermore, few studies in this area have been reported. To date, in  $H_2SO_4$  media, only complex formation of V(IV) and V(V) species has been reported. A clearer knowledge of the speciation of vanadium in  $H_2SO_4$  would provide a better understanding of some of the transport phenomena associated with the membrane in the vanadium redox cell.

Violet solutions containing V(II) (aq) ions can be prepared by dissolving the black oxide of VO. Aquo-ions of  $[V(H_2O)_6]^{2+}$  are the predominant species that exist in the absence of complexing anion. The H<sub>2</sub>O molecules can be replaced by ligands such as NH<sub>3</sub>, ethylenediamine, EDTA<sup>4-</sup>, CN<sup>-</sup> and acetylacetonate. It is hypothesed, the aquoion  $[V(H_2O)_6]^{2+}$  is a strong reducing agent and is oxidized by water with hydrogen evolution. In acid solutions, the oxidation of V<sup>2+</sup> (aq) is due to atmospheric O<sub>2</sub>. The oxidation of  $V^{2+}$  (aq) by air appears to proceed in a stepwise manner, initial formation of intermediate species like VOV<sup>4+</sup> (aq), and further reaction of this species with  $V^{2+}$  (aq) to form  $V^{3+}$  (aq). However, direct oxidation of  $V^{2+}$  (aq) to  $VO^{2+}$ (aq) in the presence of air is also possible. A few crystalline salts containing the  $[V(H_2O)_6]^{2+}$  ion have been isolated. The most important are the sulphate  $VSO_4.6H_2O$ as violet crystals and the double sulphates  $M_2[V(H_2O)_6](SO_4)_2$ , where M can be NH<sup>4+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup>.

The blue aqua ion  $[V(H_2O)_6]^{3+}$  is obtained by electrolytic or chemical reduction of V(IV) or V(V), as well as by dissolution of V<sub>2</sub>O<sub>3</sub> in acidic medium. These ions undergo partial hydrolysis to VO<sup>+</sup> and V(OH)<sup>2+</sup>. The V<sup>3+</sup> can form a number complex ions such as  $[VCl_2(MeOH)_4]^+$ ,  $[V(NCS)_6]^{3-}$ , and  $V[S_2P(OEt)_2]^3$ . The green solution of V<sup>3+</sup> in H<sub>2</sub>SO<sub>4</sub> is hypotheses to be due to the complex formation of V<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Hydrolysis of V<sup>3+</sup> ion is evident at pH's above 1, and increases as the pH increases. Hydrolysis products such as  $VOH^{2+}$  and  $V_2(OH)_2^{4+}$  are evident from potentiometric and spectrophotometric studies.

Vanadium (IV) oxide is amphoteric being equally soluble in both acidic and basic solutions. In acidic solution, V(IV) exists as VO<sup>2+</sup>, which is commonly known as the vanadyl ion, and in aqueous solutions, it is present as  $[VO(H_2O)_5]^{2+}$ . The predominant species of V(IV) in alkaline solution is VO<sub>4</sub><sup>4+</sup>. Solution of VO<sup>2+</sup> in strong acid is very stable. Hydrolysis of VO<sup>2+</sup> is similar to that of V<sup>3+</sup> and the main products are VO(OH)<sup>+</sup> and  $(VO)_2(OH)_2^{2+}$ . When VOSO<sub>4</sub>.2H<sub>2</sub>O is dissolved in water, a relatively unstable complex  $[VO(H_2O)_4OSO_3H]^+$  is formed. Strehlow and Wendt [163] reported

the equilibrium constant for the formation of  $VOSO_4$  ion pair as 3.0 x 10<sup>2</sup>, according to the following equation:

$$VO^{2+}(aq) + SO_4^{2-}(aq) \rightleftharpoons VOSO_4 (aq pair)$$
 3.5

The formation of V(IV) complexes in  $H_2SO_4$  medium was also investigated by Ivakin et.al. [164]. Complex species such as: VOSO<sub>4</sub>, [VO(SO<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> and [VOHSO<sub>4</sub>]<sup>+</sup>, with their respective stability constants:  $K_1 = 55 \pm 3$ ,  $K_2 = 320 \pm 10$  and  $K_3 = 1.7 \pm 0.3$ , have been established.

The most common compounds of Vanadium (V) are the pentoxide  $(V_2O_5)$  and ammonium metavanadate.  $V_2O_5$  is slightly soluble in water and more soluble in strong acids. It is readily soluble in basic solutions, producing a colourless solution containing the vanadate ion,  $VO_4^{3}$ .  $V_2O_5$  is a moderately strong oxidizing agent. The predominant species in strong acids are  $VO_2^+$  and  $[VO_2(H_2O)_4]^+$ . It may complex with anions to form  $[VO_2Cl_4]^{3}$ ,  $[VO_2EDTA]^{3}$  and  $[VO_2Ox_2]^{3}$ . A large number of hydrolysis products are formed at varying pH's and the pervandyl ion  $VO_2^+$  is the principal species for -0.5 < pH < 1.3. It can be easily protonated to form the  $VO(OH)^{2+}$ species. The complex formation of  $VO_2^+$  with  $SO_4^{2-}$  was investigated by Ivakin [165]. It was found that in acidic solutions with the presence of  $SO_4^{2-}$  ion, the following type of equilibrium exist and the equilibrium constant measured at 19 °C are:

$$VO_2^+ + HSO_4^- \rightleftharpoons VO_2SO_4^- + H^+ \qquad K_1 = 9.32 \pm 0.43$$
 3.6

$$VO_2^+ + SO_4^{2-} \rightleftharpoons VO_2SO_4^ K_2 = 0.73 \pm 0.14 \text{ M}^{-1}$$
 3.7  
 $VO_2^+ + VO_2SO_4^- \rightleftharpoons (VO_2)_2SO_4$   $K_3 = \text{very small M}^{-1}$  3.8

However, the equilibrium constant for  $K_3$  is very small and the species  $(VO_2)_2SO_4$  is not formed to any appreciable extent.

## 3.1.2 Vanadium electrolyte preparation.

The preparation of vanadium electrolyte for the vanadium redox flow battery is described in Section 4.3.7. A sample calculation of the concentrations of various species in the vanadium solutions prepared by electrolysis of  $V_2O_5$  powder in  $H_2SO_4$  is presented here:

In the preparation of 2 M V<sup>3 5+</sup> (i.e 1 M V(III) plus 1 M V(IV)) in 2.5 M H<sub>2</sub>SO<sub>4</sub>). The mass balance assumes H<sup>+</sup> is the only current carrying species. 1 mole of V<sub>2</sub>O<sub>5</sub> and 5 moles of H<sub>2</sub>SO<sub>4</sub> are made up to a litre. Initial solution consists of: [H<sub>2</sub>SO<sub>4</sub>] = 5 M, or [H<sup>+</sup>] = 10 M and [SO<sub>4</sub><sup>2-</sup>] = 5 M During electrolysis, to V(IV) state:

$$V_2O_5 + 6H^+ + 2e \rightarrow 2VO^{2+} + 3H_2O$$
 3.9  
 $2e = 2H^+$ 

Overall solution has lost 4H<sup>+</sup>

Therefore, the solution consists of: 3 M  $H_2SO_4$ , 2 M  $VO^{2+}$ , 2 M  $SO_4^{2-}$ .

Further electrolysis, to V(III) state:

$$2(VO^{2+} + 2H^{+} + e \rightarrow V^{3+} + H_2O)$$
 3.10  
 $2e = 2H^{+}$ 

Overall solution has lost 2H<sup>+</sup>

Therefore, the solution consists of: 2 M  $H_2SO_4$ , 2 M  $V^{3+}$ , 3 M  $SO_4^{2-}$ .

For the reaction (3.10) to be half-completed,

$$2VO^{2+} + 2H^+ + e \rightarrow VO^{2+} + V^{3+} + H_2O$$
 3.11  
e = H<sup>+</sup>

The final solution thus consists of:  $1 \text{ M V}^{3+}$ ,  $1 \text{ M VO}^{2+}$ ,  $2.5 \text{ M SO}_4^{2-}$ ,  $2.5 \text{ M H}_2\text{SO}_4$ The theoretical electrolysis time required to produce a 1:1 mixture of V(IV) and V(III) is calculated from Faraday's law using:

Moles of Vanadium (M) = 
$$It / nF$$
 3.12

where I is the current applied, t is the time, F is the Faraday's constant and n is number of equivalents per mole of vanadium, which is 1.5 in this case.

To obtain vanadium solutions of the other oxidation states, equal volumes of the 2 M  $V^{3.5+}$  solution are fed to the redox flow cell as discussed in Section 4.3.3.

During charging, the 2 M  $V^{3,5+}$  solutions would be charged to initially produce  $V^{3+}$  on the negative side and  $VO^{2+}$  on the positive side.

On the negative side,

$$VO^{2+} + 2H^{+} + e \rightarrow V^{3+} + H_2O$$
 3.13  
 $e = H^{+}$ 

The negative half-cell solution consists of: 2 M  $V^{3+}$ , 3 M  $SO_4^{2-}$ , 2 M  $H_2SO_4$ , which represents the discharged state for the negative half-cell electrolyte.

On the positive side,

$$V^{3+} + H_2O \rightarrow VO^{2+} + 2H^+ + e$$
 3.14  
e = - H<sup>+</sup>

The positive half-cell solution consists of: 2 M VO<sup>2+</sup>, 2 M SO<sub>4</sub><sup>2-</sup>, 3 M H<sub>2</sub>SO<sub>4</sub>, which represents the discharged state for the positive half-cell electrolyte.

Further charging,

On the negative side,

$$2(V^{3+} + e \rightarrow V^{2+})$$
 3.15

$$2e = 2H^4$$

The charged negative half-cell solution thus consists of: 2 M  $V^{2+}$ , 2 M  $SO_4^{2-}$ , 3 M  $H_2SO_4$ .

On the positive side,

$$2(\text{VO}^{2+} + \text{H}_2\text{O} \rightarrow \text{VO}_2^+ + 2\text{H}^+ + \text{e}) \qquad 3.16$$
  
2e = 2H<sup>+</sup>  
Overall solution gain 2H<sup>+</sup>

Therefore, the charged positive half-cell solution consists of:  $4 \text{ M H}_2\text{SO}_4$ ,  $2 \text{ M VO}_2^+$ ,  $1 \text{ M SO}_4^{-2}$ .

During discharging of the redox cell, the reverse reactions occur.

## 3.1.3 Solubility and stability of vanadium solutions.

The solubility of the vanadium solutions in their various oxidation states is important with due regard to optimizing the energy density of the vanadium redox battery. V(II), V(III) and V(IV) can undergo crystallization when their concentrations exceeded the solubility limit, as well as with a decrease in temperature. On the other hand thermal precipitation of V(V) occurs with increasing in temperatures. Variations in the ambient temperature of the surroundings is thus a crucial factor in determining the appropriate concentrations of the solutions to be used in the battery without the problems of crystallization or thermal precipitation.

Crystallization of the solutions in the vanadium redox flow battery can be detrimental to its performance. A few more obvious problems which could arise are: increase in pressure drop across the felt electrode and in serious cases, blockage of the secondary manifolds; decrease in the active electrode surface area and increase in the electrode resistance; and in extreme cases, the crystals formed may rupture the pore structure of the membrane. Besides any possible damage done to the membrane, however, the performance of the battery can be restored back to normal by redissolving the crystals formed. This is usually achieved by mixing the two half-cell electrolytes together.

Cheng studied the solubility of the vanadium solution in  $H_2SO_4$  [166,167]. The solubility values of V(II), V((III) and V(IV) at various concentrations of  $H_2SO_4$  and at different temperatures are presented in Figure 3.3.a-c.



Figure 3.3 Solubility of vanadium ions in various concentration of  $H_2SO_4$  at different temperature; a) V(II), b) V(III), c) V(IV).

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The solubility of V(II), V(III) and V(IV) species decreases, with increasing  $H_2SO_4$  concentration and decreases in temperature. In Figure 3.4, the stability of the 2 molar V(IV)/V(V) sulphate system is presented. On the other hand, V(V) in  $H_2SO_4$  does not undergo crystallization, but instead, a slow thermal precipitation of  $V_2O_5$  occurs with increasing temperature. Thermal precipitation starts to occur at temperatures as low as 30 °C for 2 M V(V) in 4 M  $H_2SO_4$  solution, although this is very slow.



Figure 3.4 Stability diagram of V(IV)/V(V) sulphate system in 4 M H<sub>2</sub>SO<sub>4</sub>. Initial total vanadium concentration is 2 M and the numbers on the curves represent the solution SOC.

#### 3.1.4 Electrodes

Early studies on the vanadium redox cell utilized graphite plates as electrodes in the laboratory test cell. Later, graphite felt materials were used together with graphite electrodes, so as to increase the electro-active surface area. The graphite felts were placed into the cavities of the two half-cellss and the compression provided the contact with the graphite plate. Energy efficiencies as high as 85 % were achieved with this type of electrode. In the scale-up prototype 1 kW battery, the use of graphite plate is not only impractical but also costly. Commercially available conductive plastic electrode substrates with graphite felts bonded to the surface were later used in substitution of the graphite plate. However, the high cost of this electrode and problems with electrolyte penetration to the copper current collector has lead to the research team at this University to develop improved an electrode.

Preparation and evaluation of the conductive plastic material for the vanadium redox battery applications have been actively pursued by Zhong [168]. The electrochemical activity of different graphite felt materials available commercially, were also screened. The conductive plastic electrode developed in this laboratory has been found to possess superior properties over the commercially available electrode tested previously. The electrodes developed consist of three layers with copper mesh bonded to one face of the conductive plastic and the graphite felt on the other to produce an end electrode. Bipolar electrodes are fabricated by bonding the graphite felt onto both ends of the conducting plastic sheet.

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## **3.2** Performance characteristics of redox flow cells [10,161].

The electromotive force (EMF) of a battery is related to the free energy change of the overall cell reaction which can be represented by the Nernst equation. However, during the passage of current, the applied potential has to be higher than the equilibrium cell potential to account for the losses due to the irreversible behaviour associated with the electrode processes (electrode polarization) and the cell resistance (ohmic potential drop). Likewise, when the current is drawn from the system, the reverse is true. The cell potential can be expressed as [10]:

$$E_{cell} = E_{c}^{o} - E_{A}^{o} - \eta_{A} - \eta_{C} - IR_{cell} \qquad 3.17$$

where  $E_c^{\circ}$  is the cathodic half-cell potential;

 $E_A^{\circ}$  is the anodic half-cell potential;

 $\eta_A$  is the activation overpotential;

 $\eta_{\rm C}$  is the concentration overpotential;

IR<sub>cell</sub> is the internal resistance of the cell.

The electrode polarization losses are equal to the sum of the individual overpotentials associated with the charge transfer kinetics (activation overpotential) at the anode and the cathode, and the mass transport of reactant species (concentration overpotential). The source of IR drop is due to the internal resistance of the bulk phase within the cell. This ohmic overpotential is directly proportional to the cell current.

For the vanadium redox battery, the activation overpotential of the electrode can be reduced by increasing its active surface area, thus reducing the effective current density, or by the use of an electro-catalyst to improve the kinetics of the reaction. In

the redox flow cell, the active species are fed from the external reservoirs to the cell. Providing the flowrate through each half-cell is greater than the stoichiometric flowrate, the polarization losses associated with concentration polarization are minimal. Concentration polarization of the cell only becomes more evident when it is at a high state of charge during charging or at low states of charge during discharge. Also, when the current density applied reaches the limiting current density, mass transport of the reactants to and products away from the electrodes become the rate controlling step. The steep rise in cell potential during the latter stages of charging can initiate side reactions such as oxygen and hydrogen evolution at the anode and the cathode respectively. This in turn will affect the coulombic efficiency of the cell. Concentration polarization losses can be minimised by providing adequate flow of the reactants through each half-cell and operating over a restricted SOC range (e.g 5 % to 95 %). The IR<sub>cell</sub> contribution to the cell voltage is the sum of the resistances from the faradic processes, the electrolyte, electrode material, electrical contacts and membrane. Minimising the resistivities of these components will invariably improve the voltage efficiency of the cell.

## 3.2.1 Electrolyte flow consideration [169].

The necessary electrolyte flowrate through the cell depends on factor such as: solution state of charge, cell operating current and total solution concentration. The theoretical minimum flow required for adequate cell performance is the stoichiometric flow ( $F_{sf}$ ), which is defined as the flowrate at which the electrolyte is totally depleted of the active ionic species just as it leave the cell. The stoichiometric flow is related to the specified current (I), solution state of charge (SOC) and the electrolytes capacity (N, A min cm<sup>-3</sup>), represented as [169]:

$$F_{sf} = I / (N * SOC) cm^3/min.$$
 3.18

The electrolytes capacity, N can be obtained from [169]:

$$N = (M \times F \times 10^{-3}) / 60$$
 3.19

where M is the concentration of the electrolyte and F is the faraday constant.

From this relationship, for a constant current, the stoichiometric flow requirements for the discharging process are seen to increase as the SOC decreases. Therefore, the  $F_{sf}$  requirements of a cell at constant current are continually changing as the electrolytes cycle between a fully charged and fully discharged state. Generally, in the vanadium redox battery, the flowrate employed is a few times that of  $F_{sf}$  to avoid significant overpotential losses due to concentration polarization.

## 3.2.2 Battery characteristics

The theoretical capacity  $(Q_T)$  of a cell is given by [10]:

$$Q_{\rm T} = \int_0^t I \, dt = m(nF) \qquad 3.20$$

where m is the theoretical number of moles of reactant associated with the complete discharge of the cell, n is the number of electrons transfer in the reaction, F is the Faraday constant, and I is the current passed for time, t. To reduce the effect of concentration polarization, the vanadium redox battery is normally cycled between 5 to 95 % SOC. Hence, the capacity for actual utilization is only 90 % of the theoretical. If the solutions for the two half-cell are out of balanced, however, the

useful capacity of the cell can be much lower.

The power (P) delivered by a battery is the product of the cell voltage and the associated current flowing [10]:

$$P = I E_{cell}$$
 3.21

The power rating specifies whether or not the battery is capable of sustaining a large current drain without undue polarization.

## 3.2.3 Cell efficiencies

Performance of the secondary battery is usually tested under constant current or constant voltage charge/discharge cycling. In applications such as load levelling and motive power, the battery is required to undergo a continuous sequence of deep discharges followed by recharge to maximum capacity. Therefore, an effective way to determine the performance of the vanadium redox cell under these applications is by evaluating it under constant current cycling operation. A typical charge/discharge curves obtained under this mode is illustrated in Figure 3.5.



Figure 3.5 A typical charge/discharge curve obtained with constant current applied.

The coulombic (amperehour) efficiency  $(\eta_c)$  of the battery is defined as [168]:

$$\eta_c = \frac{\int_0^t i_{dis} dt}{\int_0^t i_{ch} dt} \times 100\%$$
 3.22

where the  $i_{ch}$  and  $i_{dus}$  refer to the currents flowing during charge and discharge respectively. The coulombic efficiency is affected by factors such as: self-discharge across the membrane, side reactions such as hydrogen or oxygen evolution during charge, and air oxidation of the V(II) solution.

The energy (watt-hour) efficiency is defined as [168]:

$$\eta_E = \frac{\int_0^t V_{dis} i_{dis} dt}{\int_0^t V_{ch} i_{ch} dt} \times 100\% \qquad 3.23$$

where  $V_{ch}$  and  $V_{dus}$  are the cell voltages during charging and discharging respectively.

A quantitative measure of the effects of the cell polarization during charge/discharge is given by the voltage efficiency, which is defined as [168]:

$$\eta_{v} = \frac{\eta_{E}}{\eta_{c}} \times 100\% \qquad 3.24$$

The voltage efficiency is related to the cell resistance. The voltage efficiency decreases with an increase in cell resistance.

# 3.3 Transport properties of separators and membranes.

## 3.3.1 Separators [54]

For microporous separators, the mobilities and the concentrations of the current carrying ion species are identical to those of the bulk solution. Transport of ionic species generally occurs by hydrodynamic flow and the separators are not able, to any significant extend, to discriminate between specific species that pass through. The selectivity of the separator arises from the different mobilities of the ionic species passing through. Therefore, the microporous separator has poor selectivity and the rate of permeation of different ionic species across the separator depends on their mobilities. The structure and the pore size of different types of separators vary and, hence, they possess different characteristics in selectivity and conductivity.

The conductivity of the separator is directly related to the mobilities of ions, their charge, concentration, and the length and nature of migration pathways (tortuosity). An increase in the tortuosity of the separator effectively increases its selectiveness and also the resistivity. Several mathematical models [54] based on the porosity of the microporous separators have been proposed to estimate their conductivity. These include: cylinder model, particulate model and three phase model.

#### 3.3.2 Membrane

#### **3.3.2.1** Ion-exchange membranes

Ion-exchange membranes combine the ability to act as a physical barrier to the cross mixing of two solutions while also providing electrical conductivity. Moreover, these membranes are capable of discriminating co-ions over counter ions due to their fixed ionic groups. The extend of ion selective capability and the conductivity of the membrane is generally governed by the type and the total fixed ion content (IEC) and the overall degree of swelling.

When the membrane separates two electrolytes, counter ions are admitted to the membrane and have little difficulty in passing through while co-ions are partially if not totally excluded, in accordance to the Donnan exclusion principle [66,p134]. In essence, when a cation-exchange membrane is placed in a dilute solution of a strong electrolyte, there are considerable concentration differences between the two phases. The cation concentration is larger in the membrane whereas, the (mobile) anion concentration is larger in the solution. Migration of cations into the solution and anions into the membrane results in an accumulation of positive charge in the solution and negative charge in the membrane phase, resulting in a build up in electrical potential called 'the Donnan potential' between the two phases. The Donnan potential acts by pulling cations back into the (negative charged) membrane and anions back into the (positive charged) solution, thereby conferring ionic selectivity. The situation with anion-exchange membrane is analogous and the Donnan potential has a opposite sign. Therefore, if an electric field is applied across the membrane, the transport of electric current is accomplished nearly exclusively by the counter ions. This electrolyte exclusion is favoured by [66,p136] low concentration of the solution, high ion-exchange capacity and cross-linking of the membrane, low valency of counter ion, high valency of co-ion and large molar volume of the electrolyte. The electrolyte exclusion can however, be partially or completely offset by association, complex formation, or similar interactions between the ions of the electrolyte and the fixed ionic groups or the matrix, as well as by association of mobile ions with one another.

The electrical conductivity of the membrane is related to the concentration and the mobilities of the charge carriers within it. The mobility of an ion can be expressed in terms of its diffusion coefficient. High specific conductivity of the membrane is
generally favoured by [66,p322] high concentration of the fixed ionic groups, low degree of cross-linking, small size and low valency of the counter ions, high concentration of the solution which is in equilibrium with the membrane, and elevated temperature. The concentrations of the fixed ionic groups and of the solution determine the concentrations of the charge carriers in the membrane, while the degree of cross-linking, the nature of the counter ions and the temperature determine their mobilities.

The degree of swelling has important implications for the selectivity and the conductivity of the membrane. Swelling is favoured by [66,p102] a low degree of cross-linking and high ion-exchange capacity of the membrane, strong solvation tendency of the fixed ionic groups, large and strongly solvated counter ions, low valency of the counter ion and low concentration of the external solution. Generally, the self-diffusion coefficient of the counter ion decreases with progressive dehydration of the membrane as does its conductivity. However, exceptions may occur and the specific conductivity can go through a maximum at a certain swelling state. This is because, shrinkage of the membrane could reduce the 'jumping' distance of counter ion from chain to chain and thus, increase its effective self-diffusion coefficient. The increase in conductivity is also explained by the increase in the number of counter ions per unit volume of the membrane.

## **3.3.2.2** Ionomers (perfluorosulfonic type)

For PTFE-based ionomers (in particular Nafion<sup>\*</sup> type), the transport properties

[170,171] differ from those of the conventional cross-linked ion-exchange membrane. The fixed charge of the membrane affects the rate of diffusion very slightly and in general, all the diffusion coefficients are of the same order of magnitude. The ion-exchange capacities for commonly used forms of Nafion (1100-1500 EW) are about 4 times smaller than the commercial sulfonate type ion-exchange membranes and yet, they exhibit diffusion coefficient comparable to these membranes. (EW - Equivalent weight is defined as weight of dry hydrogen ion form polymer per mole of exchange sites.) Also, the swelling behaviour of these membranes is very dependent on the nature of the counter ion and its pretreatment. There is now convincing evidence to indicate that exchange sites, counter ions and sorbed water, exist as a separate microphase in the ionomer, and this phenomenon is not possible for cross-linked ion-exchange membranes.

The transport dynamics in ionomers are complicated and still not well understood. The polymer morphology [82] which influences transport properties, appears to be set by the ionic structure that exists within the polymer. A theoretical model which has been proposed to explain the transport phenomena of Nafion<sup>\*</sup> type membranes is the Cluster-Network model [100,101,170] which is based on the concept of spherical ionic regions separated by inter-connecting channels as illustrated in Figure 3.6. The possibility that ion transport in perfluorosulfonic membranes might be described by percolation theory was proposed by Hsu et.al [101].



Figure 3.6 Three region structural model for Nafion\* membrane: a) fluorocarbon,b) interfacial zone, c) ionic clusters.

For the perfluorosulfonic membranes, ionic clustering has been studied by many [100,101]. In the matrix, the ion pairs (can be described as dipoles) form aggregates through dipole-dipole interaction, lowering the internal energy of the system by 20-25 Kcal/mole for a quadrupolar aggregate relative to that of two isolated dipoles. These aggregates can act as physical cross-links in the system. However, the size of these aggregates is limited by the steric effect of the backbone to which the ion pairs are

attached. Two basic types of ionic aggregates have been postulated, small aggregates consisting of a few ion pairs (multiplets) and larger aggregates (clusters) which comprise of a non-ionic backbone and many ion pairs. Therefore the structure of ionomers can be broadly described as that of a microphase separated system in which a matrix of low ion content (due to multiplets) is interspersed with the ion-rich domains (cluster).

The effects of equivalent weight (EW) of the perfluorosulfonic membrane, ion form and water content on the dimensions and composition of the clusters is discussed in [101]. With the increase in equivalent weight of the ionomer, the cluster diameter, ion-exchange sites per cluster and water per exchange site decreases. At higher EW's, more energy is required to hydrate each exchange site and have the exchange site aggregated. This is due to the increase in crystallinity and polymer stiffness with increase in EW. An increase in the molecular weight of the counter ions (cations) increases the cluster diameter and water per exchange site decreases, but the number of exchange sites per cluster increases. An increase in swelling also increases the cluster diameter, exchange sites per cluster and waters per exchange site. The growth of clusters occurs with swelling and continuous reorganisation of exchange sites actually contributes to the decrease in clusters in a fully hydrated sample.

## **3.4.** Modelling and theoretical approaches to membrane transport properties.

At the present time no quantitative methods exist which permit the full characterization of the distribution of ions, water and matrix within an ion-exchange membrane. Models of ion and water transport through ion-exchange membrane are generally classified into one of the three categories [66,171]. Brief discussions of each approach will be present here. However, it should be noted that, none of these models can effectively predict the transport of ion fluxes across the membrane in the electrochemical processes. The main obstacles lie, in the lack of accurate electrochemical data in highly concentrated solutions and a complete understanding of the structural and chemical properties of the newly developed membranes used in these processes.

The theories of the first group consider the membrane as a surface of discontinuity separating the two adjacent phases and setting up different resistances to the passage of the various ionic species. The driving forces for particle transfer across the membrane are the differences in the general chemical potentials between the two adjacent phases. The continuum-mechanical model is based on these theories and was used to model transport for membrane with uniform pores. The model is quantitatively accurate for pore size larger than 3 nm and electrolyte concentration less than 0.1 M. The Nernst-Planck equation [64] is frequently used to described the ionic fluxes across the membrane and the imbibed solution in the membrane phase is assumed to be stationary. Therefore, transport of ionic fluxes by convection arising from osmotic and electro-osmosis flow is not considered here.

The theories of the second group are based on thermodynamics of irreversible processes. The membrane is considered as a quasi-homogeneous intermediate phase of finite thickness. The driving forces are the local gradients of the general chemical potentials in the layer. Convention may also contribute to the particle transfer within the membrane. Unlike the continuum-mechanical model, irreversible thermodynamics is a continuum approach that does not consider microscopic information about pore morphology. The Stefan-Maxwell equation is often used to describe the fluxes transported across the membrane. The TMS model which considers the membrane as a quasi-homogeneous phase in which one ionic species is immobile was first successfully applied to membranes by Teorell, and Meyer and Sievers [64].

The theories of the third group consider the membrane as a series of potential-energy barriers. Thus, the membrane is considered as an inhomogeneous intermediate layer. An (irregular) spatial lattice is formed because the probability of finding a particle is higher in the positions between the activation thresholds. The driving forces arise from the differences between the transition probabilities in opposite directions normal to the membrane. Percolation theory which comes under this group, has been applied by Hsu et.al. [101] to model the threshold value of the aqueous volume fraction for which the polymer becomes proton conductive. However, the percolation theory has not been fully developed to obtain other transport parameters such as hydraulic permeability and pore electrical conductivity.

In view of the complexities of the theoretical approach in quantitative prediction of the transport of ionic fluxes across the membrane, qualitative explanations of the transport phenomena occurring in electrochemical processes are often sought. The modified Nernst-Planck flux equation (3.25) is most frequently used to described the transport of ionic fluxes across the membrane [64,66]. In this equation (3.25), the

transport of ionic fluxes due to convection and coupling of flows are included. In equation 3.25, the over-all flux  $J_i$  of the species i is composed of three additive terms: the diffusion flux  $(J_i)_{duff}$  caused by the chemical potential gradient of the species, the electric transference  $(J_i)_{elec}$  caused by the electric potential gradient and the transfer  $(J_i)_{con}$  caused by convection.

$$J_{i} = -U_{i}RT \frac{dC}{dX} - Z_{i}C_{i}U_{i}F \frac{d\psi}{dX} + \boldsymbol{\theta}_{i}C_{i}V \qquad 3.25$$

Where  $U_1$  is the mobility of ions i.

- R is the gas constant
- T is the temperature of the system

dC/dX is the concentration gradient across the membrane

- $C_1$  is the concentration of i species
- $Z_1$  is the ion charge
- F is the faraday constant
- $d\psi/dX$  is the electric potential gradient
- $\theta_1$  coupling coefficient
- V is the rate of motion of the centre of gravity

The fixed charge theory (TMS) which uses the Nernst-Planck equation, assumes that the frame of reference is the stationary membrane. For equation 3.25, the fluxes are expressed relative to a frame moving in the membrane with the average velocity of the volume flow of solvent and ions. Even though the ions are intimately associated with the water in the membrane, the counter ions could undergo strong interaction with the fixed charges of the matrix. Therefore, the convection term in equation 3.25 is multiplied by a coupling coefficient  $\theta_i$ , which expresses the tightness of the coupling between the flow of ion i and the water.

In equation 3.25, the diffusional flux is relate to Fick's First Law as:

$$-U_{i}RT\frac{dC_{i}}{dX} = -D_{i}\frac{dC_{i}}{dX}$$
 3.26

The mobility of ion i  $(U_1)$  is related to the diffusivity of ion i  $(D_1)$ , according to Nernst-Einstein equation as [66,p332]:

$$U_i = \frac{F}{RT} D_i \qquad 3.27$$

The transport of ions across the membrane due to electro-migration and convection is generally much higher than the diffusional transport.

## **CHAPTER 4**

# **EXPERIMENTAL**

# 4.1 General

The chemicals and the equipment used for the different experiments in subsequent chapters are described in this chapter. Experimental procedures for studying various aspects of membrane processes of the vanadium redox cell as outlined in Chapter 1 are described in their respective sections.

# 4.2 Materials and chemicals

#### 4.2.1 Chemicals

The following chemicals were employed in the course of this work and they were of analytical grades unless otherwise specified. The chemicals were used as received without further purification.

- a) Vanadyl sulphate, (VOSO<sub>4</sub>. $H_2O$ ) and (VOSO<sub>4</sub>. $5H_2O$ ), Merck Chemicals Ltd., Germany.
- b) Vanadium pentoxide flakes  $(V_2O_5)$ , 98.9 % pure, Highveld, South Africa.
- c) Magnesium sulphate (MgSO<sub>4</sub>.7H<sub>2</sub>O), Ajak Chemicals Ltd., Sydney, Australia.
- d) Sulphuric acid 98 %,  $(H_2SO_4)$ , Ajak Chemicals Ltd., Australia.
- e) Sodium persulphate,  $(Na_2S_2O_8)$ , Sigma Chemical Company, U.S.A.
- f) Benzoyl peroxide, BDH Chemicals Ltd., England.

- g) Chlorosulphonic acid, Sigma Chemical Co., U.S.A.
- h) Carbon tetrachloride, Sigma Chemical Co., U.S.A.
- i) Methacrylic acid 99 %, Aldrich Corp., U.S.A.
- j) Divinyl benzene, Sigma Chemical Co., U.S.A.
- k) Styrene, Ajak Chemicals Ltd., Australia.
- 1) 4 Vinyl pyridine 95 %, Aldrich Corp., U.S.A.
- m) Polyethylimine 50 wt.% in water, Aldrich Corp., U.S.A.
- n) Methanol, Ajak Chemicals Ltd., Australia.
- o) Ethanol, Ajak Chemicals Ltd., Australia.
- p) Acetone, Ajak Chemicals Ltd., Australia.
- q) Xylene, Ajak Chemicals Ltd., Australia.
- r) Dimethyl formamide, BDH Chemicals Ltd., Australia.
- s) Polystyrene sulphonate, M.W. 500,000, National Starch & Co., U.S.A.
- t) Carboxy methyl cellulose sodium, M.W. 120,000, Tokyo Kasei Kogyo Co., Japan.
- u) Amberlite CG400, Rohm & Haas Co., U.S.A.
- v) Sodium sulphate  $(Na_2SO_4)$ , Sigma Chemical Co., U.S.A.
- w) High purity nitrogen gas, CIG, Sydney, Australia.

a) Graphite felt and Electrode:

FMI graphite felt (3 mm), Fibre Materials Inc., Maine, U.S.A.
GFA graphite felt (4.5 mm), Sigri Electrographit GmbH, Germany.
Toray graphite felt (4.5 mm), Toray Industrial Inc., Tokyo, Japan.
Graphite plate, Low porosity graphite (ATJ grade), Carbon Brush Co.,
Sydney, Australia.

Conductive plastic electrode, Toray Industrial Inc., Tokyo, Japan.

Conductive plastic electrode, University of New South Wales, Australia (inhouse development).

Platinum electrode (P101), Radiometer, Copenhagen, Denmark.

Hg/HgSO<sub>4</sub> (in  $K_2SO_4$  solution) electrode (K601), Radiometer, Copenhagen, Denmark.

b) Membranes/separators

Daramic<sup>\*</sup> (0.15, 0.20 and 0.23 mm), W.R. Grace, U.S.A. Selemion<sup>\*</sup>- CMV, CMS, AMV, DMV, ASS and DSV, Asahi Glass Co., Japan.

Selemion\*- CMF (Flemion\*), Asahi Glass Co., Japan.
New Selemion\* (polysulfone), Asahi Glass Co., Japan.
Nafion\* 117 and 324, E.I. Du Pont, U.S.A.
DOW\* XUS1 3204.10, DOW Chemical Co., U.S.A.
RAI R1010 and R4010, Pall RAI Inc., N.Y., U.S.A.

K142, Asahi Chemical Co. Ltd., Japan.

## 4.3 Equipment and Apparatus

## 4.3.1 Equipment

The following types of commercial equipment were used in the course of the study.

- a) Yokogawa Type 3057 Portable Recorder, Japan.
- b) Iwaki Magnet Pumps, Model MD-10 and MD-6, Japan.
- c) G.W. Laboratory DC Power Supply, Goodwill Instrument Co. Pty. Ltd., Taiwan.
- d) Multimeters 7060, Parameters, Korea.
- e) Varian Super Scan 3, Ultraviolet Visible Spectrophotometer, Varian Techtron
   Pty. Ltd., Australia.
- f) Varian Cary 3, Ultraviolet Visible Spectrophotometer, Varian Techtron Pty.
   Ltd., Australia.
- g) Conductivity Meter, Radiometer, Copenhagen, Denmark.
- h) Field Electron Scanning Electro Microscope (FESEM), Hitachi S-900, Japan.
- i) Ion-exchange Chromatograph, Waters Model 590, IC-Pak Column.
- j) Coulter Porometer, Coulter Electronics Limited, U.K.
- k) 910 Differential Scanning Calorimeter, Du Pont Thermal Analyst 2100 System.
- Thermogravimeter, Du Pont 951 TGA module and TA2100 software operating system.
- m) AutoPoro-9200, Micromeritics, U.S.A.

- n) Labtest ICP Spectrometer/Monochromator, Model Plasmalab, Australian
   Branch of Applied Research Laboratories, Australia.
- ATR-Infrared, Mattson Instruments Inc., Sirius 100, Liquid cooled MCT detector, ATR Accessory-KRS5 Crystal.

## 4.3.2 Diffusion test cell and Area resistance test cell

a) PVC cell used for static diffusion measurement

A schematic drawing of the PVC cell is shown in Figure 4.1. For the static diffusion test, two half-cells were mounted together with the membrane pressed in the centre between two rubber gaskets, which were used to seal the cells to prevent leakage. The two half-cells were tightened using bolt and nuts. The half-cell was constructed from a PVC block with the cavity of the cell machined out. The area of the membrane (size:  $5 \times 5$  cm) exposed to the solutions was  $25 \text{ cm}^2$ . The volume of the solutions used for each of the half-cell was  $65 \text{ cm}^3$ .



Figure 4.1 Diagram showing the components and the setup of the static diffusion test cell.

b) Flow diffusion test cell

The material used for the construction of the flow diffusion test cell is clear perspex. The set-up and the assembly of the flow diffusion test cell as shown in Figure 4.2 is similar to the redox flow test cell discussed in Section 4.3.3. However, in this case no electrode is used. The area of the membrane (size: 5 x 6 cm) exposed to the solution is 30 cm<sup>2</sup>. The volume of the solutions used for each half-cell is 100 cm<sup>3</sup>. Pumps are used to circulate the solutions through the half-cells.



Figure 4.2 Diagram showing the setup of the flow diffusion test cell.

### c) Area resistance test cell

The same cell as discussed in part (a) was used for measuring the area resistance of the membrane. The set-up used is illustrated in Figure 4.3. The membrane to be tested is glued between two rubber gaskets which have a centimetre diameter hole punched in the middle. The rubber gaskets are assembled and pressed in between the two half-cells. Silicon rubber is used to glue the membrane to the gaskets as well as providing an insulating layer to ensure that the area of the membrane exposed to the solution is of the same diameter as the hole. Care is required to ensure the silicon rubber does not cover the area of membrane to be exposed to the solution. The volume of solution used in each half-cell is 50 cm<sup>3</sup>. A pair of graphite plate electrodes is used and the electrical contact with the electrode is provided by a copper rod inserted into it and secured with silver epoxy resin. The electrical resistance of the electrode measured between the copper rod and the graphite plate was less than 0.1  $\Omega$ .



Figure 4.3 Setup of the cell used for measuring the area resistance of the membrane.

# 4.3.3 Redox flow test cell

## a) PVC redox flow test cell

The schematic drawing of the components of the PVC redox flow test cell is shown in Figure 4.4, while the setup of the redox flow test cell was presented in Figure 2.1. All the plastic components of the cell are made of PVC material. The two half-cells are of symmetrical construction. Graphite felt electrodes (2 mm thickness) are used with graphite plates as the current collectors. The graphite plates used are pretreated by soaking in molten wax under vacuum for an hour. This procedure seals off the pores in the graphite plates, thus ensuring no reaction occurs in the pores which can be detrimental to the electrodes. The electrical contact with the electrode is provided by the copper rod inserted into the graphite plate and secured by using silver epoxy resin. The cavity of each half-cell is 1 mm. The electrical contact between the felt (2 mm) and the graphite plate is provided by compression when the cell is assembled. The membrane is placed in between two rubber gaskets which provide the seal. Rubber gaskets of different thickness can be used to vary the degree of compression on the felt. Clear polyethylene tubing is used to connect the cell to the solution reservoirs and to the pumps. The volume of the reservoir can be varied by using different sizes of glass tubing sealed at one end. The electrode and the membrane areas are 25 cm<sup>2</sup> and 30 cm<sup>2</sup> respectively. The experimental set-up for the charging/discharging test is shown in Figure 4.5.



Figure 4.4 The schematic drawing of the components of the PVC redox flow test cell.



Figure 4.5 The experimental set-up for the charging/discharging test.

b) Redox flow test cell using graphite felt bonded to the conductive plastic electrode.

The components and the assembly of the cell is shown in Figure 4.6 and the set-up of the experiment is similar to that shown in Figure 4.5. The front view of the flow frame used in this cell is shown in Figure 4.7. All the plastic components used in the construction are PVC material. The rubber gasket is made from Neoprene rubber. Copper plate is used as the current collector. Stainless steel end-plates are used to ensure even compression pressure over the entire surface of the test cell components.

Threaded stainless steel tie rods are placed with even spacings around the test cell to compress and hold all the components in place.

The design of the flow frame is to ensure uniform electrolyte flow through the felt electrode. The electrolytes are pumped through the primary manifold (Figure 4.7) entering the half-cell cavities. At this point, the electrolytes enter the secondary manifold which distributes the electrolytes in a 'laminar' manner through the felt electrode. The electrolytes exit the test cell via the primary manifold and re-enter the circulating electrolyte circuit.



Figure 4.6 Diagram showing the components of the redox flow test cell using conductive plastic-graphite felt electrode.



Figure 4.7 Redox cell flow frame showing flow ports and manifolds.

The superficial area of the graphite felt is  $138 \text{ cm}^2$  and the membrane area is  $160 \text{ cm}^2$ . Conductive plastic-felt electrodes are produced using the procedure described in [168]. The thickness of the graphite felt used in the present cell is 4 mm. Graphite felt obtained from different suppliers (Section 4.2.2 (a)) can be thermally bonded to the conductive plastic to produce either bipolar or end electrodes. Multi cells battery stack can be constructed by using bipolar electrodes and additional flow frames. The bipolar electrodes have graphite felts bonded on both side of the conductive plastic,

while end electrodes are fabricated by bonding graphite felt onto one side and copper or brass mesh onto the back of a conducting plastic sheet.

The major differences between the PVC test cell and this test cell are the type and the area of the electrode used, and the flow pattern of the electrolytes introduced to the cell. Moreover, in this design, multi cells can be easily constructed by using bipolar electrodes and flow frames.

## 4.3.4 Automatic controller

An automatic controller developed in-house is used to control and deliver or withdraw preset constant current from the vanadium redox cell during charging/discharging. The connection of the controller to the whole set-up for the charge/discharge experiment is shown in Figure 4.5. The schematic diagram of the controller box as shown in Figure 4.8 has features such as: adjustable knobs to preset upper and lower voltage limit for the battery to be cycled, a dial to preset discharge current, automatic or manual control - with switches to put the battery in the charging or discharging mode, and connection terminals to the battery and the power supply. The voltage limit can be set from 0 to 20 V while the current can be varied from 0 to 10 A.

The automatic controller box monitors the cell voltage and continuously charge and discharges the cell between the preset upper and lower voltage set points. The cell voltage is also displayed in the digital readout on the controller panel. The charge

and discharge currents are set independently by switching the controller knob to manual mode. The charging current is set by adjusting the current knob on the power supply while the discharge current is set by adjusting the discharge current setting knob on the automatic controller box.



Figure 4.8 Automatic controller box used for charge/discharge cycling.

## 4.3.5 Osmotic cell

The osmotic cell shown in Figure 4.9 is used to measured the osmotic water transfer across the membrane separating two solutions. Clear perspex is used for the construction of the cell. The cavity of each half-cell is 40 cm<sup>2</sup> and the area of the membrane exposed is 15.9 cm<sup>2</sup> (membrane radius 2.25 cm). Each half-cell consists of

a perspex tubing, 45 cm in length with internal diameter of 7 mm, inserted into a hole drilled through the perspex block down into the compartment. The membrane is pressed between the two half-cells with rubber "O" rings acting as seals and the cell is tightened using bolts and nuts. Solution is transferred to the half-cell cavity through the port adjacent to the perspex tubing. The port can be sealed with a rubber stopper.



Figure 4.9 Osmotic cell

# 4.3.6 Hydraulic permeation cell

The schematic drawing of the hydraulic permeation cell is shown in Figure 4.10. Clear perspex is used in the cell construction. The area of the membrane exposed to the solution is 15.9 cm<sup>2</sup>. Nitrogen gas from cylinder is connected to the cell and delivers a set pressure on the solutions side. The solution in the cell is vigorously stirred using a magnetic stirrer. The membrane is supported on a porous ceramic disc. The permeate can flow freely in the porous ceramic disc and is collected through a stainless steel tubing connected to the permeate side of the cell. An "O" ring is used on the solution side to seal off any leakage of solution over the edge of the membrane.



Figure 4.10 Hydraulic permeation cell

#### 4.3.7 Technique employed in the vanadium electrolyte preparation.

The technique used for the preparation of vanadium electrolytes used in the vanadium redox battery is described here. The preparation of vanadium solution in  $H_2SO_4$  is achieved by the electrolytic dissolution of  $V_2O_5$  powder, finely suspended in  $H_2SO_4$  [161,166]. The theoretical aspects of the vanadium electrolyte preparation are discussed in Section 3.1.2. The electrolysis cell used is shown in Figure 4.11. The two compartments of the cells are separated by an ion-exchange membrane, and flat sheet lead electrodes are used for both the anode and the cathode. The electrolytic reduction of  $V_2O_5$  proceeds in the cathode compartment while at the anode side,  $O_2$  evolution occurs.  $H_2SO_4$  of the same concentration is used in both of the compartments so as to reduced any osmotic transfer of water across the membrane. A cation-exchange membrane is used to ensured  $H^+$  ion is the major current carrying ion. Nitrogen gas is bubbled through the cathode compartment to promote stirring and assist in mass transfer. Electrolysis is allowed to proceed until the catholyte consists of 1:1 mixture of V(III) and V(IV).

The concentration of vanadium ions can be readily determined by redox titration with KMnO<sub>4</sub>. In determining the concentration of a vanadium solution containing V(V) ions, zinc is usually used to reduced the V(V) present in the solution to a lower oxidation state before titration. The determination of  $SO_4^{2-}$  ions concentration is done using Inductively Couple Plasma (ICP) technique. Since the ICP technique can only determine concentration in ppm, dilution of the sample is required, and this can introduce significant errors in the result obtained.



Figure 4.11 A schematic drawing showing the set-up of an electrolysis cell for the preparation of vanadium electrolytes.

#### **CHAPTER 5**

## **EVALUATION OF COMMERCIAL MEMBRANES**

#### 5.1 Introduction

The primary functions of a membrane/separator in the vanadium redox cell are to prevent cross-mixing of the positive and the negative side electrolytes, prevent short circuiting of two half-cell electrodes and at the same time, permit the transport of charge balancing ions during the passage of current. Commercially available membranes with low area resistance and low diffusivity would be ideal. However, other factors which are not related to the membrane's performance such as mechanical strength, chemical inertness and cost, should also be taken into consideration.

Screening of commercially available membranes was conducted to identify suitable membranes to be used as separators for the vanadium redox battery. The requirements of the separator are listed in Chapter 1. Initial screening of the membranes involved measuring the area resistance and the diffusivity of the membrane. These tests were simple, quick and relatively easy to conduct compared to the charge/discharge test. In the charge/discharge test, other variables such as cell polarisation and side reactions could affect the efficiencies obtained even when the same membrane is used. General inspection of the whole membrane sheet for pinhole defects was also carried out. Membranes which exhibited low resistance and diffusivity were further tested in charge/discharge cycling of the vanadium redox

flow test cell. Extended charge/discharge cycle testing was conducted for those membranes which had exhibited excellent performance in the initial cycling test. The long term charge/discharge cycling revealed the stability of the membrane and its performance with time. Promising membranes selected from the screening test were also subjected to accelerated life testing in the highly oxidative environment consisting of 2 M V(V) in  $H_2SO_4$ .

The following types of membranes were evaluated:

- a) Conventional cross-linked ion-exchange membrane
- b) PTFE-based membrane (cation-exchange type)
- c) Radiation grafted membrane

The properties of some of these membranes provided by the manufacturers are presented in Table 5.1. It should be noted that the values shown are very dependant on the methods by which the measurements are done. Therefore, direct comparison of these values can be erroneous.

Flemion<sup>\*</sup> refers to a family of Asahi Glass Co. products ranging from all-carboxylate and all-sulphonate membranes to composites of sulphonate/carboxylate membranes. The Flemion<sup>\*</sup> membrane shown in Table 5.1 is a cation-exchange sulphonate membrane.

	Table 5	.1 Pr	operties	of	some	commercial	membranes
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Membrane type	Thickness (mm)	Area resistance $(\Omega \text{ cm}^2)$	Transport number	Water content (g H <sub>2</sub> O/g dry form)	Ion-exchange capacity (meq/g dry form)
Anion-exchange membrane Selemion <sup>*</sup> AMV Selemion <sup>*</sup> DMV Selemion <sup>*</sup> ASS Selemion <sup>*</sup> DSV	0.15 - 0.13 0.14	3.0 - 2.5 -	>0.94 - >0.95 -	16 - 16 -	2.3 - 2.3 -
Cation-exchange membrane Selemion <sup>*</sup> CMV Selemion <sup>*</sup> CMS	0.15 0.13	3.5 2.0	>0.92 >0.92	16 16	1.8 1.8
PTFE-based ionomer Nafion <sup>*</sup> 117 Nafion <sup>*</sup> 324 Flemion <sup>*</sup> DOW <sup>*</sup> XUS1 3204.10	- 0.28 0.1	1.5 4.5 2.7 1.0	- - 0.65-0.75 -	- - 20-24 52	- - 1.1 -

1) For Selemion<sup>\*</sup> membrane, resistance measurement is done in 0.5 M NaCl at 25 °C, transport number for Na<sup>+</sup> is calculated from membrane potential of 0.5/1.0 M NaCl at 25 °C.

2) For Nafion<sup>\*</sup> membrane, resistance measurement is done in 0.6 M KCl at 23 °C.

3) For Flemion<sup>\*</sup> membrane, resistance measurement is done in 12 % NaOH at 25 °C.

4) Measurements are for membrane in  $H^+$  form.

The Selemion<sup>\*</sup> type membranes are made from styrene-divinyl benzene polymeric material. The cation-exchange type have sulphonate ionic groups while the anion-exchange type have quaternary ammonium groups. All the PTFE-based membranes shown in Table 5.1 have sulphonate groups. Swelling and expansion of the membranes is less pronounced with the Selemion<sup>\*</sup> type, but for the teflon<sup>\*</sup>-based ionomer, this is quite substantial.

## 5.2 Experimental

## 5.2.1 Membrane diffusion measurement

The diffusivity of the membrane was measured with the method described in [9,10]. It involved measuring the absorbance of the diffusate (VOSO<sub>4</sub>) using UV-Visible spectrophotometry technique and relating the absorbance to its concentration using Beer's law.

## a) Static diffusion test

The membrane diffusivity was evaluated by measuring the diffusion rate of VOSO<sub>4</sub> across the membrane. The cell used is described in Section 4.3.2.a. The membrane was exposed to 1 M VOSO<sub>4</sub> in 2 M  $H_2SO_4$  on one side and 1 M MgSO<sub>4</sub> in 2 M  $H_2SO_4$  on the other side. 65 cm<sup>3</sup> of the solutions were transferred to each half-cell. MgSO<sub>4</sub> was added to equalise the ionic strength of the two half-cell solutions, thus reducing the osmotic pressure effect. Periodically, a 3 cm<sup>3</sup> sample of the solution on the initial vanadium free solution side was taken and the absorbance of the solution

measured using a UV-Visible spectrophotometer. The sample solution was then returned to the cell. The experiment was terminated when the absorbance of the sample reached 1.

#### b) Flow diffusion measurement

Flow diffusion measurements of some membranes were conducted to compare their diffusivities with the values obtained in the static case. The diffusivity obtained in the flow system would relate more closely to the diffusional flux in the actual vanadium redox cell system. The setup of the flow diffusion cell is described in Section 4.3.2.b. Pumps were used to circulate the solutions through the cell, volume of solutions used for each side being 100 cm<sup>3</sup>. The procedure employed for the measurement was similar to that described for the static case.

## 5.2.2 Area resistance measurement

The area resistance of the membrane was measured using the cell described in Section 4.3.2.c. The membrane was glued using silicone rubber between two rubber gaskets which had a 1 cm diameter hole in the middle. Only this area of the membrane was exposed to the solution. The electrolyte used for the cell was 2 M  $VOSO_4$  in 3 M  $H_2SO_4$  for both half-cells (volume used was approximately 40 cm<sup>3</sup> for each side). The electrodes used were flat graphite plates, with area significantly larger than the area of the membrane exposed to the solution. The resistance of the membrane was determined by measuring the conductance using a radiometer conductivity meter which employed a low voltage, high frequency AC signal (2 kHz)

to ensure no significant reaction occurred at the electrodes. The value of conductance was taken once the reading on the conductivity meter stabilised. For some membranes, this could take more than 24 hours. Also measured was the conductance with the same setup where no membrane was attached to the gaskets. The area resistance was calculated from the measured conductance using equation 5.1.

Where R is the area resistance of the membrane ( $\Omega$  cm<sup>2</sup>)

C is the conductance of the membrane (mS)

The area resistance of the membrane was obtained by subtracting the cell resistance without the membrane present to that with the membrane present.

# 5.2.3 Charging/discharging test

The laboratory redox flow test cell used in the charge/discharge testing of the membrane is described in Section 4.3.3. During the course of the project, different designs of the laboratory redox flow test cell were developed employing different electrode materials. The different cell designs were tested to demonstrate the maximum achievable efficiency obtained by the vanadium redox battery. However, by using the same cell type with identical electrode materials but different membranes, any differences in the cell efficiencies obtained can attributed to the membrane.

For the charge/discharge test, the test membrane was used as the separator for the cell. For the initial cycle, the solution used for the two half-cells consisted of equal volumes of 1 M V(III) + 1 M V(IV) in 2.5 M H<sub>2</sub>SO<sub>4</sub>. The preparation of the electrolytes is discussed in Section 4.3.7. The volume of electrolyte used for each of the half-cells was 65 cm<sup>3</sup> for the PVC redox flow cell (Section 4.3.3.a) and 250 cm<sup>3</sup> for the Redox flow cell using the conductive plastic electrode (Section 4.3.3.b).

Charging/discharging of the cell was conducted at constant current and the cell performance was evaluated over a range of different current densities. The initial solution was first charged up to V(IV) on the positive side and V(III) on the negative side representing 0 % SOC. The cell was then charged further to produce V(V) on the positive side and V(II) on the negative side when the cell attained 100 % SOC. In the single cell cycling test, the cell was charged to an OCV of 1.6 V (above 99 % SOC) corresponding to the charging cell voltage of 1.70 to 1.80 V, depending on the cell electrical resistance and the current density applied. When the cell reached the upper limit of the charging voltage which could be set, the automatic controller reversed the current direction to discharge the cell. The cell was discharged to a lower voltage limit of 0.8 V corresponding to about 1 % SOC. When the cell voltage reached the lower limit, the automatic controller switched the cell to charging.

The V(II) solution on the negative half-cell was prone to air oxidation, and in the experimental setup, the opening of the reservoir was sealed with a double layer of flexible polyethylene sheet (PE). The PE sheet would expand outward if any hydrogen gas was released. A thin film of paraffin oil was also used in some tests to

cover the surface of the V(II) solution and was found to be capable of eliminating the air oxidation.

Polarisation measurements were also conducted to evaluate the cell resistance during charging and discharging. The cell resistance was measured at 50 % SOC for both the charging and discharging cycles. The automatic controller was switched to charging and discharging modes alternate to obtain the polarisation voltage at various applied current densities. With this technique, the OCV of the cell before and after the polarisation measurements remained the same, indicating the SOC of the battery remained at 50 % SOC.

## 5.2.4 Long term stability testing of commercial membranes.

The oxidative nature of V(V) solution tends to degrade the membrane material, reducing its cycle life. Accelerated degradation of the membrane was thus carried out in the V(V) solution. The stability of the membranes was tested by immersion in 2 M V(V) solution which was obtained from the charged positive half-cell solution. Periodically, the membrane area resistance and the diffusivity values were measured using the methods discussed earlier. Degradation of the membrane could also be evaluated by physical examination. Any erosion of the membrane material or pinholes developed were due to the deterioration of the polymeric material.

The long term stability of the membrane tested in the charge/discharge cycling represented a more accurate measure of the membrane life in the vanadium redox
cell. Cycle testing of the membrane was continued until the membrane failed, which manifested itself with low coulombic efficiency. However, during the cycle testing, the cell capacity dropped off gradually as a result of volumetric crossover of electrolyte across the membrane, or the side reactions occurring such as oxygen evolution on the positive side or hydrogen evolution on the negative side. Hence, it was necessary to rebalance the cell periodically with the techniques described in Section 5.3.3. The cell was rebalanced when the capacity dropped to half of its initially capacity.

## 5.3 Results and discussion

#### 5.3.1 Diffusivity and area resistance of commercial membrane.

 $VOSO_4$  in sulphuric acid medium was selected for the resistance and diffusivity measurements since it is a more stable vanadium species compared with other oxidation states. Moreover, the predominant vanadium species present in the separator of the vanadium redox cell are V(III) and V(IV).

In the diffusion experiment, the absorbance of the vanadium solution measured using the UV-visible spectrophotometer is related to its concentration according to Beer's law. The mathematical derivation of the equation relating absorbance and the diffusivity of the membrane is represented by equation 5.2 [9,10].  $\ln[abs B^{\circ} - 2abs A] = \ln [abs B^{\circ}] - [2K_sAt]/V_A \qquad 5.2$ 

where abs B° is the initial absorbance of the solution on the concentrated side.

abs A is the absorbance of the solution on the permeate side at time t (min).

A is the area of the membrane  $(cm^2)$ 

 $V_A$  is the volume of the permeate side (cm<sup>3</sup>)

t is the time (min)

 $K_s$  is the diffusivity of V(IV) ion across the membrane (cm/min)

A plot of ln [abs B° - 2 abs A] versus t will give a straight line with a slope equal to  $-2K_sA/V_A$  (from which the membrane diffusivity,  $K_s$  can be determined) and with an intercept equal to ln [abs B°]. The linearity of the plots of the experimental data confirms the validity of equation 5.2. The values of diffusivity ( $K_s$ ) calculated from the slope obtained from linear regression, are shown in Table 5.2. The  $K_s$  value determined from equation 5.2 is actually the permeability of the membrane, however, to be consistent with the previous published works [9,10] which use the term - diffusivity, this term is also used throughout this thesis.

Before commencing the diffusion experiment, the UV-visible spectrographs of solutions of different concentration of V(IV) were obtained to find their peak absorbances wavelengths and the concentration at which deviation from Beer's law occurs. Figure 5.1 shows the UV-visible spectrographs for various concentrations of V(IV) in 2 M  $H_2SO_4$ . Figure 5.2 is a plot of peak absorbance (from Figure 5.1) versus V(IV) concentration, showing that Beer's law is obeyed up to an absorbance of 1, corresponding to a V(IV) concentration of about 0.06 M. In the diffusion experiment, the wavelength of 760 nm corresponding to the peak maxima for

concentration up to 0.05 M V(IV) was used for the absorbance measurements. All the tests were terminated when the absorbance reached a value greater than 1 to avoid deviation from linearity according to Beer's law. Figure 5.3 is a typical plot obtained by using equation 5.2 for evaluation of the diffusivity of the membrane.



Figure 5.1 UV-visible spectrographs of 0.01 M to 0.1 M V(IV) in  $H_2SO_4$ .



Figure 5.2 Plot of peak absorbance versus V(IV) concentration.



Figure 5.3 A typical plot of ln [abs B° - 2 abs A] versus t for diffusion test cell experimental data.

The diffusivity of two commercial membranes, CMV and Daramic<sup>\*</sup> was also measured using the flow diffusion method discussed in Section 4.3.2.b. Their diffusivity values are presented in Table 5.2. Also included in the same table for comparison purpose are diffusivity values of the same membranes obtained from the static diffusion test.

Table 5.2Diffusivity of membrane obtained from flow diffusion and static<br/>diffusion tests.

	Diffusivity, K <sub>s</sub> (cm min <sup>-1</sup> )		
Membrane type	CMV	Daramic*	
Flow diffusion test value	3.0 x 10 <sup>-5</sup>	1.6 x 10 <sup>-3</sup>	
Static diffusion test value	2.6 x 10 <sup>-5</sup>	1.4 x 10 <sup>-3</sup>	

The diffusivity values obtained from the flow diffusion test are marginally higher than those obtained with the static test. According to Helfferich [66,p346], the overall diffusion rate from bulk solution on one side to bulk solution on the other side may be controlled by diffusion in either the membrane (membrane diffusion control) or in the films-the Nernst diffusion layers (film diffusion control). For ion-exchange membranes and diffusion of electrolytes, membrane diffusion control predominates. The rate controlling step in the diffusion process is not affected by the thickness of the film which invariably can be affected by stirring. Hence, the diffusivity values obtained in the flow or the static case should not differ appreciably. Therefore, all the latter diffusivity values reported were based on the static diffusion test. The area resistance and the diffusivity of some commercial membranes tested are shown in Table 5.3. It should be pointed out that the measured values of the area resistance and the diffusivity presented in Table 5.3 are only to serve as comparison rather than an absolute measure of resistance and diffusivity of the membranes. The membranes when used as separators in the vanadium redox cell would be exposed to vanadium ions of different oxidation state on either side of the membranes. Hence, the actual resistance and the permeation of the vanadium ions across the membranes could be different compared to the to the values predicted by the diffusivity data. However, it was found that the values of the measured area resistance and diffusivity were quite reliable in predicting the efficiency expected of the redox flow cell employing a particular membrane.

From Table 5.3, it can be seen that the area resistance of all the membranes tested is low with the exception of Nafion<sup>\*</sup> 324 and RAI R4010 membranes. NASA research on the Fe/Cr NASA redox battery had set a criterion for membrane area resistance values less than 3  $\Omega$  cm<sup>2</sup> as acceptable [133]. However, membranes with the lowest area resistance were sought to reduce ohmic losses and increase the power output of a battery of similar size.

# Table 5.3 Area resistance ( $\Omega$ cm<sup>2</sup>) and diffusivity (cm min<sup>-1</sup>) for some

Membrane type	Thickness (mm)	Area resistance $\pm 0.1 (\Omega \text{ cm}^2)$	Diffusivity $\pm 0.05$ x10 <sup>5</sup> (cm min <sup>-1</sup> )
Anion-exchange membrane Selemion <sup>*</sup> AMV Selemion <sup>*</sup> DMV Selemion <sup>*</sup> ASS Selemion <sup>*</sup> DSV	0.16 0.14 0.13 0.11	2.8 2.1 2.7 1.0	0.32 2.40 0.10 7.90
Cation-exchange membrane Selemion <sup>*</sup> CMV Selemion <sup>*</sup> CMS	0.14 0.11	2.6 1.7	2.60 3.90
Teflon <sup>*</sup> -based ionomer Nafion <sup>*</sup> 117 Nafion <sup>*</sup> 324 Flemion <sup>*</sup> DOW <sup>*</sup> XUS1 3204.10	0.21 0.26 0.27 0.13	1.5 3.4 2.4 0.5	19.4 11.3 3.25 84.1
RAI R1010 RAI R4010	0.04 0.06	0.4 8.4	3.02 0.21
K142	0.12	0.9	6.65

commercial membranes tested.

Membranes thicknesses quoted in Table 5.3 were obtained when the membranes had been equilibrated in  $V^{3.5+}$  solution. Generally, the thickness of the membrane also affects its resistance, being higher with increase in thickness for the same type of membrane. This is due to the increase in the tortuosity of the membrane. Tortuosity is defined as the effective path length divided by the thickness of the membrane.

For an ion-exchange membrane equilibrated in the electrolyte, the concentration and the mobility of ionic species present in the membrane also affect its electrical conductivity [55]. For charged membranes, the concentration of mobile counter ions should increase with increase in ion-exchange capacity, which in turn lowers the resistance of the membrane. For a cation-exchange membrane which is equilibrated in VOSO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub>, the counter ions are the H<sup>+</sup> ions and the vanadium ions. In the case of an anion-exchange membrane, the counter ions are the SO<sub>4</sub><sup>2-</sup> ions. Higher conductivity would be expected of the cation-exchange membrane since the mobility of H<sup>+</sup> ions is substantially higher than the SO<sub>4</sub><sup>2-</sup> ions. However, from the area resistance values shown in Table 5.3, both cation and anion-exchange membranes exhibit low resistance in the VOSO<sub>4</sub> electrolyte. The possible reason being the presence of H<sup>+</sup> ions in high concentration within both types of membranes, which is not effectively excluded by their fixed ionic groups. Hence, it will be expected, in the vanadium redox cell, the H<sup>+</sup> ions will be the major current carrying ions when these membranes are employed.

The permeation rate of V(IV) ions are lower for AMV and DSV membranes compared to DMV, DSV and other cation-exchange membranes shown in Table 5.3. The fact that AMV and DSV membranes have lower permeation rate of V(IV) ions compared to DMV and DSV could be due to their difference in the ion-exchange capacity. According to the Donnan exclusion principle, co-ions (vanadium species) are partially excluded from the anion-exchange membranes whereas a cationexchange membrane is incapable of restricting vanadium species from entering [66,p134]. The higher the ion-exchange capacity, that is, the higher the fixed charges, the greater is the exclusion effect. With the membranes exposed to high ionic strength test solutions, it should be expected that the repulsion of the co-ions by the fixed positive charges will be greatly reduced, as they are effectively shielded.

Besides the shielding effect of the fixed positive charges of anion-exchange membrane in the high ionic strength vanadium solution, the presence of negatively charged V(IV) complexes could also reduce its efficiency in excluding the V(IV) species. Studies done by Ivakin et.al.[164] for the V(IV) complexes with sulphuric acid confirm the existence of the complexes VOSO<sub>4</sub>, VO(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup> and VOHSO<sub>4</sub><sup>+</sup> The stability constants for the VOSO<sub>4</sub> and VO(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup> are large, indicating the presence of both complexes in the V(IV) solution. Therefore, it will be expected that the diffusivity of both cation and anion-exchange membranes is effectively increased by the presence of both positive and negative species.

The hydraulic permeability of the membranes shown in Table 5.3 was also measured using the permeation cell discussed in Section 4.3.6. No flux across all the membranes was recorded when the differential pressure of up 101.3 kPa was applied for more than 24 hours. The minimum flow that could be measured from the hydraulic permeation cell is approximately 0.05 ml.

### 5.3.2 Charge/discharge test.

## 5.3.2.1. Capacity loss

In the charge/discharge tests, the cell was cycled from an upper cell voltage limit of 1.8 V to the lower cell voltage limit of 0.8 V. With this type of cycling, any one of the following three situations would prevail:

# First case

In the first case, if the total vanadium content for each half-cell is the same and both

half-cell solutions are at the same SOC, then the maximum cell capacity can be realised.

#### Second Case

In the second case, the SOC of the two half-cell solutions is different and the vanadium content in the two solutions is the same. In this instance, the SOC of one half-cell solutions would lag behind the other. When one half-cell solution is fully charged, polarization of that half-cell will occur, causing the automatic controller to switch to discharge mode. During discharge, the other half-cell solution will be fully discharged first. Therefore, the available capacity of the solutions will be reduced by 2 times the difference in the SOC of the solutions.

## Third Case

In the third case, which is the predominant case in the latter stages of the cycling test, the total vanadium content of one half-cell solution is higher than the other and the SOC of the two solutions at any stage of charging and discharging is different. During cycling, differences in the diffusion of the different vanadium ions across the membrane leads to the preferential transport of vanadium ions from one half-cell to the other. Thus, the vanadium content of the negative half-cell solution becomes depleted in the cell using a cation-exchange membrane, while when an anion-exchange membrane is used, the positive half-cell solution would be depleted (refer Chapter 7). In this situation, the half-cell solution with the lower vanadium content will be fully charged or fully discharged faster than the other half-cell solution. The capacity of the cell will be governed by the half-cell solution with lower vanadium content.

When a fully balanced cell is charged to the upper limit of 1.8 V and discharged to the lower limit of 0.8 V at current densities in the range of 10 to 40 mA cm<sup>-2</sup>, about 98 % utilization of the cell capacity is realised. With continuous cycling, however, the cell capacity drops off steadily. The rate of capacity loss for some membranes has been investigated further in Chapter 8, however, the most significant loss in cell capacity was found to arise from the imbalance in the SOC of the two half-cells resulting from ion transport through the membrane during the cycle testing, which alters the concentration of the vanadium and the sulphate ions in both reservoirs. In serious cases, crystallization occurred which could affect the conductance of the solution as well as reducing the active electrode surface area. This manifested itself as a continuing decline in voltage efficiency during cycle testing. Crystallization of V(III) sulphate on the felt electrodes was also shown to be detrimental to the stability of the otherwise very chemically inert Flemion<sup>\*</sup> membrane.

The air penetrating the 'unsealed' (since the flexible polyethylene sheet used to seal the reservoir, was not completely effective) negative half-cell also caused oxidization of V(II) to V(III), leading to a drop in cell capacity of 0.1 to 0.5 % per cycle. But this could be prevented by using paraffin oil to form a thin film on the solution surface, thereby preventing any air contact.

During charging, when the cell was out of balance, side reactions for either oxygen and hydrogen evolution occurred depending on which half cell reached the upper limit first. This would further increase the difference in the SOC's of the two halfcell solutions and also, decreased the coulombic efficiency of the cell. Oxygen

evolution could be avoided by stopping the charging when polarization occurred. But hydrogen evolution was harder to control since its potential and the V(III) reduction potential are close together. For the graphite felt electrode used, the loss in coulombic efficiency due to hydrogen evolution was less than 0.5 % (from measurement of gas collected during cycling test). However, the cell capacity and the cell efficiencies could be fully restored by equalizing the SOC's of the two half-cell electrolytes. This was achieved by mixing the anolyte and the catholyte and flushing the mixed solutions through the cell to ensure consistency in the vanadium ion concentration throughout the whole system and then exchanging an appropriate volume of the 'mixed' solutions with V(III) solution. Alternatively, the addition of oxalic acid to the positive half-cell electrolyte can also be used to reduce the appropriate fraction of V(V) to V(IV), thereby equilizing the SOC's of the solutions.

#### 5.3.2.2 Cell efficiencies

All the membranes tested for their diffusivity and resistance shown in Table 5.4 were subjected to charge/discharge tests in the vanadium redox test cell. From these tests, the coulombic efficiency was the ratio calculated from measurement of coulombs input and output during charge and discharge respectively. Since, both the charging and discharging currents are the same and constant for the full cycle, the energy efficiency could be obtained by integrating the areas (equation 3.23) under the charge and discharge curves recorded by the chart recorder and taking their ratios. The voltage efficiency was obtained by dividing energy efficiency by coulombic efficiency. The coulombic, voltage and energy efficiencies obtained using each

membranes in the charge/discharge test, could be related back to their resistance and the diffusivity values established earlier. Criteria for the membrane resistance and diffusivity values which would produce acceptable performance when being employed in the vanadium redox cell could then be established. The efficiencies of the vanadium redox test cell utilising a variety of membranes are presented in Table 5.4. Unfortunately, during the tests on the DOW<sup>\*</sup> and RAI R1010 membranes, problems associated with membrane splitting or electrode deterioration meant that the results obtained for these membranes are unreliable and therefore are not included in Table 5.4.

Table 5.4Cell efficiencies obtained from charge/discharge tests of the vanadiumredox cell employing different commercial membranes.

Membrane type	Testing conditions	Coulombic	Efficiency (%) Voltage	) Energy
Anion-exchange membrane Selemion <sup>*</sup> AMV Selemion <sup>*</sup> DMV	1 1	98.5 98.1	81.4 87.2	80.2 85.5
Selemion <sup>*</sup> ASS Selemion <sup>*</sup> DSV	2 2	96.0 91.0	77.0 86.9	74.1 79.0
Cation-exchange membrane Selemion <sup>*</sup> CMV (1) " (2) Selemion <sup>*</sup> CMS	2 1 2	94.1 97.2 94.2	82.0 86.2 80.9	77.2 84.1 76.2
PTFE-based membrane Nafion <sup>*</sup> 117 Nafion <sup>*</sup> 324 Flemion <sup>*</sup>	1	95.2 - 96.1	87.3 - 87.0	83.1 - 84.1
K142	2	93.0	87.2	81.1

1) obtained using the cell discussed in section 4.3.3.b. employing Toray felt bonded to the conductive plastic at constant charge/discharge current density of 30 mA cm<sup>-2</sup>. 2) obtained using the PVC cell discussed in Section 4.3.3.a. employing FMI felt at the constant charge/discharge current density of 40 mA cm<sup>-2</sup>. The cell efficiencies presented in Table 5.4 are the average efficiencies obtained over the first 10 cycles using the different membranes in the vanadium redox test cell. All the membranes employed in the vanadium redox test cell produced acceptable energy efficiencies as shown in Table 5.4. Further charge/discharge testing on DOW<sup>\*</sup> was abandoned because of the poor mechanical properties (which is susceptible to splitting) of this membrane for the redox flow cell application. The voltage efficiency for RAI R1010 membrane is 77.2 % even though the resistance of the membrane is low (Table 5.3). This was due to the degradation of the FMI felt electrode after more than 2 months of usage for other membrane testings and further testing was abandoned because of the chemical attack on the membrane by vanadium solution, revealed from physical inspection of the membrane.

As described earlier (Section 4.3.3), two types of redox flow test cell were developed during the course of the project. The first generation redox flow test cell (PVC cell) utilized graphite plates with graphite felt electrode pressed together to achieve electrical contact, whereas the latter type used graphite felts thermally bonded to conductive plastic sheets as electrodes. Using the same type of separator, the cell resistance was reduced by up to 0.3  $\Omega$  cm<sup>2</sup> with the conductive plastic electrodes compared with the graphite plate electrodes.

Evaluation of a range of graphite felt material was conducted simultaneously by other co-workers [168]. Different graphite felt materials, such as the FMI, Sigri and the Toray felt were also tested here. The electro-chemical properties of these materials were extensively studied by Zhong [168]. Initially, the redox test cell was constructed using the FMI graphite felt which was inferior in performance compared to the Toray and the Sigri graphite felt used at the latter stage of the studies. The voltage efficiency during the charge/discharge test was about 5 % higher for the cell using the Toray or the Sigri felt electrodes. The increase in voltage efficiency of the battery using these felt materials was attributed to the higher electro-active surface area present.

The cell efficiencies in Table 5.4 were obtained under various testing conditions. Different current densities were applied for the charge/discharge test for the two types of test cell and the felt material. Hence, direct comparison of the energy efficiency values shown in Table 5.4, obtained with the different membranes is not possible. A new FMI felt electrode showed a slight improvement in electro-chemical activity with cycling but after a month, started to degrade. For the Toray felt material, the electro-chemical activity increased with cycling and this was maintained after more than 12 months usage. In spite of these variations in conditions, however, consultation of both Table 5.3 and Table 5.4 should give a reliable indication of the performance of the membranes for the vanadium redox cell. Generally, a membrane which exhibited low area resistance and diffusivity gave high voltage and coulombic efficiency when tested in the charge/discharge using the same electrode felt material and cell design. However, it should be noted that the voltage and coulombic efficiency obtained in charge/discharge test is also dependent on other factors such as the type of electrode felt used and the cell design rather than just the type of membrane used.

Referring to Table 5.3 and Table 5.4, it is observed that, for membranes with area resistance less than 2.5  $\Omega$  cm<sup>2</sup> and diffusivity less than 2.0 x 10<sup>-4</sup> cm min<sup>-1</sup>, voltage and coulombic efficiencies above 80 and 95 % respectively, could be achieved in the vanadium redox cell. These values of area resistance and membrane diffusion coefficient, measured with the methods described could thus be used as the criteria for undertaking further testing during the screening process.

# 5.3.3 Long term stability testing of membranes in cycle testing.

For all the commercial membranes tested shown in Table 5.4, the energy efficiencies obtained in the charge/discharge tests are considered acceptable with the exception of DOW<sup>\*</sup> membrane. Some of the membranes were selected for stability testing in the long term charge/discharge cycling using the redox flow cell discussed in Section 4.3.3.b. The cell efficiencies obtained as well as the stability of the different membranes tested are illustrated in Figure 5.4 to Figure 5.9. The cell capacity values measured during the cycle testing are also included in the same set of figures.

It should be noted that the cell efficiencies shown in Figure 5.4 to Figure 5.9 are the average cell efficiencies over the entire cycling test, and may differ from those shown in Table 5.4. For the long term charge/discharge cycling, when the cell capacity dropped by more than 50 %, the cell was rebalanced. The numbers shown on the curves in the figures for cell capacity versus cycle number indicate cell rebalancing.

Several techniques used to rebalanced the cell and thereby restore the capacity of the cell were explored. If the anolyte was at a higher SOC than the catholyte, rebalancing could be achieved by exchanging an appropriate volume of the charged positive V(V)solution with an equivalent volume of V(IV) solution or adding an appropriate amount of oxalic acid to the analyte to reduce the V(V) to V(IV). However, both of these methods was shown to be incapable of restoring the cell capacity fully since during cycle testing, there was a gradual accumulation of vanadium ions on either the positive or the negative half-cells depending on the type of membranes used. These observed phenomena will be discussed in detail in Chapter 7. Complete rebalancing could however, be achieved by mixing the anolyte and the catholyte and flushing the mixed solutions through the cell to ensure consistency in the vanadium ion concentration throughout the whole system and then exchanging an appropriate volume of the 'mixed' solutions with V(III) solution. The solution was considered fully balanced if the ratio of V(III) to V(IV) ions was unity. This could be readily confirmed by measuring the half-cell potential of the solutions and compared it with the calibration curve shown in Figure 5.10. The calibration curve was obtained by measuring the cell potential at various ratios of V(III) and V(IV) using a platinum indicator electrode with respect to the Hg/HgSO4 reference electrode. This technique of rebalancing the cell was shown to be capable of restoring the full capacity of the cell.

In the case of the AMV, DMV and CMV membranes shown in Figures 5.4 to 5.6 respectively, a gradual chemical degradation of the membranes resulted in an irreversible decrease in performance. In Figure 5.5, the performance of the DMV

membrane is also seen to drop significantly after 155 cycles. Both the coulombic and the voltage efficiencies decreased giving an overall energy efficiency of 65 %. In Figure 5.4, the performance of AMV membrane was similar to that observed with DMV membrane except the life span of the former was longer. Failure of AMV membrane was characterized by wild variations in coulombic efficiency from cycle to cycle. Examination of both membranes under the microscope showed fractures and erosion of the polymeric material at the fracture sites, thus producing pinholes. The presence of pinholes on the membrane would cause significant self-discharge if the hydraulic pressures on both sides were not the same. If the pinholes were not numerous at the initial stage of deterioration, the impurities present in the solution were capable of sealing them off, thereby improving the coulombic efficiency for a few cycle until more pinholes were developed. Moreover, the erosion of the polymeric material occurring at the anode side confirmed the oxidative nature of the V(V) solution as being responsible for the degradation.





Figure 5.4 Cycle charge/discharge of the vanadium redox cell employing AMV membrane as separator at the current density of 30 mA cm<sup>-2</sup>: a) cell efficiencies versus cycle number for the first 80 cycles, b) cell capacity versus cycle number for the first 80 cycles, c) and d) are for the complete cycling test.







Figure 5.5 Cycle charge/discharge of the vanadium redox cell employing DMV membrane as separator at the current density of 30 mA cm<sup>-2</sup>: a) cell efficiencies versus cycle number for the first 80 cycles, b) cell capacity versus cycle number for the first 80 cycles, c) and d) are for the complete cycling test.







Figure 5.6 Cycle charge/discharge of the vanadium redox cell employing CMV membrane as separator at the current density of 30 mA cm<sup>-2</sup>: a) cell efficiencies versus cycle number for the first 80 cycles, b) cell capacity versus cycle number for the first 80 cycles, c) and d) are for the complete cycling test.



In Figure 5.6, the coulombic efficiency of the CMV membrane is seen to drop to an undesirable level at the 160th cycle. The overall energy efficiency is less than 70 percent compared to the initial 85 percent. Unlike the other membranes, this drop in efficiency is associated with the reduction in the coulombic efficiency of the cell, the voltage efficiency remaining essentially constant or even higher. Physical examination of the membrane after the test showed that the polymeric material had been uniformly eroded by the electrolytes. The highly oxidizing nature of the V(V) solution was also responsible for the observed degradation.

From physical examination of the membranes used in the charge/discharge test, the failure of AMV and DMV membranes were characterised by pinholes formation whereas the CMV membrane showed gradual and uniform erosion of the whole membrane sheet. The deterioration of the membranes also resulted in an increase in both the rate of capacity drop and the volume of solution flux being transfer across during cycling test.

The degradation of the active sites of ion-exchange membranes has tentatively been attributed to the presence of tertiary hydrogen which are particularly susceptible to oxidative attack [158]. The chemical instabilities of the CMV, AMV and DMV membranes was further investigated by soaking in V(V) solution. The CMV membrane showed erosion of the polymeric material in less than one month, whereas DMV and AMV membranes were remarkably stable after eight months of testing. The latter observation was not consistent with the results obtained in the cycling tests and further studies are needed to fully understand the behaviour of this membrane in the vanadium redox cell.

Apart from the gradual drop in efficiency associated with electrolyte imbalance, the performance of both the Nafion<sup>\*</sup> 117 and Flemion<sup>\*</sup> membranes presented in Figure 5.7 and Figure 5.8 was maintained during the entire test period. These two types of membranes had previously been used in charge/discharge cycling to study other transport phenomena associated with the membranes for more than 7200 and 3000 hours respectively. The coulombic efficiency can fluctuate by 4 to 5 percent from cycle to cycle. No appreciable decrease in performance was observed during the testing period. Moreover, no sign of chemical degradation of the membranes was observed when the membrane was soaked in the V(V) solution for a period of 12 months. In the case of the DOW<sup>\*</sup> membrane, as shown in Figure 5.9, the performance of the vanadium redox test cell did not vary significantly even though the diffusivity of this membrane was higher. However, DOW<sup>\*</sup> membrane has poor mechanical property and is susceptible to splitting when it is assembled in the cell. Therfore, the poor coulombic efficiency obtained in the cycling test could be due to mechanical defects of the membrane.





Figure 5.7 Charge/discharge cycle tests of the vanadium redox cell employing Nafion\* 117 membrane as separator at a current density of 30 mA cm<sup>-2</sup>: a) cell efficiencies versus cycle number for the first 80 cycles, b) cell capacity versus cycle number for the first 80 cycles, c) and d) are for the complete cycling test.







Figure 5.8 Charge/discharge cycle tests of the vanadium redox cell employing Flemion<sup>\*</sup> membrane as separator at a current density of 30 mA cm<sup>-2</sup>: a) cell efficiencies versus cycle number and b) cell capacity versus cycle number.



Figure 5.9 Charge/discharge cycle tests of the vanadium redox cell employing DOW<sup>\*</sup> membrane as separator at a current density of 30 mA cm<sup>-2</sup>: a) cell efficiencies versus cycle number and b) cell capacity versus cycle number.



Figure 5.10 Half-cell potential of V(III)/V(IV) measured using platinum indicator electrode w.r.t Hg/HgSO<sub>4</sub> electrode.

In the long term charge/discharge cycle tests, the coulombic efficiency obtained seemed to fluctuate from cycle to cycle by about 4 to 5 % with all the membranes tested. Slight variation in voltage efficiency of 1 % from cycle to cycle was also observed. The most likely explanation was the daily ambient temperature fluctuation, leading to temperature variation in the solutions reservoirs which were not maintained at constant temperature. Studies conducted by NASA with the Fe/Cr battery also showed that increasing the operating temperature of the system did decrease the selectivity of the membrane while increasing its conductance [41]. Moreover, in the vanadium redox cell using 2 M vanadium solutions, temperature

excursions below 15 °C or above 45 °C could cause crystallization on the negative half-cell or thermal precipitation on the positive side half-cell, which would affect the ionic strength of the solutions and also reduce the electro-active sites for the reaction.

In the cycling tests for all the membranes, there was a trend observed in the voltage efficiency which decreased gradually and could be recovered by rebalancing the cell. This is believed to be associated with transfer of water across the membrane, resulting in concentration of one half-cell solution and dilution of the other, consequently altering the conductivity of both half-cell solutions.

The voltage efficiency of the cell in the long term cycle testing using Nafion<sup>\*</sup> 117 membrane seemed to show a steep increase when the cell was rebalanced as illustrated in Figure 5.7. The cell resistance measured at 50 % SOC shown in Table 5.5 actually decreased with time. A typical polarization curve of the cell measured at 50 % SOC in the current density range 10 to 40 mA cm<sup>-2</sup>, is shown in Figure 5.11. The Nafion<sup>\*</sup> 117 membrane was chemically stable during the course of the test period, hence the membrane resistance as well as the permeation rate did not change considerably. Therefore the decrease in the cell resistance is attributed to the decrease in the electrode polarization resistance. The properties of the Toray graphite felt used as the electrode was extensively studied by Zhong [168]. It was found that the initial decrease in the electrode resistance is due to the increase in active surface area, since new graphite felt is slightly hydrophobic and it usually takes some time for the solution to fully wet the whole electrode. Furthermore, by thermally treating the graphite felt at 400 °C, the wettability of the felt and the oxygen functional groups increased. The oxygen functional groups are believed to increase the hydrophilicity of the graphite felt as well as serving as active-sites to catalyse the reaction on the positive half-cell, hence lowering the activation over-potential for the V(IV)/V(V) reaction.

Table 5.5Cell resistance measured at 50 % SOC for vanadium redox cellemploying Nafion\* 117 membrane during the cycling test.

Cycle number	Cell resistance measured at 50 % SOC during ( $\Omega$ cm <sup>2</sup> )		
	R <sub>ch</sub>	R <sub>dis</sub>	<b>R</b> <sub>average</sub>
190	3.50	3.60	3.55
290	3.10	3.08	3.09
420	3.12	3.18	3.16
650	2.89	2.95	2.92

Although the evolution of oxygen on the positive electrode is also believed to create oxygen functional groups. Any lowering of the electrode resistance is not immediately realised in the charge/discharge cycling until the cell is rebalanced. This is because the evolved oxygen which adheres to the surface of the electrodes actually decreases the active sites for the reaction, consequently increasing the resistance of the felt. However, with high and more uniform electrolyte flow through the felt, the oxygen bubbles can be dislodged once formed and hence increase the active surface site. It was also found that if the positive electrode was overcharged for extended periods (more than 1 hour), the oxygen evolution could be detrimental to the electrode performance as a result of disbonding of the graphite felt from the conducting plastic substrate.

In a separate charge/discharge cycle of the vanadium redox cell employing Nafion<sup>\*</sup> 117 membrane and the test cell described in Section 4.3.3.b, the performance of the cell was evaluated at various current densities. The cell efficiencies obtained at various current densities are shown in Figure 5.12. The efficiencies presented here are the average of 5 cycles obtained at each current density.



Figure 5.11 Typical polarization curve of the vanadium redox cell employing Nafion<sup>\*</sup> 117 membrane.



Figure 5.12 Cell efficiencies obtained at various current density with the vanadium redox cell employing Nafion<sup>\*</sup> 117 membrane.

There was not much variation in the coulombic efficiency at the range of the current densities investigated. However, by increasing the current density from 20 mA cm<sup>2</sup> to 50 mA cm<sup>-2</sup> the voltage efficiency drop from 92 % to 82 %. This was mainly due to the increase in IR loss with the increase in the current density. The overall energy efficiency was thus slightly higher at the lower current density.

# 5.3.4 Chemical stability testing of commercial membranes.

The method used to evaluate the chemical stability of the membranes was described in Section 5.2.4. The membranes were soaked in 2 M V(V) solution for different length of times and their area resistance and diffusivity measured. The membranes were also soaked in 2 M V(II) solution to test whether the reducing nature of the solution might have any effect on the membrane stability. Values of area resistance and diffusivity of the membranes after soaking in V(V) solution are presented in Table 5.6.

Table 5.6Long term testing of the stability of some commercial membrane in<br/>V(V) solution.

Membrane	Resistance ( $\Omega$ cm <sup>2</sup> )		$\Omega \text{ cm}^2$ )	Diffusivity (cm min <sup>-1</sup> )	
	Initial	l 4mont	hs 8months	Initial 4months 8months	
ASS in V(V)	2.7	1.7	1.4	1.0x10 <sup>-6</sup> 1.9x10 <sup>-5</sup> 3.4x10 <sup>-5</sup>	
ASS in V(II)	2.7	2.4	2.6	1.0x10 <sup>-6</sup> 1.6x10 <sup>-6</sup> 1.4x10 <sup>-6</sup>	
DSV in V(V)	1.0	0.95	0.74	$7.9 \times 10^{-5}$ $1.8 \times 10^{-4}$ >1.0 $\times 10^{-3}$	
DSV in V(II)	1.0	0.98	1.04	7.9x10 <sup>-5</sup> 6.3x10 <sup>-5</sup> 8.5x10 <sup>-5</sup>	
AMV in V(V)	2.8	3.0	2.7	3.2x10 <sup>-6</sup> 4.1x10 <sup>-6</sup> 4.9x10 <sup>-6</sup>	
DMV in V(V)	2.1	1.7	1.5	2.4x10 <sup>-5</sup> 3.5x10 <sup>-5</sup> 3.3x10 <sup>-5</sup>	
CMV in V(V)	2.6	0.8	-	$2.6 \times 10^{-5} > 1 \times 10^{-3}$	
The CMV membrane was shown to degrade very quickly, in less than 4 months and the diffusivity is above  $1 \times 10^{-3}$  cm min<sup>-1</sup>. The uniform erosion of the polymeric material was consistent with that observed in the charge/discharge tests. The erosion of the polymeric material also increased the conductivity of the membrane, again, consistent with the observations from the charge/discharge tests which showed an increase in voltage efficiency when the coulombic efficiency of the cell decreased.

Remarkable stability was exhibited by AMV, ASS and DMV membranes in V(V) solution for up to 8 months with no appreciable change in resistance and diffusivity. Physical examination of these membranes under the microscope after soaking in the V(V) solution for 8 months did not show any sign of polymeric material breaking down except for the DMV membrane where slight deterioration occurred. Further testing was discontinued since these membranes did actually deteriorate in the long term charge/discharge test. Hence, the deterioration of these membranes could also be due to the presence of other ions such as H<sup>+</sup> ions.

The DSV and CMV membranes both deteriorated rapidly. In the case of CMV, nearly all the polymeric material dissolved in the solution in less than 4 months. The degradation of the CMV membrane reduced the V(V) to V(IV) ions which was indicated by the disappearance of the yellow colour of the V(V) solution with membrane soaking in it. Further test conducted with a new piece of CMV membrane using 0.1 M V(V) in 0.4 M  $H_2SO_4$  showed reduction of V(V) ions to V(III) ions in less than 48 hours.

During the testing, the AMV, DMV, ASS and DSV anion-exchange membranes were observed to undergo a colour change, suggesting that vanadium species were entering the membrane. This was confirmed by soaking samples of these membranes in V(V) solution which resulted in the samples turning a reddish colour. The presence of negatively charged complexes of V(V) were believed to be responsible for this colour change which could in fact be reversed by immersing the same membrane in a V(IV) solution. In the paper by Ivakin et.al.[165], studies of the complex formation for the VO<sub>2</sub><sup>+</sup> ions in sulphuric acid, confirmed the existence of VO<sub>2</sub>SO<sub>4</sub><sup>-</sup> ions. Moreover, in the charge/discharge test, the presence of high ionic strength electrolytes would greatly diminish the effects of Donnan exclusion of the co-ions.

From the membrane diffusivity results obtained in the stability test shown in Table 5.6, the degradation of the cation selective CMV membrane could have been due to the oxidative nature of V(V) ions, whereas the anion-exchange membranes (such as AMV, ASS and DMV) were shown to be resistant when soaked in V(V) solution. V(II), V(III) and V(IV) ions showed no effect on the ASS and DSV membranes which were rigorously tested. The failure mode of anion-exchange membranes such as DMV and AMV during charge/discharge testing in the vanadium redox cell is still not well understood even though these membranes are stable when they are soaked in the oxidative V(V) solution.

Similarly, stability testing of Nafion<sup>\*</sup> 117 and Flemion<sup>\*</sup> in V(V) solution did not show any sign of deterioration for more than 24 months and 18 months respectively. Measurement of the membrane area resistance and diffusivity carried out after the membrane have been soaking in V(V) solution did not produce any significant changes. However, crystallization of V(III) in the Flemion<sup>\*</sup> membrane was capable of rupturing the polymeric material. This failure mode of the membrane was localised, occurring at spots where crystals were present on the surface. Confirmation testing was conducted by soaking Flemion<sup>\*</sup> membrane in saturated V(III) solution and similar observations were established.

## 5.4 Treatment of Selemion<sup>\*</sup> CMV membrane to enhance chemical stability in V(V) solution.

#### 5.4.1 Introduction

The use of CMV membrane in the vanadium redox cell produced excellence efficiencies and in the 1 kWh battery prototypes energy efficiencies above 90 % have been achieved, making it the most efficiency battery system reported to date [4,50]. However, the coulombic efficiency of the battery started to decrease quite rapidly after a month of cycle testing, and any slight difference in hydraulic pressure across the membrane caused appreciable solution transfer. In this part of the study, attempts were made to improve the chemical resistance of the CMV membrane in the V(V) solution. Cost estimations for vanadium battery based on the use of this membrane shown it to be attractive compared with existing commercial systems [4]. The CMV membrane was also extensively used in the development of Fe/Cr battery by Japanese researchers who have also attempted to modify its chemical properties to improve its selectivity [129,172]. Similar treatment methods on the CMV membrane were tried

here and the stability of the modified CMV membrane evaluated.

#### 5.4.2 Treatment methods.

The following modifications were applied to CMV membrane samples and any enhancement in its chemical stability evaluated by immersing in 2 M V(V) in 4 M  $H_2SO_4$  solution.

- i) Formation of acid amide bonds to the ion-exchange sites [172].
- ii) Treatment with 4 vinyl pyridine and DVB to increase the cross-linking and hence, chemical stability [129].

Previous studies have shown that degradation of CMV membrane in V(V) solution is accompanied by reduction of the vanadium ions to a lower oxidation state. However, before commencing any stability tests, the resistance of the modified CMV was first measured with the methods described in Section 5.2.2. The treatment methods were regarded as unsuitable if the resistance of the treated membrane increased above the value of 3.5  $\Omega$  cm<sup>2</sup> compared to the initial value of 2.6  $\Omega$  cm<sup>2</sup>.

#### 5.4.2.1 Experimental

i) Formation of acid amide bonds to the ion-exchange sites [172].

A CMV membrane sample of size:  $5 \times 5$  cm was soaked in 50:50 Vol. % of chlorosulphonic and carbon tetrachloride for 2 hours. The resulting membrane was transferred to solutions containing varying amount of polyethylimine (PEI) and

reacted at 25°C for a further 2 hours to form the acid-amide bond.

Treatment of CMV using 4 vinyl pyridine, DVB and sodium persulphate initiator.

The treatment methods employed here were similar to those described by Ohya et.al. [129]. The CMV membrane (5 x 5 cm) was immersed for 1 hour in a mixture: 5 ml 4 Vinyl pyridine and DVB (3 ml-12 ml), made up to 25 ml by adding methanol. The 'soaked' membranes were then polymerised using sodium persulphate as initiator in distilled water at 90 °C for 2 hours.

### iii) Treatment of CMV using 4 vinyl pyridine, DVB and benzoyl peroxide initiator [129].

This treatment method was similar to that described in (ii) above, except that the initiator used was benzoyl peroxide. The CMV samples (5 x 5 cm) were immersed in the following mixtures:

Sample	4VP	DVB	Methanol
1	10ml	2.5ml	Balance to
2	20m1	2.5ml	make vol. to
3	30m1	2.5ml	50ml.
4	40m1	2.5ml	

0.1 g of benzoyl peroxide was added to the mixtures and the membrane was soaked for 1.5 hours. The resulting membranes were placed between two glass plates and polymerised in the oven at 60 °C for 3 hours.

#### 5.4.2.2 Results and discussion

i) Formation of acid amide bonds to the ion-exchange sites.

The area resistance of CMV membrane samples treated with varying amounts of PEI is presented in Table 5.7.

 Table 5.7
 Resistance of CMV membrane-after treatment and after stability test.

Sample	Area resistance ( $\Omega$ cm <sup>2</sup> )	Area resistance ( $\Omega$ cm <sup>2</sup> )
treated	after treatment	after soaking in 0.1 M
with		V(V) solution for 1 week
5% PEI	6.4	1.4
10% PEI	10.3	1.9
15% PEI	26.3	2.2

The treatment thus increased the resistance of the membrane quite significantly as compared with the original material which has a resistance of about 2.6  $\Omega$  cm<sup>2</sup>. Also shown in Table 5.7 are the resistance values of the treated samples after soaking in V(V) solution for a week. The value is greatly reduced indicating the instability of the acid amide bonding. Moreover, the base membrane also showed signs of degradation and the V(V) solution was reduced to a lower oxidation state when the membrane was immersed. These observations suggest that the acid amide layer formed does not protect the base material.

 Treatment of CMV using 4 vinyl pyridine, DVB and sodium persulphate initiator.

The resistance values of the treated samples are shown in Table 5.8 and they compare favourably with their initial values (before treatment). The membrane samples were however tested for stability in V(V) solution.

Sample	DVB (ml)	Area resistance ( $\Omega$ cm <sup>2</sup> )
1	3	2.59
2	6	2.52
3	9	2.46
4	12	3.37

The treated membranes samples after soaking in 0.1 M V(V) solutions also showed signs of deterioration and the V(V) solution was reduced to a lower oxidation state, indicating the treated material was still unstable in the oxidizing solution. iii) Treatment of CMV using 4 vinyl pyridine, DVB and benzoyl peroxide initiator.

The values of resistance and diffusivity of the treated samples are presented in Table 5.9 and show that this treatment did produce a slight improvement in the stability of the membrane. Initial testing of the samples in 0.1 M V(V) solution did not reduce the vanadium ion to a lower oxidation state, however, the treated samples were also soaked in 2 M V(V) solution to further test its chemical stability. The membrane after being soaked in V(V) solution for 3 months showed degradation of some of the polymeric material. Even though the stability of the sample showed slight improvement with this treatment, it was decided to abandon any further modification of the CMV membrane in favour of the use of a lower cost substrate for membrane modification studies.

Table 5.9Resistance and diffusivity of CMV membrane modified with 4 vinylpyridine and DVB.

Sample	Resistance ( $\Omega$ cm <sup>-2</sup> )	Diffusivity (cm min <sup>-1</sup> )
1	15.1	1.92x10 <sup>-5</sup>
2	4.7	3.77x10 <sup>-6</sup>
3	3.6	1.28x10 <sup>-5</sup>
4	14.4	3.70x10 <sup>-5</sup>

#### 5.5 Evaluation of new Selemion<sup>\*</sup> membrane.

Recent communication and reports from Japanese workers at ETL and Kashima Kita Power Corporation in Japan, who have been evaluating the vanadium redox battery, revealed a new Selemion<sup>\*</sup> membrane which exhibited remarkable stability and excellent performance characteristics in the vanadium redox cell. They have shown that the efficiencies obtained by employing this membrane in the vanadium redox cell was slightly higher than using the costly Nafion<sup>\*</sup> 117 membrane. Moreover, the cost of the new Selemion<sup>\*</sup> membrane is expected to be several times less than Nafion<sup>\*</sup> 117 membrane, making it particularly attractive for commercial application in vanadium redox battery.

The new Selemion<sup>\*</sup> membrane is still a developmental product from Asahi Glass Co., Japan and was prepared from a block copolymer containing polysulfone units. Preparation of both cation and anion-exchange membranes using this polymer have been reported [91]. Samples of the new Selemion<sup>\*</sup> membrane were recently acquired from Asahi Glass Co., Japan. The membrane is a composite consisting of PVC cloth as the substrate (0.1 mm) and an active anion-exchange layer (1  $\mu$ m).

The values of resistance and the diffusivity of this membrane as determined by the techniques described in Section 5.2, were 1.2  $\Omega$  cm<sup>2</sup> and 2.7 x 10<sup>-5</sup> cm min<sup>-1</sup> respectively. Charge and discharge tests of the vanadium redox test cell (Section 4.3.3.b) using this membrane produced the results given in Figure 5.13 which shows cell efficiencies as a function of current density. An overall energy efficiency of 91

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% was observed at 20 mA cm<sup>-2</sup>, while the coulombic efficiency obtained with this membrane remained essentially constant (above 98 %) over the range of current densities tested.



Figure 5.13 Cell efficiencies versus current density for the new Selemion<sup>\*</sup> membrane.

From the polarization plot of Figure 5.14, the cell resistance is calculated as 2.7 and  $3.0 \ \Omega \ cm^2$  for the charge and discharge respectively. The low resistance exhibited by this membrane is particularly attractive since a higher power output could be obtained with the same sized battery by operating at a higher current density.

The membrane is still undergoing long term cycling tests in the laboratory together with stability tests in V(V) solution.



Figure 5.14 Polarization plot at 50 % SOC for the new Selemion<sup>\*</sup> membrane.

#### 5.6 Conclusion

Evaluation of the commercial membranes AMV, DMV, CMV, CMS, DSV, ASS, Nafion\* 117, Nafion\* 324, DOW\* XUS1 3204.10, RAI 1010, RAI 4010 and K142 showed acceptable area resistance values and that possess low diffusivities with the exception of the DOW membrane. Energy efficiencies above 85 % were achieved when these membranes were employed in the vanadium redox battery. Generally, anion-exchange membranes gave marginally higher coulombic efficiencies than the cation-exchange membranes, but the gain was offset by the lower voltage efficiency obtained. However, since the two properties stated are mutually exclusive and there is no 'ideal' membrane available commercially, selection of the type of membrane to achieve optimum performance for the vanadium redox battery, depends on its application. Generally, for minimal maintenance applications such as Remote area power supply systems (RAPSS), energy self-sufficient solar houses and emergency backup power source, membranes with low diffusivity and stability should be selected. Whereas, for traction or mobile application, maximum power output is an important criteria, hence the membrane which is most suited for this application must possess the lowest possible resistance with coulombic efficiencies above 90 % being acceptable.

For all the commercial membranes evaluated, most gave acceptable performance in the short term, less than 6 months, after which the performance of the battery dropped off rapidly. The exception was the Nafion<sup>\*</sup> 117 membrane, which offered consistent performance for more than 18 months of acceralate cycle testing and

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showed no sign of impairment in performance. The Flemion<sup>\*</sup> membrane also exhibited excellent stability in the cycling tests.

The CMV membrane, although an excellence membrane for vanadium redox battery application in terms of performance showed very poor stability. Various treatments applied to this membrane failed to appreciably improve the stability and moreover, the resistance of the membrane after treatment also increased significantly, making it unsuitable for redox cell applications. The most promising membrane to date, however, is a second type of 'New' Selemion\* membrane recently developed by Asahi Glass Co. (Japan), for Kashima-Kita Power Corporation vanadium battery development program. Recent discussions with these workers have revealed that excellent stability and area resistance values of less than 1  $\Omega$  cm<sup>2</sup> have been achieved with this new membrane which also promises to have an acceptable cost (~\$200/kW) for most energy storage applications.

For larger scale load levelling applications, a membrane cost of less than \$100/kW is essential if battery storage is to compete with other forms of energy storage. The development of a low cost, stable membrane for such application was thus the objective of the following phase of this study.

#### **CHAPTER 6**

#### **MODIFICATION OF MICROPOROUS SEPARATOR, Daramic\*.**

#### 6.1 Introduction

In this part of the study, the development of a technique to improve the selectivity of the microporous separator, Daramic<sup>\*</sup> was undertaken. Daramic<sup>\*</sup> is a polyethylenesilica based material with a silica content as high as 55 %. It was selected for this study due to its low cost and chemical stability in the vanadium electrolytes. However, without any further treatment, this separator is unsuitable for use as a separator in the vanadium redox cell because of its non selectiveness to the vanadium ions [10]. A simple treatment method to impart selectivity to this separator could lead to significant cost reduction for the vanadium redox battery system.

The approach taken to impart selectivity to the Daramic<sup>\*</sup> separator was to partially block and/or reduce the pore size as well as incorporate ionic selective capability to the separator. Various methods of treating the separator were initially investigated to find the most effective means of improving its selectivity. Further studies were conducted for those treatment methods which produced promising results. The methods of treatment included:

i) Formation of an interpenetrating network (IPN) with the porous structure of Daramic<sup>\*</sup>.

In this part of the study, three different techniques of ionic IPN formation with the

substrate, Daramic<sup>\*</sup>, were investigated. Even though these methods had been widely investigated by many with low density polyethylene material, however, the high silica content of the Daramic<sup>\*</sup> was expected to result in very different properties after the treatment. The first method involved the incorporation of carboxylic networks in the porous structure of the substrate, similar to those described in [173]. The second method was similarly to those described by Cox et.al [174], which involved cross-linking of 4 vinyl pyridine and divinyl benzene with the substrate. In the third case, preparation of IPN based on styrene and divinyl benzene with subsequent sulfonation, was investigated. The procedure was similar to that described by Rozek-Galina et.al [76].

ii) Sorption of polyelectrolyte/ion-exchange resins onto the porous structure of the membrane with or without further cross-linking with divinyl benzene.

Sorption of polyelectrolyte/ion-exchange resin onto the porous structure of the membrane has been widely investigated. Various investigations have been described [10,148,154] using this technique to improve the selectivity of Daramic<sup>\*</sup> separator, with varying success. A review of these studies is covered in Section 2.4. However, treatment involving sorption of polyelectrolyte with further cross-linking had not previously been reported.

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#### 6.2 Formation of IPN with porous structure of Daramic<sup>\*</sup> separator.

#### 6.2.1 Experimental

Preparation of IPN with carboxylic networks. a)

The Daramic<sup>\*</sup> (0.23 mm) was soaked in a mixture of methacrylic acid (MA) and divinyl benzene (DVB), 95:5 vol. %, with 0.5 wt. % of benzoyl peroxide added as an initiator. The mixture was heated in a water bath at 50 °C for 1 hour and the membranes placed between two glass plates and transferred to the oven at 80 °C for 2 hours to interpolymerize the monomer.

Preparation of IPN using 4 vinyl pyridine (VP) and divinyl benzene. b)

Daramic<sup>\*</sup> samples (0.15 mm) were soaked in the mixtures specified in Table 6.1.

Table 6.1	Ratio of	solution	mixtures	used	in	the	treatment.
Table 6.1	Ratio of	solution	mixtures	used	1N	the	treatment.

Sample	4 VP (ml)	DVB (ml)	Methanol
1	10	2.5	Balanced to
2	20	2.5	make vol. to
3	30	2.5	50ml.
4	40	2.5	

0.1 g of benzoyl peroxide was added to the mixtures and the membranes were soaked for 1.5 hours. The resulting membranes were placed between two glass plates and were polymerised in the oven at 60 °C for 3 hours.

c) Preparation of IPN based on styrene and Divinylbenzene with subsequent sulfonation.

Daramic<sup>\*</sup> (0.15 mm) was soaked in the mixture of styrene and DVB (95:5 vol. %), with 0.5 wt. % of Benzoyl peroxide added as initiator, for 1 hour at 50 °C in the water bath. The resulting membrane was transferred to the oven at 80 °C for 2 hours to interpolymerise the monomer. The polymerised membrane was sulfonated with chlorosulphonic acid and carbon tetrachloride (70:30 vol. %) for 16 hours. It was converted to the sodium form by immersing in 0.1 M sodium hydroxide for 2 hours.

Polymerisation using the initiator, sodium persulphate in the place of Benzoyl peroxide was also investigated. The 'soaked' membrane with styrene/DVB as described before, was transferred to the reactor where 1 g of sodium persulphate was added to 200 ml of distilled water. The membrane was polymerised at 85 °C for 1 hour and at 95 °C for 2 hours. The resulting membrane was sulfonated with the method described earlier.

#### 6.2.2 Results and discussion

a) Preparation of IPN with carboxylic networks.

The Daramic<sup>\*</sup> sample after the treatment had poor hydrophilicity and was brittle in nature. This was due to non-uniform polymerization across the sheet of the membrane. The treatment also resulted in excessive shrinkage of the membrane. The physical properties of the membrane did not warrant further testing and this technique was not further investigated.

b) Preparation of IPN using 4 vinyl pyridine and divinyl benzene.

Using this treatment method, the resulting membrane samples were hydrophilic, and physical examination did not show any adverse effects on its properties. The resistance and the diffusivity of the treated samples were thus measured using the methods described in Sections 5.2.1 and 5.2.2, and their values are presented in Table 6.2.

Table 6.2	Resistance and diffusivity values of samples treated using 4	
	vinylpyridine and divinyl benzene.	

Resistance $\pm 0.1$ ( $\Omega$ cm <sup>2</sup> )	Diffusivity $\pm (0.05 \times 10^{-3})$ (cm min <sup>-1</sup> )
2.0	1.35 x 10 <sup>-3</sup>
2.9	3.77 x 10 <sup>-3</sup>
1.3	1.37 x 10 <sup>-3</sup>
2.4	1.43 x 10 <sup>-3</sup>
0.4	1.40 x 10 <sup>-3</sup>
	Resistance $\pm 0.1$ ( $\Omega$ cm <sup>2</sup> ) 2.0 2.9 1.3 2.4 0.4

As shown in Table 6.2, the resistance of the samples increased with treatment and there was no decrease in the diffusivity. No further effort was devoted to this treatment method.

c) Preparation of IPN based on styrene and Divinylbenzene with subsequent sulfonation.

The Daramic<sup>\*</sup> membrane polymerised using benzoyl peroxide was brittle and hydrophobic in nature. No further testing was carried out for the treated samples.

The Daramic<sup>\*</sup> sample polymerised using sodium persulphate however, was flexible and hydrophilic. The resistance and the diffusivity of the treated sample were measured and their values were:

Resistance =  $0.6 \pm 0.1 \ \Omega \ cm^2$ 

Diffusivity =  $8.10 \pm 0.05 \times 10^{-4} \text{ cm min}^{-1}$ 

As the sample treated with this method produced a slight decrease in diffusivity compared to the untreated Daramic<sup>\*</sup>, further testing was conducted by employing this membrane in the vanadium redox test cell described in Section 5.2.3 for the charge/discharge cycling. The cell efficiencies obtained in the charge/ discharge test are shown in Table 6.3.

Efficiency (%)							
Cycle no.	Coulombic	Voltage	Energy				
2	79.0	76.3	60.2				
3	80.3	75.8	60.9				
Untreated	47.0	86.0	40.0				

Table 6.3Cell efficiencies of the vanadium redox test cell employing treatedDaramic\* at a current density of 40 mA cm<sup>-2</sup>.

The treated membrane thus shows an improved coulombic efficiency and overall energy efficiency compared with the untreated membrane. However, the coulombic efficiency obtained with this treated membrane is still too low for practical application in the vanadium redox battery.

6.3 Sorption of polyelectrolyte/ion-exchange resins with or without crosslinking with DVB.

#### 6.3.1 Experimental

#### 6.3.1.1 Materials and reagents

The microporous separator, Daramic<sup>\*</sup> (W.R Grace) of thickness 0.15 and 0.23 mm was used for the study. The polyelectrolytes employed were polystyrene sulphonate (PSS), and carboxy methyl cellulose sodium (CMCS). The ion-exchange resin used was Amberlite CG400 (Amb).

#### 6.3.1.2 Membrane preparation and treatment

a) Treatment involving sorption of polyelectrolyte/ion-exchange resin.

The first part of the treatment involved sorption of the polyelectrolyte/ion-exchange resin dissolved in various solvents onto the porous structure of the Daramic\* membrane, (0.23 mm, size: 10 x 12 cm). The solvents used for dissolving the polyelectrolyte/ion-exchange resins were dimethyl formamide (DMF), 1 M H<sub>2</sub>SO<sub>4</sub> and ethanol/water (1:1 vol. %) mixture. The polyelectrolyte solutions/mixtures were prepared by dissolving 0.25 g of polyelectrolyte in 50 ml of solvent. The ionexchange solutions/mixtures were prepared by adding 1.0 g of ion-exchange resin to 50 ml of the solvent. The ion-exchange resin, Amberlite CG400, was not soluble in the solvents tried such as ethanol, methanol and acetone. However, it formed a fine suspension and the resin could adhered itself to the surface or enter the large pores of the separator samples. (The particle sizes of the resins were 0.4 µm and below, while the average pore size of Daramic<sup>\*</sup> membrane was 0.1 µm. From the FESEM viewing at magnification of 3000 to 4000 times, scattered pores above 1 µm could also be observed.) The separator samples were immersed in the polyelectrolyte solutions or mixtures at 20 °C or 60 °C for 24 hours. The resulting membranes were washed with distilled water and dried in a vacuum oven at 50 °C for 2 hours.

## b) Treatment involving sorption of polyelectrolyte/ion-exchange resin and further cross-linking with DVB.

In the second part of the experiment, Daramic<sup>\*</sup> samples that were soaked in the polyelectrolyte/ion-exchange resin as in Part (a), were further cross-linked using

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divinyl benzene (DVB). To achieve cross-linking, the membranes 'soaked' at 20 °C for 24 hours were transferred to a mixture containing DVB (30 vol. %) and methanol, and soaked for a further 2 hours. The membranes were transferred to the reactor containing 2 g of sodium persulphate in 400 cm<sup>3</sup> distilled water. Polymerization was carried out for 1 hour at 90 °C and for a further hour at 95 °C. The treated membranes were washed with 5 % methanol to remove the initiator, sodium persulphate and any unreacted DVB.

#### 6.3.1.3 Membrane evaluation

The area resistance and the diffusivity of the membrane were evaluated by the methods described in Section 5.2. In this case, however, a static diffusion experiment was conducted to avoid cross-over of the solutions due to different rates of pumping on either side of the membrane. The microporous separator, Daramic<sup>\*</sup>, unlike ion-exchange membranes, does permit hydraulic permeation due to differential pressure across it. The static diffusion cell is described in Section 4.3.2.a., while the area resistance was determined using the cell described in Section 4.3.2.c. The membrane resistance was obtained by subtracting the cell resistance without the membrane from the cell resistance with the membrane present.

Measurement of the hydraulic permeability of the membrane was done using the apparatus described in Section 4.3.6. The solution used was 2 M VOSO<sub>4</sub> in 3 M  $H_2SO_4$  and the area of the membrane exposed to the solution was 15.9 cm<sup>2</sup>. The flux of the permeate was recorded at regular intervals while maintaining the differential

pressure across the membrane at 101.3 kPa.

Charge/discharge tests using the redox flow test cell (Section 4.3.2.a) using the treated Daramic<sup>\*</sup> were conducted to evaluated the cell efficiency obtained. The experimental procedure was similar to those described in Section 5.2.3. The electrode and the membrane area were 25 cm<sup>2</sup> and 30 cm<sup>2</sup> respectively while the volume of the electrolytes was 65 ml for each half-cell. The cell was charged and discharged at the constant current density of 40 mA cm<sup>-2</sup>.

#### 6.3.2 Results and Discussion

## 6.3.2.1 Treatment involving sorption of polyelectrolyte/ion-exchange resin onto Daramic<sup>\*</sup>.

Treatment of Daramic<sup>\*</sup> membrane with different polyelectrolyte/ion-exchange resin would be expected to result in varying properties. Several kinds of polyelectrolytes/ion-exchange resins dissolved in different solvents were investigated in the preparation of an ionic membrane/separator. The effect of temperature on the sorption of polyelectrolytes into the substrate was also investigated.

The functional electrochemical and hydraulic properties of polyelectrolyte-activated interpolymer membranes [115], depend primarily on the pore size and the pore size distribution of the membrane, the number and the nature of the ionizable groups of the polyelectrolytes molecules, and the distribution of the polyelectrolyte within the membrane. An adequate quantity of inorganic groups must be present to control all geometrically possible pathways across it, and a higher charge density is also favoured so as to reduce the ohmic resistance.

The polyelectrolyte used must have a high enough molecular weight to be sorbed by the membranes in an irreversible manner. Studies by Caplan and Sollner [116] indicated that the absorption of polyelectrolyte onto the porous substrate is also influenced by the ionic strength of the polyelectrolyte solution used.

The various conditions used for the treatment of the Daramic<sup>\*</sup> and their effects on the area resistance, diffusivity and hydraulic permeability of the resulting membranes are summarised in Table 6.4, along with the area resistance, diffusivity and hydraulic permeability of the untreated Daramic<sup>\*</sup>. The hydraulic permeability ( $K_{b}$ ) was calculated as:

$$K_{\rm h} = Q / \Delta P \tag{6.1}$$

Where Q is the solution flowrate  $(cm^3 s^{-1})$  and P is the pressure (kPa).

Conditions for		Daramic <sup>*</sup> soaked in				Daramic <sup>*</sup> soaked in			
treatment		solution at 20 °C				solution at 60 °C			
Polyelectrolytes/ ion-exchange resins in various solvents	S	$ m R$ $\Omega.cm^2$	Dx10 <sup>4</sup> cm min <sup>-1</sup>	K <sub>h</sub> x10 <sup>6</sup> cm <sup>3</sup> cm <sup>-2</sup> s <sup>-1</sup> kPa <sup>-1</sup>	S	R Ω.cm²	Dx10 <sup>4</sup> cm min <sup>-1</sup>	K <sub>b</sub> x10 <sup>6</sup> cm <sup>3</sup> cm <sup>-2</sup> s <sup>-1</sup> kPa <sup>-1</sup>	
PSS in DMF	X1	1.0	7.0	1.2	X4	3.3	6.3	1.0	
PSS in 1 M H <sub>2</sub> SO <sub>4</sub>	X2	1.1	7.5	1.0	X5	2.4	7.5	1.6	
PSS in 50 % Ethanol	X3	1.2	7.5	1.0	X6	1.9	5.9	1.6	
CMCS in DMF	X7	1.1	5.4	1.1	X10	2.0	7.3	1.1	
CMCS in $H_2SO_4$	X8	1.1	7.5	1.5	X11	4.1	7.9	1.3	
CMCS in 50 % Ethanol	X9	0.9	5.3	1.1	X12	2.2	8.8	1.1	
Amb in 50 % Ethanol	X13	1.2	6.8	1.6	X14	1.5	6.2	1.5	
Untreated Daramic <sup>*</sup> 0.23 mm thick 0.15 mm thick		0.3 0.4	8.1 14.0	230 288					

samples (S) under different treatment conditions obtained from a single measurement for each sample.

Area resistance (R,  $\Omega$  cm<sup>2</sup>), diffusivity (D, cm min<sup>-1</sup>) and hydraulic permeability (K<sub>h</sub>, cm<sup>3</sup>cm<sup>-2</sup>s<sup>-1</sup>kPa<sup>-1</sup>) of the

Daramic\* of thickness 0.23 mm were used for samples X1 to X12 and 0.15 mm for samples X13 and X14.

Table 6.4

The area resistance values of the samples (X1 to X14) presented in Table 6.4 seem to increase quite significantly, while the decrease in the diffusivity of the membrane is only marginal. Also, the area resistance values of the samples treated at 60 °C are slightly higher than those samples treated at 20 °C and there is no appreciable difference in the diffusivity values of the samples for the treatment at the two temperatures investigated. Generally, it would be expected that an increase in the resistance of the membrane after treatment be accompanied by a decrease in the diffusivity of the membrane.

The hydraulic permeability  $(K_h)$  for the treated Daramic was significantly reduced by the same order of magnitude for all the treatments as shown in Table 6.4. The reduction in hydraulic permeability could be due the resistance to flow caused by the absorbed polyelectrolyte/ion-exchange resin in the membrane pores or the blockage of larger pores by the resin. The average pore size of Daramic provided by the manufacturer was 100 nm compared with ion-exchange membranes which have a typical value of a few nanometres. With such a large initial pore size however, the absorbed polyelectrolyte/ion-exchange resin on the Daramic still produced a significant reduction in the hydraulic permeability. These results are consistent with those observed by Idol and Anderson [120].

The results in Table 6.4 also show that the absorbed polyelectrolyte was more effective in restricting the hydraulic flow of the solution than the diffusion of vanadium ions. This could be due to the low ion-exchange capacity of the treated membrane which was ineffective in excluding the vanadium ions. Moreover, in the presence of the high ionic strengths of the diffusion test electrolytes used, the absorbed polyelectrolyte could adopt a collapsed conformation - where the polyelectrolyte coils up instead of existing as a long flexible chain. Also, the ionic groups of the polymeric material would be effectively shielded [120].

The absorption of polyelectrolyte had been shown to depend strongly on the charge of the polyelectrolyte and on the difference between the dielectric constants of the solution and the substrate [115]. The charge of the substrate also influenced the absorption affinity of the polyelectrolyte [115]. The use of different solvents to dissolve the polyelectrolyte/ion-exchange resin employed for the treatments did not show any definite trends in the measured resistance and diffusivity values. Only small differences in the measured parameters were observed, so no conclusive indications of the effects of the different solvents could be found. Moreover, both the diffusivity and resistance tests employed solutions with high ionic strength which had invariably reduced the effectiveness of the absorbed polyelectrolytes.

The effect of the above treatments was further evaluated by charge/discharge cycling in a vanadium redox cell. Table 6.5 shows the cell efficiencies obtained for the second charge/discharge test cycle at a constant current density of 40 mA cm<sup>-2</sup> for each of the treated samples X1-X14 and for the untreated Daramic<sup>\*</sup>. A comparison of the voltage efficiencies for the treated and untreated separators showed that a decrease in the voltage efficiency was observed after each treatment, this being consistent with the increase in resistance of the membranes. Significant increases in the coulombic efficiency were however produced by the different treatment methods,

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showing that the membrane modification had retarded the electrolyte cross-over in the cell and therefore, the self-discharge rate during cycling.

Table 6.5Vanadium redox cell efficiencies of the second charge/discharge testcycle for samples X1 to X14 and untreated Daramic\* at a currentdensity of 40 mA cm<sup>-2</sup>.

Daramic <sup>*</sup> sample	Efficiencies (%)						
-	Coulombic	Energy					
X1	76.9	77.5	59.6				
X2	81.2	81.2	60.0				
X3	84.2	82.1	69.1				
X4	85.3	78.6	67.0				
X5	76.9	76.4	58.7				
X6	81.1	83.1	67.4				
X7	81.8	81.3	66.5				
X8	79.8	76.8	61.3				
X9	84.4	76.3	64.4				
X10	83.7	78.0	65.2				
X11	82.9	75.6	62.7				
X12	79.8	82.2	65.6				
X13	80.2	79.1	63.4				
X14	81.4	77.8	63.3				
	Untreated Daramic*						
0.23 mm	48-77	88-87	42-70				
0.15 mm	47	86	40				

The coulombic and the voltage efficiencies obtained by the charge and discharge tests do not however, correlate closely with the resistance and the diffusivity values of the treated samples. In each of the charge/discharge tests summarised in Table 6.5, the same electrolytes, cell configuration and electrodes were employed so that any variations in the coulombic and voltage efficiencies should be attributed to the differences in the membrane properties.

For the untreated Daramic<sup>\*</sup>, the differential pressure caused by different pumping rates between the two sides of the membrane produced significant volumetric cross-over of the solutions giving rise to large variations in the coulombic efficiency. As can be seen in Table 6.5, values as high as 77 % could be obtained for the untreated Daramic<sup>\*</sup> with proper control of the pumping rates on the two sides of the cell. The improvement in coulombic efficiency for the treated membranes can thus be attributed to the decrease in convective transport across the membrane.

From Table 6.5, the treatment method for the Daramic<sup>\*</sup> sample designated X3 showed the greatest improvement in terms of cell efficiencies from the charge/discharge tests. The stability of sample X3 or the irreversibility of the absorbed polyelectrolyte on the membrane for this treatment was further tested for 34 charge/discharge cycles which was equivalent to 160 hours. The cell efficiencies versus cycle number are shown in Figure 6.1.

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Figure 6.1 Cell efficiencies for sample X3 in vanadium redox cell charge/discharge cycling test at current density of 40 mA cm<sup>-2</sup>.

As can be seen in Figure 6.1, the coulombic efficiencies obtained in charge/discharge cycling fluctuate between 77 and 85 % and there was no apparent decrease in coulombic efficiency after 160 hours of testing. The cycling test indicates that the absorbed polyelectrolyte in the membrane did not redissolve in the vanadium electrolytes. The slight drop in voltage efficiency was associated with a gradual flow of electrolytes from the positive to the negative half-cell, resulting in an imbalance in the state-of-charge of the two solutions and a loss of capacity. At the 31st cycle the solutions from the anolyte and the catholyte were rebalanced to restore the capacity of the redox cell and the performance of the cell recovered to its initial value.

For all the remaining treated membrane samples (X1-X14) shown in Table 6.5, the coulombic efficiencies obtained in the charge/discharge tests were too low for practical application as separators in a battery application.

## 6.3.2.2 Treatment involving sorption of polyelectrolyte/ion-exchange resin and further cross-linked using DVB.

In Section 6.3.2.1, it was shown that the absorption of polyelectrolyte/ion-exchange resin onto Daramic<sup>\*</sup> membrane is capable of significantly reducing its hydraulic permeability. However, the treated Daramic<sup>\*</sup> was prone to swelling and this effectively increased its pore size. Studies conducted by Idol and Anderson [120] showed that the absorbed polyelectrolyte would be more effective in reducing membrane diffusional and hydraulic permeability if the absorbed polymer dimension was not too much greater than its pore size. Therefore, with Daramic<sup>\*</sup> membrane, the reduction in its diffusivity and hydraulic permeability would be more substantial if the treatment could also reduced its swelling behaviour and thus the pore size.

DVB was used in this study to effect cross-linking of the absorbed polyelectrolyte and the substrate, Daramic<sup>\*</sup>, to produce a more rigid membrane. The experimental procedures are described in Section 6.3.1.2.b. The area resistance, diffusivity and hydraulic permeability of the treated Daramic<sup>\*</sup> samples that were further cross-linked by DVB are shown in Table 6.6.

# Table 6.6Area resistance, diffusivity and hydraulic permeability of the<br/>treated Daramic\* with cross-linking using DVB (obtained from single<br/>measurement for each sample).

Polyelectrolytes/ ion-exchange resins	Daramic <sup>*</sup> Sample	$\frac{R}{(\Omega \ cm^2)}$	D $x10^4$ (cm min <sup>-1</sup> )	$K_{h} \times 10^{7}$ (cm <sup>3</sup> cm <sup>-2</sup> s <sup>-1</sup> kPa <sup>-1</sup> )
PSS in 50 % ethanol	Y1	2.0	6.9	4.0
CMCS in 50 % ethanol	Y2	1.3	5.0	3.4
Amb in 50 % ethanol	Y3	2.2	2.1	1.2
Daramic <sup>*</sup> treated With DVB only	Y0	0.7	11.3	11.2

From Table 6.6, the diffusivity of the samples, Y1-Y3 are seen to be lower than those treated with the polyelectrolyte/ion-exchange resin only. The most significant decrease in diffusivity was achieved by the treatment using Amb in 50 % ethanol and cross-linking with DVB. The cross-linking also produced a marginal increase in the resistance and a reduction in hydraulic permeability of about 8 fold for the treated membranes, compared to samples which were not cross-linked as shown in Table 6.5. Moreover, as shown in Table 6.6 Daramic<sup>\*</sup> membrane treated with DVB only, show only slight decrease in its diffusivity. The decrease in diffusivity for treated Daramic<sup>\*</sup> with cross-linking could be attributed to a decrease in swelling due to the more rigid physical structure of the membrane and the ion-exchange sites incorporated into the cross-linked element.

The vanadium redox cell efficiencies obtained for the second cycle of the charge/discharge tests using the treated Daramic<sup>\*</sup> with cross-linking, are shown in Table 6.7.

Table 6.7Cell efficiencies for the second charge/discharge cycle for treatedDaramic\* with cross-linking using constant charging and dischargingcurrent of 40 mA cm<sup>-2</sup>.

Daramic <sup>*</sup>	aramic <sup>*</sup> Cell efficiencies (%)			
sample	Coulombic	Voltage	Energy	
Y1	83.5	81.4	68.0	
Y2	89.8	79.7	71.6	
Y3	92.2	78.9	72.7	
¥0	55.3	79.7	44.1	

The coulombic efficiency of the treated Daramic<sup>\*</sup> with cross-linking (sample Y1-Y3) as shown in Table 6.7, has thus increased significantly and there is negligible reduction in the voltage efficiency. The absorbed polyelectrolyte/ion-exchange resin thus appears to be more effective in reducing both the diffusional permeability and the hydraulic permeability with the reduced pore size due to cross-linking. In fact, cross-linking is also expect to increase the tortuosity of the treated membrane, causing the diffusing ions to follow extended pathways, thereby decreasing their mobility.

Treatment using CMCS with further cross-linking also produced promising results. However, the membrane sample designated Y2 was slightly distorted due to uneven shrinkage. Charge/discharge cycling was carried out to test the stability of the membrane and the efficiencies of the cell are shown in Figure 6.2. The total number of hours tested was 90 hours which was equivalent to 17 cycles. Figure 6.2 shows that the coulombic efficiency of the cell was maintained, indicating that no deterioration of the membrane had occurred.



Figure 6.2 Cell efficiencies for sample Y2 in vanadium redox cell charge/discharge cycling test at the current density of 40 mA/cm<sup>2</sup>.

Sample Y3, which produced the highest overall energy efficiency was further tested in a charge/discharge cycling test to evaluate the long term stability of the treated Daramic<sup>\*</sup>. The cell efficiencies versus cycle number are shown in Figure 6.3 for a constant charge and discharge current density of 40 mA cm<sup>-2</sup>. The total number of hours tested was 130 hours for 26 charge/discharge cycles. As illustrated in Figure 6.3, the coulombic efficiency remained fairly constant with some slight fluctuations during cycling whereas the voltage and the energy efficiencies decreased slightly with each successive cycle. This was again a result of an imbalance in the SOC of the anolyte and the catholyte caused by volumetric crossover. The Daramic\* treated with Amberlite and cross-linking was thus shown to be chemically stable in the cell cycling tests, yielding average coulombic, voltage and energy efficiencies of 92, 79 and 73 % respectively. It should be emphasised that by using the optimum graphite felt material bonded onto conductive plastic electrodes, an increased voltage efficiency (up to 90 %) could be expected for the vanadium redox cell employing the modified membrane.



Figure 6.3 Cell efficiencies for sample Y3 in vanadium redox cell charge/discharge cycling test at the current density of 40 mA cm<sup>-2</sup>.
# 6.3.3 Conclusion

In the present study, a range of treatment conditions were investigated for the microporous separator, Daramic<sup>\*</sup>, with the aim of producing a membrane having the selectivity required for redox battery applications. The treatment method that produced the most selective membrane from the microporous separator, involved soaking in Amberlite with 50 % ethanol/water mixture and cross-linking using divinyl benzene. The cell efficiencies obtained by employing this membrane in a vanadium redox cell at a current density of 40 mA cm<sup>-2</sup> were 92, 79 and 73 % for coulombic, voltage and energy efficiency respectively. The long term stability of the modified membrane (with cross-linking) has been shown to be excellent in the charge/discharge cycling test.

Other techniques used to modify Daramic<sup>\*</sup> such as formation of IPN: with carboxylic networks, 4 vinyl pyridine and DVB, and styrene - DVB with subsequent sulfonation, failed to produce a membrane with properties required for the vanadium redox battery.

# 6.4 Optimization and characterization of the modified Daramic<sup>\*</sup> based on absorption of Amberlite CG400 and cross-linking with divinyl benzene.

### 6.4.1 Introduction

From the preliminary study on the different treatment methods to modify the properties of Daramic<sup>\*</sup>, it was shown that sorption of Amberlite CG400 and crosslinking with divinyl benzene produced the most significant effects on decreasing the diffusivity of the treated membrane. Following the treatment procedure described in Section 6.3.1.2., optimization of the treatment process was carried out to produce a membrane with improved performance for use as a separator in the vanadium redox battery.

As described in Section 6.3.1.2, the treatment for the Daramic<sup>\*</sup> membrane involved 3 steps; sorption of the membrane in Amberlite CG400 and ethanol mixture, further soaking in the DVB and methanol mixture, and finally, polymerization of the 'soaked' membrane in water using  $Na_2S_2O_8$  as the initiator. In this part of the optimization study of the treatment process, the Daramic<sup>\*</sup> membrane was soaked in a mixture of methanol, DVB and Amberlite CG400, and then polymerized using  $Na_2S_2O_8$ , thereby eliminating a step in the preparation of the "composite" membrane (a term used for the treated membrane in this section, so as to differentiate it from the previous Section). The objective of treating Daramic<sup>\*</sup> membrane was to reduce the diffusivity of vanadium ions, and thereby, produce a low cost membrane for vanadium redox battery utilization.

# 6.4.2.1 Preparation of the composite membrane

The composite membranes were prepared by immersing Daramic<sup>\*</sup>, of size 12 x 14 cm, in a mixture of divinyl benzene (DVB) and methanol (total vol. 50 ml) containing 1 g of Amberlite CG400, for 24 hours. The ratio of DVB:methanol (vol. %) was varied from 10-60 %. The 'soaked membranes' were transferred to the reactor in which 1 g of  $Na_2S_2O_8$  (Sigma Chemical Co.) was added to 200 ml of distilled water at 80 °C. The temperature of the reactor was slowly increased to 90 °C, which took about 10 minutes. Polymerization was continued for 1 hour at 90 °C and 1 hour at 95 °C.

Methanol was used as diluent for DVB and also helped to facilitate the penetration of the initiator,  $Na_2S_2O_8$ , into the membrane during polymerization. The thickness of the Daramic<sup>\*</sup> separators used were 0.15, 0.20, and 0.23 mm.

# 6.4.2.2 Membrane characterization

The diffusivity of V(IV) ions through the membrane and area resistance were evaluated by the methods described in Section 5.2.1.a and 5.2.2 respectively.

For the composite membrane prepared, the increase in weight of the membrane was determined by taking the initial weight  $(W_i)$  of the membrane before treatment and the final weight  $(W_f)$  of the membrane. The percentage increase in weight (T %) of

the membrane after treatment is calculated from:

$$T = (W_{f} - W_{1}) / W_{1} \times 100 \%$$
(6.2)

The electrolyte uptake of the membrane was determined by soaking the dry sample (weight  $W_d$ ) in 1 M V(III) + 1 M V(IV) (referred to as 2 M V<sup>3 5+</sup>) in 2.5 M H<sub>2</sub>SO<sub>4</sub> for 24 hours. The membrane was taken out of the solution, wiped with filter paper and weighed to determine the final weight ( $W_s$ ). The percent of electrolyte uptake (E) was calculated as:

$$E = (W_s - W_d) / W_d \times 100 \%$$
 (6.3)

The water uptake (H) of the membrane (using eqn.6.3) was determined in the same way as the electrolyte uptake except in this case distilled water was used.

The ion-exchange capacity (IEC) of the composite membrane was determined using the method described by Fisher and Kuin [175]. The composite membrane was converted to Cl<sup>-</sup> form by soaking the membrane in 0.1 M NaCl solution for 24 hours. The excess Cl<sup>-</sup> ions in the membrane were leached out by washing with ultra pure water until the Cl<sup>-</sup> concentration was less than 1 ppm. The ion-exchange capacity of the sample was obtained by leaching the Cl<sup>-</sup> form membrane with 0.05 M Na<sub>2</sub>SO<sub>4</sub> solution. The leached membrane was further soaked in fresh 0.05 M Na<sub>2</sub>SO<sub>4</sub> solution for 5 days to ensure all the chloride was leached out. The ion-exchange capacity of the membrane was determined by analysing the amount of chloride in the leachate using ion-exchange chromatography (Waters, model 590, with IC-Pak column). The ion-exchange capacity of the sample is expressed as milliequivalents per gram dry sample (meq/dg) as:  $\frac{\text{millimole of chloride}}{\text{dry sample weight}} = \frac{\text{meq. anion exchange capacity}}{\text{gram of dry chloride form membrane}}$ (6.4)

The average pore size distribution of the membrane was determined using the bubble point technique with a Coulter porosimeter (Coulter Electronics Limited). The membrane was cut into discs of the required size for testing. The fluid used to wet the membrane was Porofils supplied by Coulter Electronics Limited. Due to the limitation of the instrument in analysing the pore size range, Hg-Intrusion technique (using AutoPoro-9200) was used to characterize the pore size distribution of the composite membrane. Hg-intrusion technique detects pore size of the sample to the lower limit of 0.0036  $\mu$ m. However, the average pore size determined by the bubble technique is more accurate than the Hg-intrusion technique, since in the latter, the high pressure used could rupture the pores in the lower range. For the Hg-intrusion technique applied to determine the pore sizes, the membrane pores are assumed to be parallel and cylindrical. This is not strictly the case for the membranes used in this study, however the pore diameter values extracted from the experimental data give an indication of any changes occurring from the modification of the samples.

The pore size and the structure of the composite and untreated Daramic<sup>\*</sup> were also characterized by field emission scanning electron microscopy (FESEM) using a Hitachi S-900. Samples of cross-sectional view were prepared by fracturing them in liquid nitrogen. The membrane samples were mounted on a sample holder using silver epoxy glue and were gold coated to provide electrical conductivity for viewing.

The composition of the Daramic<sup>\*</sup> membrane was determined by Thermogravimetric

analysis (TGA) using Du Pont 951 TGA module. In this technique, the different components inside the sample will decompose at different temperature while any inorganic filler ( such as silica) will not decompose. The percentage of various components could be evaluated from the thermogram which plots the percent residual weight against temperature.

Differential scanning calorimetry (DSC) was employed to determine the crystallinity of the membranes investigated. The 910 Differential Scanning Calorimeter, Du Pont Thermal Analyst 2100 System was used. With this technique, the sample and an inert reference substance are heated simultaneously at the same rate. Any change in the specific heat of the sample will create a small temperature difference with the reference substance which is recorded as a function of the sample temperature. The heat of fusion ( $H_r$ ) can be calculated from the area of the thermogram peak, and the crystallinity of the sample is expressed by:

Crystallinity (%) = 
$$H_{f*} / H_{fo} \times 100$$
 (6.5)

Where  $H_{fo}$  is the heat of fusion for 100 % crystallinity of the polymer (polyethylene) and  $H_{f*}$  is the heat of fusion of the sample.

The surface chemical composition of the composite membrane and the untreated Daramic<sup>\*</sup> were determined by ATR-Infrared technique (Mattson Instruments Inc., SIRIUS 100, Liquid Cooled MCT detector and ATR Accessory KRS5 Crystal), to confirm the incorporation of Amberlite CG400 onto the substrate, Daramic<sup>\*</sup>, during treatment. Transmission Infrared was not employed because of the opaque nature and the thickness of the substrate.

#### 6.4.2.3 Membrane stability and performance in charge/discharge tests.

The redox flow cell and the procedure for the charge/discharge test were described in Sections 4.3.3.a. and 5.2.3. respectively. The cell was charged/discharged at constant current densities ranging from 20 to 80 mA cm<sup>-2</sup> where in each case, charging and discharging current densities were maintained at equal values. The long term charge/discharge cycle test was conducted at a constant current density of 40 mA cm<sup>-2</sup>. The state-of-charge (SOC) of the electrolytes in both half cells was balanced periodically when the performance of the cell dropped to an undesirable level. The cell was periodically rebalanced using the technique discussed in Section 5.3.3.

# 6.4.3 Results and Discussion

#### 6.4.3.1 Composite membrane properties

As described in Section 6.3.1.2, the preparation of the membrane involved a 3 steps process: sorption of Daramic<sup>\*</sup> in Amberlite CG400/ethanol mixture, further soaking in DVB and methanol mixture and finally, polymerization in water using  $Na_2S_2O_8$  as the initiator. As discussed earlier, the absorption of polyelectrolyte/ion-exchange depended on the dielectric constant of the solvent and the substrate. Since methanol, ethanol and acetone have very close dielectric constant values, it was decided to initiate the absorption of the ion-exchange resins in the mixture of methanol, DVB and Amberlite. This was to eliminate a step in the preparation of the composite membrane. Similar trials were also carried out using ethanol and acetone solvents to

produced the composite membrane. The properties (such as resistance and diffusivity values) of the composite membranes obtained did not differ appreciably with the different solvents used.

Figures 6.4 and 6.5 show the respective TGA thermograms for the untreated Daramic<sup>\*</sup> and the composite membrane. The TGA thermogram for the untreated Daramic<sup>\*</sup> indicates a SiO<sub>2</sub> content of about 58 wt. % and the onset of decomposition temperature was 304 °C. The composite membrane showed a slight decrease in the SiO<sub>2</sub> content, with a value of 51 wt. % and the decomposition temperature was increased quite significantly to 402 °C. Results presented in Section 6.4.3.1. (page 209) show that the modification process results in a weight gain of the sample. The decrease in the SiO<sub>2</sub> wt. % of the composite membrane is due to the weight gained during treatment rather than a loss of SiO<sub>2</sub>.

The DSC thermograms for untreated Daramic<sup>\*</sup> and the composite membrane gave similar values in melting point  $(T_m)$  as shown respectively in Figure 6.6 and Figure 6.7. The  $T_m$  of 135 °C for the Daramic<sup>\*</sup> membrane showed that the polyethylene used was highly linear and/or of ultrahigh molecular weight. The same melting point of both membranes also indicated that the molecular weight of the backbone polymer remained relatively unchanged with treatment. However, the degree of crystallinity, as indicated by the heat of fusion of the composite membrane decreased as compared to the untreated Daramic<sup>\*</sup>. The reduction in the heat of fusion also indicated possible structural changes to the Daramic<sup>\*</sup> membrane with treatment.



Figure 6.4 TGA thermogram of the untreated Daramic<sup>\*</sup> sample.



Figure 6.5 TGA thermogram of the composite membrane.



Figure 6.6 DSC thermogram of the untreated Daramic<sup>\*</sup> sample.



Figure 6.7 DSC thermogram of the composite membrane.

The resistance and diffusivity of the composite membrane after modification, are shown in Table 6.8 as a function of the ratio of DVB:methanol used in the treatment.

Table 6.8Area resistance and diffusivity values1 of composite membranes

(0.15 mm) with different treatment solution composition (Amberlite used was 1 g per 50 cm<sup>3</sup> of solution).

DVB:Methanol Vol. %	Area resistance $\Omega \text{ cm}^2$	Diffusivity (K <sub>s</sub> x 10 <sup>4</sup> ) cm min <sup>-1</sup>
0:100	1.0	6.8
10:90	1.2	11.0
20:80	0.8	9.5
30:70	1.4	6.4
40:60	1.3 ±0.4	1.6
50:50	7.7	1.1
60:40	7.1	3.2
Untreated Daramic <sup>*</sup> 0.15 mm 0.20 mm 0.23 mm	0.3 0.4 0.3	13.0 12.0 8.1

1) Values given are based on single measurement for each treatment except for 40 % DVB treatment where the resistance value shown is the average of 6 measurements on treated sample.

As illustrated in Table 6.8, the area resistance of the composite membrane was seen to rise sharply when more than 40 vol. % DVB was used in the treatment of the membrane. On the other hand, the diffusivity ( $K_s$ ) of the composite membrane was lowered by a factor of 10 with the 40-50 vol. % DVB used. Therefore, the optimum vol. % used for preparation of the composite membrane is about 40 and further

resistance measurements on this sample were conducted to validate the value shown in Table 6.8. Based on the values obtained from 6 measurements on the composite membranes produced with 40 vol. % DVB, a variation in the resistance values of about 30 % across the area of the treated Daramic<sup>\*</sup> sample (size: 10 x 12 cm) was observed. The resistance values of the samples obtained from different batches of treatment using 40 % DVB were also found to lie within the error range specified above.

The degree of cross-linking would be expected to increase with the volume of DVB used in the treatment. The degree of cross-linking is usually determined by solvent extraction. A suitable solvent which could dissolve the polymeric membrane material but not the cross-linked polymer is employed. The percentage of the undissolved polymeric material give the degree of cross-linking. In the present study, however the actual percentage of cross-linking of the composite membrane could not be determined since the base material was not soluble in any of the solvents trialled. This could be due to the silica which was incorporated (about 58 wt. %) in the base material. In the original Daramic<sup>\*</sup> material, the highest percentage of extraction (with Soxhlet extractor) obtained using xylene was about 20 wt. %. With the composite membrane (40 Vol. % DVB), the value obtained was less than 5 wt. %.

In Table 6.8, the diffusivity value was reduced from  $1.3 \times 10^{-3}$  to  $6.8 \times 10^{-4}$  cm/min when a Daramic sample was soaked in a mixture of Amberlite and methanol without cross-linking. As was mentioned earlier (see page 130), a membrane with a diffusivity value higher than 2.0 x  $10^{-4}$  cm/min was deemed to be unsuitable for

application in vanadium redox battery. As is also shown in Table 6.15, when Daramic was treated with DVB (without using Amberlite) to modify the membrane (samples A1 to A4), all the diffusivity values are greater than 2.0 x  $10^{-4}$  cm/min. Therefore, it seems that both the cross-linking and the incorporation of ion-exchange resin to the modified Daramic are essential in reducing the flux of the vanadium ions permeating across the membrane.

The resistance and diffusivity values of the composite membranes prepared with 40 vol. % DVB using Daramic<sup>\*</sup> of different thickness are presented in Table 6.9.

Table 6.9Area resistance and diffusivity of composite membrane of differentthickness prepared with 40 % DVB.

Composite membrane thickness (mm)	Area resistance ( $\Omega$ cm <sup>2</sup> )	Diffusivity $K_s$ , ± 0.1 x 10 <sup>4</sup> cm min <sup>-1</sup>
0.15	$1.3 \pm 0.4$	1.6
0.20	$1.6 \pm 0.1$	2.5
0.23	$1.5 \pm 0.1$	2.4

\* Area resistance for the 0.15 mm sample is the average value based on measurement of 6 samples on the same piece of treated membrane while the values for 0.20 and 0.23 mm samples is based on 4 repeated measurements on the same piece of membrane sample.

Referring to Table 6.9, Composite membranes obtained with substrates of different thickness showed slight variation in area resistance (1.3 to 1.5  $\Omega$  cm<sup>2</sup>) and diffusivity (1.6 to 2.5 x 10<sup>-4</sup> cm min<sup>-1</sup>). For each of the different thicknesses employed, a significant reduction in diffusivity was achieved with the treatment (cf., untreated

Daramic<sup>\*</sup> shown in Table 6.8). The composite membrane with the lowest diffusivity however, was obtained with the 0.15 mm Daramic<sup>\*</sup>, which is contrary to expectation since for the untreated membrane shown in Table 6.8, the 0.23 mm Daramic<sup>\*</sup> had the lowest diffusivity value. The probable reason could be due to the different structural properties of the 0.15 mm and the 0.23 mm untreated Daramic<sup>\*</sup>. The technical information provided by the manufacturer revealed that the 0.15 mm membrane was in fact obtained from the 0.23 mm membrane by a hot rolling process. This could change the tortuosity of the 0.23 mm membrane, or the microscopic defects introduced during hot rolling could be removed during the composite membrane preparation and thus explain the results observed.

The properties of the composite membrane (0.15 mm) produced with 40 Vol. % DVB and those of the untreated microporous membrane, Daramic<sup>\*</sup> (0.15 mm) are shown in Table 6.10. The values given in Table 6.10 are based on 2 measurements. The percentage of electrolyte uptake of the membrane shown in Table 6.10 was also used to calculate the porosity of the membrane (cm<sup>3</sup>/g), by dividing with the density of the electrolyte used (which is 1.35 g/cm<sup>3</sup>). The pore volume values thus calculated are 1.03 and 0.44 cm<sup>3</sup>/g for the untreated Daramic<sup>\*</sup> and the composite membrane respectively.

# Table 6.10Summary of the properties of composite membrane (40 Vol. % DVB)and Daramic\* (0.15 mm).

Properties (units)	Daramic <sup>*</sup> (0.15 mm)	Composite membrane
Area resistance ( $\Omega$ cm <sup>2</sup> )	$0.3 \pm 0.1$	$1.3 \pm 0.4$
Diffusivity $\pm 0.1 \times 10^{-4}$ (cm min <sup>-1</sup> )	1.3x10 <sup>-3</sup>	1.6x10 <sup>-4</sup>
Average pore <sup>1</sup> ±0.005 size (µm)	0.095	0.020
Ion-exchange ±0.2 capacity (meq/dg)	-	0.4
Electrolyte ±5 uptake (%)	140	60
Pore volume <sup>2</sup> $\pm 0.04$ (cm <sup>3</sup> /g)	1.03	0.44

The average pore size (diameter) is calculated from 4 V (total pore volume of membrane) / A (total pore area of membrane), see Appendix I).
 Calculated from electrolyte uptake.

From Table 6.10, it can be seen that the composite membrane produced with 40 Vol. % DVB showed a four-fold increase in area resistance while the diffusivity was reduced by 8 times. Even though the diffusivity of the membrane was dramatically reduced, it is desirable to have a membrane with much lower diffusivity.

The average pore size for Daramic<sup>\*</sup> determined using the bubble point technique was 0.095  $\mu$ m corresponding to the manufacturer's specification of 0.1  $\mu$ m. In fact the average pore size for all the 3 different thickness of Daramic<sup>\*</sup> (0.15, 0.20 and 0.23 mm) was 0.095  $\mu$ m. Figure 6.8 shows the differential pore number distribution of Daramic<sup>\*</sup> (0.15 mm). The differential number of pores expressed as a percentage, corresponds to the percentage of pores at each pore size. The pore size distribution of

Daramic<sup>\*</sup> is seen to fall within a very narrow range. The composite membrane on the other hand has pore sizes <0.06  $\mu$ m, which was beyond the limit detectable by the Coulter porosimeter. Mercury intrusion technique was employed to determine the pore size distribution of both the composite and the untreated Daramic<sup>\*</sup>. The results obtained for the pore size distribution of the untreated Daramic<sup>\*</sup> and the composite membrane are shown in Figures 6.9 to 6.13. For the different thicknesses of both the composite and the untreated Daramic<sup>\*</sup> are very similar as shown in Figures 6.9 and 6.11. Figure 6.13 shows the comparison of the pore size distribution for the composite and the untreated membrane and a shift to smaller pore size after treatment is evident.



Figure 6.8 Differential pore number versus pore size distribution for the untreated Daramic<sup>\*</sup> (0.15 mm) obtained by Coulter porosimeter.



Figure 6.9 Plot of cumulative pore volume (%) versus pore diameter for the untreated membrane obtained by mercury intrusion technique.



Figure 6.10 Plot of incremental pore volume (%) versus pore diameter for the untreated membrane obtained by mercury intrusion.



Figure 6.11 Plot of cumulative pore volume (%) versus pore diameter for the composite membrane obtained by mercury intrusion.



Figure 6.12 Plot of incremental pore volume (%) versus pore diameter for the composite membrane obtained by mercury intrusion.



Figure 6.13 Comparison of cumulative pore volume (%) for the composite and the untreated membrane. Average pore size : Untreated Daramic<sup>\*</sup> =0.095  $\mu$ m, Treated Daramic<sup>\*</sup> = 0.020  $\mu$ m.

A summary of the results obtained from mercury intrusion for both the composite and the untreated Daramic<sup>\*</sup> is presented in Table 6.11 and the composite membranes show a significant reduction in porosity. This reduction in porosity is expected because of the interpenetrating polymeric networks formed in the porous substrate during the treatment process. The pore volume obtained from electrolyte uptake measurement (Table 6.10) for the treated and untreated membranes (0.15 mm) agrees (within the experimental error) with the Hg-intrusion measurement shown in Table 6.11.

Daramic*	Total intrusion volume $\pm 0.05$ (cm <sup>3</sup> /g)		Percentage
thickness (mm)	Untreated	Treated	decrease (%)
0.15	1.18	0.45	62
0.20	1.07	0.63	40
0.23	1.28	0.55	57

 Table 6.11
 Summary of the results of the membranes obtained by mercury intrusion.

From the Field Electron Scanning Electron Microscope (FESEM) micrographs shown in Figure 6.14 a,b, the membrane morphology of the untreated Daramic<sup>\*</sup> membrane for both the surface and cross-section are quite similar. However, the pores on the surface of the membrane are fewer and not as well defined, compared with those in the cross-sectional micrograph. The surface and cross-section FESEM micrographs of composite membrane are shown in Figure 6.15 a,b. From Figure 6.15 a, it can be seen that the surface of the membrane after treatment is coated with a non-uniform layer of the ion-exchange resin and these deposits on the surface are partially covering the surface pores. From the cross-sectional micrograph shown in Figure 6.15.b, the structure of the membrane appears to be more porous than the untreated Daramic<sup>\*</sup>, however it is difficult to draw any quantitative conclusions from these micrographs. Further details study on the surface properties on the composite membrane (treated Daramic) may tell us more on the screening effects and selectivity of these membrane but however, is beyond the scope of the present study.



Figure 6.14 FESEM micrographs of untreated Daramic\*: a) surface, b) cross-sectional.



Figure 6.15 FESEM micrographs of composite membrane: a) surface, b) cross-sectional.

In Figures 6.16 and 6.17, a comparison of the hydraulic permeability of the untreated and composite membrane, shows a huge reduction in hydraulic permeability of the composite membrane and the convective transport across the membrane in the vanadium redox cell could be significantly reduced. This also explain the large improvement in coulombic efficiencies (from 48 % to 94 %) observed in the vanadium redox cell employing this membrane. Moreover, for the untreated Daramic<sup>\*</sup> employed in the vanadium redox cell, it was very sensitive to the differential pressure which could cause significant convective transport.



Figure 6.16 Hydraulic permeability for the composite membrane at different pressures.



Figure 6.17 Hydraulic permeability for the untreated Daramic<sup>\*</sup> at different pressures.

The electrolyte uptake of the composite membrane (0.15 mm) was tested by soaking in a solution of 2 M V<sup>3 5+</sup> in 2.5 M H<sub>2</sub>SO<sub>4</sub>, since in the vanadium redox battery application, the predominant vanadium species in the pores of the membrane are V(III) and V(IV). As seen in Table 6.10, the electrolyte uptake of the composite membrane shows a significant decrease from 140 to 60 %. The increase in area resistance of the composite membrane could thus be attributed to the decrease in the percentage of electrolyte uptake [8]. The electrical conductivity is directly proportional to the concentration of the current carrying species in the membrane which is predominantly H<sup>+</sup> ions in the vanadium redox cell.

The ion-exchange capacity (IEC) of the composite membrane (0.15 mm) was determined to be 0.4 meq/dg. This was low compared with ion-exchange membranes which have typical values in the range of 1-2 meg/dg. The technique used to measure the IEC was found to be subject to large errors (about 50 %). In fact, two samples prepared in the same batch had ion-exchange capacity values differing by 50 % while repeated measurements on the same sample showed a variation about 20 %. In the procedures for determining IEC, the treated membrane was converted to Cl<sup>-</sup> form by soaking the membrane in 0.1 M NaCl solution for 24 hours and the excess Cl<sup>-</sup> ions in the membrane was leached out by washing with ultra pure water until the Cl<sup>-</sup> concentration was less than 1 ppm. It is suspected that due to the high porosity of the membrane, excess Cl<sup>-</sup> may still be residing in the pores of the membrane and was not leached out by the distilled water even though the leachate analysis indicated that the concentration was less than 1 ppm.

Part of the discrepancy could be attributed to the fact that some PE also dissolved in the treatment solution and this is discussed on page 208.

Because of the large errors associated with this technique, IEC determination was not carried out for other treated membranes in the later part of the Chapter. The two important parameters used here to determine the suitability of the membrane for redox flow cell application therefore are the diffusivity and resistivity values as well as performance of the membrane in the charge/discharge cycling tests. These tests were given priority in this study and less emphasis was placed on the full characterization of the membrane although this is obviously an area for further work beyond the present study.

During treatment of the Daramic<sup>\*</sup> membrane, the amount of the Amberlite CG400 resin which actually entered the pores of the membrane and those that was coated onto the surface, was not possible to determine. The particle size distribution of Amberlite CG400 resin was not measured and therefore, the percentage of the resin bead with size less than 0.4  $\mu$ m was unknown. But, as it is shown in Figure 6.9, there are pores on the untreated Daramic<sup>\*</sup> membrane which are larger than 0.1  $\mu$ m and the cumulative pore volume with pore size > 0.1  $\mu$ m is about 30 %. Therefore, it would be expected that some of the resin bead could enter the larger pores presented in the membrane.

The gain in weight of the Daramic<sup>\*</sup> membrane after treatment (with 40 % DVB) was found to be about 18 %. Assuming that all of the weight gain was due the Amberlite

and since the IEC of Amberlite CG400 is 1.6 meq/dg, it is possible to estimate the IEC of the composite membrane as 0.3 meq/dg which is 0.1 meq/dg lower than that measured above. However, not all the weight gain is due to the Amberlite resins incorporated, since part of the weight gain would be contributed by the cross-linker (DVB). Furthermore, it would also be expected that some of the PE (from Daramic<sup>\*</sup>) which dissolved during treatment would reduced the measured weight gain and this would further explain the discrepancy in the estimated IEC value.

The ATR-IR spectra of the untreated and composite membranes are shown in Figure 6.18 and 6.19, respectively. In Figure 6.18, the characteristic absorption peaks at 2940-2855 cm<sup>-1</sup> (C-H stretching), 1450 cm<sup>-1</sup> (C-H bending band) and 1373 cm<sup>-1</sup> (for C-H bending band of the -CH<sub>3</sub> group) indicate the presence of high density PE.

The presence of  $SiO_2$  is indicated by the strong absorption at 1103 cm<sup>-1</sup>, while another strong absorption peak at 1722 cm<sup>-1</sup> could be due to the processing oil used during manufacturing. The presence of quaternary ammonium groups from the ionexchange resin (Amberlite CG400) in the composite membrane is indicated by the medium absorption peaks at 1375-1450 cm<sup>-1</sup> and 3200-3400 cm<sup>-1</sup> in Figure 6.19. Confirmation of these characteristic spectra was also undertaken in consultation with the Atlas of IR spectra (Aldrich) [177].

Experimental measurements also showed that the swelling of the membrane was greatly reduced by cross-linking using DVB. This was indicated by the reduced porosity and electrolyte uptake values measured. The degree of swelling decreased

with increased cross-link density. The more highly cross-linked membranes would be less permeable because of the reduced internal volume of the network and lower average pore size due to decreased swelling. Generally, for ion-exchange membranes, an increase in cross-linking is accompanied by a reduction in diffusivity without sacrificing the resistance.

From the measured properties of the composite membrane therefore, the reduction in diffusivity of the composite membrane can be attributed to the combined effects of the decrease in pore size or the change in tortuosity of the membrane and the incorporation of ion exchange sites into the cross-linked element. Tortuosity is defined as the effective path length of the migrating ions through the membrane which is made of a network of interlocking pores. Incorporation of even a very small quantity of ion-exchange capability to the initially uncharged membrane could produce pronounce differences in its transport properties. This network acts as a physical barrier to the migrating ions so that the ion mobility is effectively reduced with the increase in tortuosity. For the large pore sizes, the transport of the co-ions would be hindered by the ion-exchange resin only near the pore walls. With the decrease in pore size due to cross-linking, the ion exchange sites incorporated into the cross-linked element would be expected to be more effective in excluding the vanadium co-ions.







Figure 6.19 ATR-IR spectra of composite membrane.

# 6.4.3.2 Membrane stability and performance in Charge/Discharge test.

The composite membrane (0.15 mm) produced with 40 vol. % DVB was chosen for performance testing in a small vanadium redox test cell (Section 4.3.3 a) of electrode area 25 cm<sup>2</sup>. The cell employed 65 ml of 2 M V<sup>3 5+</sup> in 3 M H<sub>2</sub>SO<sub>4</sub> in each half cell and had a theoretical capacity of 3 Ahr. A typical charge/discharge voltage profile obtained at 20 mA cm<sup>-2</sup> with the redox cell employing the composite membrane is shown in Figure 6.20. From this figure, the coulombic, voltage and energy efficiencies were calculated as 94, 90 and 85 % respectively. The efficiencies of the cell obtained at various current densities are shown in Figure 6.21.



Figure 6.20 A typical cell potential profile for a complete charge/discharge cycle.



Figure 6.21 Cell efficiencies obtained at various current density for vanadium redox cell employing composite membrane.

The coulombic efficiency remained fairly constant within the range of current densities investigated, while the voltage efficiency dropped with increasing current density due to increased IR losses. The overall energy efficiency thus dropped off with increasing current density, a maximum of 85 % being observed at 20 mA cm<sup>-2</sup>. The efficiencies obtained for the composite membrane were comparable with those obtained with the cation-exchange membranes - CMV and Nafion\* 117 even though the diffusivity value of CMV (Table 5.3) is 6 times lower. Therefore, the high

coulombic efficiency obtained with the vanadium redox cell employing the composite membrane was due to the huge reduction in its hydraulic permeability (Figures 6.16 and 6.17) compared to the untreated Daramic<sup>\*</sup>.

The long term cycling test data for the composite membrane (40 vol. % DVB) obtained at a charge/discharge current density of 40 mA cm<sup>-2</sup> are shown in Figure 6.22. The average current, voltage and energy efficiencies over 1650 cycles (8000 hr) are 94, 86 and 81 % respectively. The coulombic efficiency fluctuates between 93 % and 100 %, while the voltage efficiency shows a gradual decrease due to the air oxidation of the negative half-cell electrolytes leading to an imbalance in the SOC of the electrolytes. The imbalance in the SOC of the electrolytes in the two half-cells was also influenced by a volumetric crossover of the electrolytes across the membrane in either direction during cycling. At points indicated by numbers in the figure, the solutions of the cell were rebalanced so as to bring the SOC of each of the half-cell electrolytes to the same level and restore the capacity of the system. This procedure also allowed the voltage efficiency of the cell, which dropped after successive cycles, to recover.



Figure 6.22 Charge/discharge cycle test data for of the vanadium redox cell employing composite membrane as separator at current density of 40 mA cm<sup>-2</sup>: a) cell efficiencies versus cycle number and b) cell capacity versus cycle number.





At the 10th cycle, the cell resistance measured at 50 % SOC was 3.10  $\Omega$  cm<sup>2</sup> for charging and 3.20  $\Omega$  cm<sup>2</sup> for discharging. At the 550th cycle, the cell resistance at 50 % SOC was 2.33  $\Omega$  cm<sup>2</sup> and 2.54  $\Omega$  cm<sup>2</sup> for charging and discharging respectively. The decrease in the cell resistance during cycling is believed to be due to the activation of the graphite felt electrodes which reduces the activation overvoltage during charging/discharging and results in a steady overall increase in voltage efficiency as observed in Figure 6.22.

Table 6.12 summarises the cell resistance values over the period of charge/discharge cycling of the redox cell employing the composite membrane.

Table 6.12Summary of the cell resistance measured at certain cycle during the<br/>longterm cycle charge/discharge of the redox cell.

	Cell resistance measured at 50 % SOC $\pm 0.05$ ( $\Omega$ cm <sup>2</sup> )		
Cycle number	R <sub>ch</sub>	R <sub>dis</sub>	<b>R</b> <sub>average</sub>
10	3.20	3.10	3.15
206	2.65	2.75	2.70
550	2.33	2.54	2.44
813	2.19	2.26	2.23
1200	2.13	2.22	2.18
1611	2.33	2.49	2.42

The long term stability test on the composite membrane, which involved soaking the membrane in 2 M V(V)/ 3 M  $H_2SO_4$  solution, did not show any sign of deterioration after more than 12 months and further testing is still continuing. The values of area

resistance and diffusivity of the membrane were quite constant for the 12 months period. Furthermore, as illustrated in Figure 6.23, the appearance of the membrane remained unchanged after the 12 month exposure test, while the untreated sample showed significant deterioration after similar exposure to the oxidizing  $V(V)/H_2SO_4$  solution.

From these long term cycle tests, the composite membrane was thus shown to be chemically stable and resistant to fouling in the vanadium redox cell system. The composite membrane produced in this study has therefore been shown to possess the properties required of a separator for the redox battery application.


Figure 6.23 Photo showing deterioration of untreated Daramic<sup>\*</sup> compared with the composite membrane.

## 6.5 Scale-up of membrane treatment.

The Amberlite/DVB treatment process is currently being scaled up in the laboratory to allow preparation of 2400 cm<sup>2</sup> membrane sheets which will be employed in a 3 kW vanadium redox battery in the near future. The manufacturer (W.R.Grace) was unable to supply the size (60 x 40 cm) of the Daramic<sup>\*</sup> membrane required for the 3 kW battery, however, an alternative Daramic<sup>\*</sup> membrane with the required size was provided. This Daramic<sup>\*</sup> membrane, according to the manufacturer, was similar in all properties to the previous samples of Daramic<sup>\*</sup> membrane provided by them, except for the colouring pigment. Previous samples were grey coloured, whilst this batch of sample was white in colour.

The white Daramic<sup>\*</sup> sample (size:  $10 \times 12 \text{ cm}$ ) was treated according to the procedure described in Section 6.4.2.1 and the various properties of the composite membrane were evaluated for comparison with the grey coloured sample.

#### 6.5.1 Results and discussion

Any differences in the white and grey Daramic<sup>\*</sup> samples were analysed using TGA and DSC techniques. Comparing the white coloured sample and the grey coloured sample before any treatment, the TGA analysis showed a silica content of about 54 wt. % (Figure 6.24), lower by 4 % compared with the grey sample (Figure 6.4). Moreover, the highest percentage weight loss in the TGA analysis for the white sample is at a temperature 14 °C higher than the grey sample. Comparing Figures 6.6 and 6.25, the DSC results show that the melting points for both samples are the same and the crystallinity of the white sample as indicated by the heat of fusion, is slightly higher than the grey sample, probably due to the higher PE content in the white sample.

The TGA and DSC results for the white sample (Figures 6.26 and 6.27), treated with 40 vol. % DVB and Amberlite CG400, show similar trends to the treated grey sample (Figures 6.5 and 6.7)- that is both of the grey and white samples after treatment had a higher decomposition temperatures and a reduction in the heat of fusion, while the melting points remained the same.



Figure 6.24 TGA thermogram of white untreated Daramic<sup>\*</sup>.



Figure 6.25 DSC thermogram of white untreated Daramic<sup>\*</sup>.



Figure 6.26 TGA thermogram of white treated Daramic.



Figure 6.27 DSC thermogram of white treated Daramic.

Table 6.13 shows the resistance and the diffusivity of the white sample (size:  $10 \times 12$  cm) treated with different degrees of cross-linking using 1 g of Amberlite CG400 in 50 cm<sup>3</sup> of the solution mixture, while the weight change and the water intake of these samples are shown in Table 6.14. The lowest diffusivity value for the white sample was also achieved with the treatment employing 40 vol. % DVB but the resistance and the diffusivity values obtained was slightly higher than the grey sample (Table 6.9). Moreover, above 40 vol. % DVB, the resistance and diffusivity values obtained with those for the grey sample (Table 6.8).

Table 6.13Properties of composite membranes\* prepared by different degrees of<br/>cross-linking (Amberlite used was 1 g per 50 cm³ of solution).

Sample	DVB:Methanol ratio	Area resistance $\Omega \text{ cm}^2$	Diffusivity x 10 <sup>4</sup> (cm min <sup>-1</sup> )
X1	0:100	0.96	9.14
X2	10:90	1.07	8.45
X3	20:80	1.37	8.93
X4	30:70	1.57	4.63
X5	40:60	1.95	2.24
X6	50:50	1.09	4.02
X7	60:40	0.74	6.20
X8	70:30	1.50	8.23
Untreated (White 0.22 mm) (grey 0.22 mm)	-	0.33 0.30	12.0 8.1

\* Obtained from single measurement for each sample.

Besides the 30 and 40 vol. % DVB treatment (samples X4 and X5), all other samples show a negative weight gain (Table 6.14) and the percentage water intake (as defined on 187) is also the lowest for the same samples, X4 and X5. Also presented in Table

6.14 is the percentage PE extracted by Xylene using the soxhlet extractor for both treated (X5 and X9) and untreated samples. The PE content of the untreated white and grey samples as determined by TGA method however, is 46 and 42 % respectively, so that not all the PE is extracted by this method.

The percentage of PE extracted is slightly higher in the case of the white samples, both treated and untreated, compared with the grey samples and inspite of the fact that all of the PE is extracted, the results shown in Tables 6.14 are consistent with the TGA results which showed a PE content of 4 % higher in the white sample.

Sample	DVB:Methanol ratio	% change in weight	% of water intake
X1	0:100	-7.8	86
X2	10:90	-7.0	81
X3	20:80	-4.7	80
X4	30:70	3.6	74
X5	40:60	3.6	68
X6	50:50	-6.2	72
X7	60:40	-11.3	81
X8	70:30	-11.4	82
Untreated (white 0.22 mm) (grey 0.22 mm) Composite X5 X9 (grey 0.22 mm)	% extraction by Xylene 21.3 19.3 4.7 2.3		115 120

Table 6.14Properties of composite membrane with different degrees of cross-<br/>linking (Amberlite used was 1 g per 50 cm³ of solution).

\* X5 and X9 were treated in the same solution mixture.

Table 6.15 shows the area resistance and the diffusivity of the samples prepared using different amounts of Amberlite CG400 in 50 cm<sup>3</sup> of the solution mixture. Other properties of the corresponding composite membrane samples are also presented in Table 6.16. From Tables 6.15 and 6.16, when no Amberlite was used, the measured properties of the membranes obtained did not differ much from the untreated membrane (Table 6.13 and 6.14). The properties of the treated membranes obtained with 0.1, 0.5 and 1.5 g of Amberlite used in the corresponding DBV:methanol ratio, did not differ significantly and seem to follow a similar trend. This could also indicate that the weight gain by the treated membranes due to Amberlite incorporated would be quite low compared to the those contributed by DVB. The trends seem to show that treatment with 30 or 40 Vol. % DVB and Amberlite CG400, results in lower diffusivity and intermediate resistance values (Table 6.15), higher values of % weight gain, lower values for % extraction of PE by Xylene and lower % of water intake (Table 6.16). The membranes treated with 10 or 50 % DVB show no significant improvement in diffusivity values compared with the original material (Table 6.13). The percentage of water intake for these membranes was also high. The highest percentage in weight gain after treatment was 24.8 %, recorded for sample Y3. In general, low values of the diffusivity of the treated membranes (in Table 6.15) are associated with high percentage weight gain values, low % extraction by xylene and low percentage water intake (Table 6.16). It seems that the weight gain of the treated membrane actually decreases its pore volume and hence, reduces the water uptake.

Sample V2 seems to have a low resistance value even though the values obtained for

other properties was similar to sample V3. Also, for sample Y4, the diffusivity value was low while its weight gain and water intake values would indicate otherwise. For sample Z3, the weight gain value was low while its diffusivity value would indicate a high weight gain.

Sample	DVB:methanol ratio	Area resistance $\Omega \text{ cm}^2$	Diffusivity X 10 <sup>4</sup> cm min <sup>-1</sup>
A1	20:80	0.26	10.7
A2	30:70	0.31	7.23
A3	40:60	0.34	9.45
A4	50:50	0.33	12.5
V1	20:80	0.27	11.5
V2	30:70	0.42	5.12
V3	40:60	1.24	4.33
V4	50:50	0.56	10.5
Y1	20:80	0.43	9.82
Y2	30:70	1.40	4.59
Y3	40:60	2.21	4.05
Y4	50:50	1.78	1.62
Z1	20:80	0.42	13.4
Z2	30:70	0.85	8.55
Z3	40:60	1.29	3.68
Z4	50:50	1.47	11.5

Table 6.15Resistance and diffusivity values of composite membranes (0.22 mm)using different amount of Amberlite CG400.

Sample	DVB:methanol ratio	% change in weight	% Extraction by Xylene	% of water intake
A1	20:80	-6.5	-	85
A2	30:70	4.2	-	63
A3	40:60	-6.6	_	80
A4	50:50	-14.3	_	104
<b>V</b> 1	20:80	2.6	6.1	82
V2	30:70	22	3.6	55
V3	40:60	14.8	3.0	53
V4	50:50	-1.8	8.8	72
	-			
<b>Y</b> 1	20:80	2.2	11.2	83
Y2	30:70	18.9	9.4	58
Y3	40:60	24.8	3.5	48
Y4	50:50	2.8	5.1	73
<b>Z</b> 1	20:80	-3.7	6.4	99
Z2	30:70	12.1	9.9	67
Z3	40:60	5.6	4.2	73
Z4	50:50	-1.0	3.3	99

Table 6.16Properties of the composite membrane treated using different amount<br/>of Amberlite CG400.

Sample size : 10x12 cm

Thickness : 0.22 mm (white sheet)

Amount of Amberlite used per 50 cm<sup>3</sup> of solution.

Code A : no Amberlite used

Code V: 0.1 g of Amberlite used

Code Y : 0.5 g of Amberlite used

Code Z : 1.5 g of Amberlite used

Based on the measured properties of the composite membranes prepared using the white Daramic<sup>\*</sup>, it was thus decided to prepare composite membranes for the 1 kW redox battery using the composition of the solution mixture specified for sample X5 in Table 6.14.

### 6.6 Conclusion

A composite membrane has been developed using Daramic<sup>\*</sup> as substrate and the ionexchange resin, Amberlite CG400. Further cross-linking using 40 Vol. % DVB and methanol has resulted in properties which are suitable for application in redox batteries. The performance of the treated membrane in the charge/discharge testing of a vanadium redox cell is comparable with that observed with ion-exchange membranes available commercially, with an overall energy efficiency of 85 % being achieved. The improvement in the coulombic efficiency obtained in the vanadium redox cell for the Daramic<sup>\*</sup> membrane after treatment is mainly due to cross-linking which effectively reduces its pore size and also decreases the hydraulic permeability. Furthermore, the chemical stability of the membrane is excellent and the membrane is not susceptible to fouling.

#### **CHAPTER 7**

### TRANSPORT PROPERTIES OF MEMBRANES

#### 7.1 Introduction

As described in Chapter 5, during charge/discharge cycling of the vanadium redox cell, preferential transfer of solution from one half-cell to the other was observed. Even though this solution transfer is not detrimental to the shelf life of the battery it does cause capacity losses which can be recovered by remixing of the two half-cell electrolytes. Other factors such as air oxidation and hydrogen evolution which also contribute to loss in battery capacity can be rigorously controlled. This is done by using paraffin oil as a barrier layer on the surface of the negative half-cell electrolyte to eliminate air oxidation and lowering the upper cell voltage charging limit to prevent excessive hydrogen evolution. Maintenance intervals to restore the capacity of the battery, could be extended if the rate of capacity loss could be reduced. Studies of the individual contribution of different transport processes to the overall ionic fluxes across the membrane during charge/discharge cycling would thus provide a better understanding of the observed phenomena.

Quantitative representation of the mass transport of ions across the membrane during charge/discharge of the vanadium redox cell can be described by the Nernst-Planck flux equation (eqn. 3.25). The overall flux  $J_1$  of the species i, is composed of three additive terms; the diffusion flux  $(J_1)_{duff}$  caused by the chemical potential gradient of the species, the electric transference  $(J_1)_{elec}$  caused by the electric potential gradient

and, the transfer  $(J_1)_{con}$  caused by convection. The direction of ionic fluxes and the transport of water across the membrane during charge/discharge of the vanadium redox cell are depicted in Figure 7.1.a,b, for both cation and anion-exchange membranes respectively.

Referring to Figures 7.1 a and b, the diffusional fluxes consist of both V(V) and V(IV) species from the positive half-cell crossing the membrane to the negative half-cell, while the V(II) and V(III) species move in the opposite direction.  $H_3O^+$  (generally referred to as H<sup>+</sup>) and hydrated (usually 6  $H_2O$ ) HSO<sub>4</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup> ions will also diffuse across the membrane due to their concentration gradient across the membrane, however, they would not effect the coulombic efficiency of the battery. It should be noted that where there is a pH gradient, an anion-exchange membrane would exhibit a higher acid permeation rate than does a cation-exchange membrane.

Under electromigration, the H<sup>+</sup> ion is the main current carrying species for both cation and anion-exchange membranes. However, in the case of anion-exchange membranes, the HSO<sub>4</sub><sup>-</sup> ion (moving in opposite direction to the H<sup>+</sup> ion) also carries part of the current. H<sub>2</sub>O molecules which are bound to the charge balancing ions (H<sup>+</sup> and/or HSO<sub>4</sub><sup>-</sup>) as well as the vanadium ions are also transported across the membrane under the influence of the applied electric field during charging and discharging of the redox cell. The transport of the charge balancing ions (H<sup>+</sup> and/or HSO<sub>4</sub><sup>-</sup>) will also drag along water molecules in the direction of the flow (electro-convection). The electro-osmosis flow of water through a membrane is the algebraic sum of that transport by the solvation shells of the charge balancing ions and electro-convection.

It is expressed as the total quantity (moles of water) transported per Faraday of electricity passed [54].

The convective transport of  $H_2O$  which arises from the osmotic pressure gradient (due to the  $H_2SO_4$  concentration difference) across the membrane could also carry other hydrated ions such as  $H^+$ ,  $HSO_4^-$ ,  $SO_4^{-2-}$  and vanadium ions.

The term osmosis is usually applied to membranes that are permeable to the solvent (water), but impermeable to the solute. Most, if not all, of the commercially available membranes are at least slightly permeable to some hydrated ionic species. The transport of these hydrated ionic species could increase or decrease the osmotic water flux.

For an ideal system where there is no transfer of solute and the concentration of solutions separated by a microporous separator is less than 0.1 M, the osmotic pressure could be calculated from the ionic strength of the solutions [10,178,186]. Hence, the decrease or the increase in water flux due to the transfer of solutes in a non ideal system could be deduced. In the present system however, the ionic strength of the solutions cannot be theoretically calculated due to the complex equilibria which are known to exist between the various vanadium ions and the HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions, the equilibrium constants for which are not known.

Using the simplifying assumption that there no complex equilibria present and  $HSO_4^$ is the predominant ion from the  $H_2SO_4$  dissociation, however, the ionic strengths of the solutions were calculated for the respective fully charged positive and negative half-cell solutions as 7 M and 12 M, and for the respective fully discharged positive and negative half-cell solutions as 12 M and 17 M. This suggests that the osmotic water flow should be from the positive half-cell to the negative half-cell solutions. Since no available microporous separator can totally exclude the vanadium and other ions in solution, however, osmotic pressure measurements would not be possible.

For the work described in this Chapter therefore, osmotic water transfer/flow is used as a general term to describe the net volumetric flow in the absence of any electric field due to both the osmotic pressure difference of the solutions and the flow hydrated ionic species due to concentration difference, since the contribution from each process cannot be determined separately. Electro-osmosis, on the other hand is used here to describe the transport of water associated with the solvation shells of the charge balancing ions and electro-convection under the influence of an electric field. Referring to Figures 7.1 a and b, the direction of the water fluxes due to osmosis could reverse at a latter stage as is shown in the experimental results for some of the membranes presented in Section 7.3.2. This is due to changes in the concentrations of the two half-cells solutions in the latter stages of the experiments. Therefore, in Figures 7.1 a and b, a double headed arrow is used.

In addition to the above processes, a phenomenon referred to as anomalous osmosis frictional interaction between solutes and water, has also been described by several workers [66,178-180] and quantitatively treated by Sasidhar et.al [181,182]. It involves solving the theoretical equations that govern the momentum and mass transport for membranes with cylindrical pores, taking into account: (i) the electric field generated by the charged surface of the pores, and (ii) the axial and radial variations of concentration, electrical potential and pressure. As is shown by Sasidhar et.al [182] however, such a phenomenon is only likely to be significant with  $H_2SO_4$  solutions of lower than 1 M concentration. Since the present system involves concentrations of over 2 M, however, this phenomenon should only make a minor contribution to the observed solvent transfer compared with the other transport processes. For simplicity, therefore it is not included in Figure 7.1.



\*Notes: 1) For a discharged electrolyte containing 2 M vanadium ions, the initial  $H_2SO_4$  concentration is 2 M and 3 M for the negative and positive half-cells respectively.

2) The predominant V(IV) and V(V) species are assumed to be  $VO^{2+}$  and  $VO_{2}^{+}$  respectively, while V(III) and V(II) exist as solvated  $V^{3+}$  and  $V^{2+}$  ions respectively.

Figure 7.1 Diagram depicting ionic and water fluxes across the membrane during charge/discharge in the vanadium redox cell: a) cation-exchange membrane, b) anion-exchange membrane.



\*Notes: 1) For a discharged electrolyte containing 2 M vanadium ions, the initial  $H_2SO_4$  concentration is 2 M and 3 M for the negative and positive half-cells respectively.

2) The predominant V(IV) and V(V) species are assumed to be  $VO^{2+}$  and  $VO_2^+$  respectively, while V(III) and V(II) exist as solvated  $V^{3+}$  and  $V^{2+}$  ions respectively.

In this Chapter the transport of ionic fluxes due to diffusion, electro-migration and convection were measured for some of the commercial membranes and the composite membranes prepared as described in Section 6.4. The experimental aspects involved measurement of:

- a) Permeability of V(II), V(III), V(IV) and V(V) species, referred to in this study as diffusivity.
- b) Water transfer across the membrane separating the two half-cell electrolytes at different SOC.
- c) Transport numbers of vanadium, sulphate and hydrogen ions.
- e) Transport of  $H_2O$  during charging/discharging.
- f) Self-discharge current for different types commercial membranes.

### 7.2 Experimental

### 7.2.1 Measurement of diffusivity of V(II), V(III), V(IV) and V(V) ions.

The diffusivity of each of the vanadium ions-V(II), V(III), V(IV) and V(V), across different types of membranes were measured using the set-up and procedures for the diffusion experiment described in Section 4.3.2.a and Section 5.2.1.a, respectively.

Vanadium solutions of various oxidation states were prepared by charging a solution consisting of 1 M V(III) sulphate + 1 M V(IV) sulphate in 2.5 M  $H_2SO_4$  (generally referred to as 2 M  $V^{3.5+}$  in 2.5 M  $H_2SO_4$ ) in the redox flow cell described in Section 4.3.3.b. The prepared vanadium solutions in their various oxidation states consisted

of: i)  $2 \text{ M VSO}_4$  (V(II)) in  $3 \text{ M H}_2\text{SO}_4$ 

- ii) 1 M  $V_2(SO_4)_3$  (V(III)) in 2 M  $H_2SO_4$
- iii) 2 M VOSO<sub>4</sub> (V(IV)) in 3 M  $H_2SO_4$
- iv) 1 M  $(VO_2)_2SO_4$  (V(V)) in 4 M H<sub>2</sub>SO<sub>4</sub>

The V(II) and the V(V) solutions prepared by this method did however, contain a small quantity of V(III) and V(IV) ions respectively, which would be less than 1 % as determined by potentiometric titration using potassium permanganate solution.

In all of the diffusion tests, the blank solution (which was the initial vanadium free solution) consisted of 3 M  $H_2SO_4$  and 1 M MgSO\_4. MgSO\_4 was added to minimise the osmotic pressure effects which would result in the transfer of solution to the concentrated side. During measurement of the diffusivity of V(II) ions, the V(II) solution in the diffusion test cell was covered with a film of paraffin oil to prevent the oxidation V(II) to V(III).

The absorbance of the different vanadium ions in the visible wavelength range was initially measured using UV-visible spectrophotometry to determine the wavelengths corresponding to the peak absorbance for the various vanadium ions. The diffusivity was computed from equation 5.2.

# 7.2.2 Measurement of water transfer for the vanadium electrolytes with different membranes.

Water transfer measurements were performed for the vanadium electrolytes corresponding to each of the different states-of-charge (SOC). The solutions at 0, 50 and 100 % SOC in both the positive and negative half-cells were investigated. The solutions at 0 % SOC correspond to the two half-cell solutions of the vanadium redox battery when it is fully discharged and likewise, 100 % SOC corresponds to a fully charged state. The experimental set-up is described in Section 4.3.5. The vanadium solutions at different SOC were prepared by charging and discharging the redox flow cell similar to that described in Section 7.2.1. For measuring the water transfer of the solutions at 0 % SOC, V(III) and V(IV) solutions were used on opposite sides of the membrane, while V(II) and V(V) solutions were used to measure the water transfer at 100 % SOC. For the intermediate 50 % SOC, equal volumes of V(II) and V(III), or V(IV) and V(V) were mixed for the negative and positive half-cell solutions respectively. It should be noted that the SOC's quoted refer to the initial SOC's of the solutions used, since self-discharge would be occurring as a result of diffusion of the vanadium ions across the membrane during the experiment. The SOC's of the solutions will thus vary during the course of the experiments. The extent of this self-discharge can be determined from the change in the cell voltage with time as discussed in Section 7.3.4.

For these experiments  $65 \text{ cm}^3$  of each solution was used in each of the half-cells. The solutions were at the same initial level which was about half-way up the tubes.

Periodically, the levels attained by the solutions in the tubes were recorded and the experiment was adjourned when the height attained by the solutions remained constant.

# 7.2.3 Measurement of the transport numbers for vanadium, sulphate and hydrogen species.

Transport numbers of vanadium, sulphate and hydrogen across the membrane were determined by electrolysis using a redox flow test cell similar to the one described in Section 4.3.3.b. The solutions were prepared from vanadyl sulphate (Merck); one half-cell solution consisted of 0.1 M V(IV) in 0.1 M H<sub>2</sub>SO<sub>4</sub> and the other half-cell solution was 0.2 M H<sub>2</sub>SO<sub>4</sub>. The electrode used in the vanadium solution was graphite felt bonded to a conductive plastic substrate while a lead electrode was immersed in the H<sub>2</sub>SO<sub>4</sub> solution. Lead was used as the positive electrode in the H<sub>2</sub>SO<sub>4</sub> solution since the evolved oxygen would be detrimental to a graphite electrode. Each electrode had an area of 33 cm<sup>2</sup> and the area of the membrane was 36 cm<sup>2</sup>. The current applied for the electrolysis was 1.09 A (30 mA cm<sup>-2</sup>).

Initially, before the passage of electricity, samples of solution from both half-cells were taken and the total volume of each cell was recorded. Electrolysis was allowed to proceed to the stage where nearly all the V(IV) ions were converted to V(V), this being indicated by the colour of the solution changing from blue to yellow. At the end of the electrolysis samples of the solutions were taken and the contents analysed for vanadium and sulphate using ICP. The transport number of hydrogen ions was

deduced from the balance of the current carried by vanadium and the sulphate ions.

# 7.2.4 Vanadium redox cell self-discharge current measurement for different types of membranes.

The redox flow test cell used for the experiments is described in Section 4.3.3.b. To each half-cell, 250 cm<sup>3</sup> of the electrolyte 2 M V<sup>3 5+</sup> in 2.5 M H<sub>2</sub>SO<sub>4</sub> was added. In the negative half-cell reservoir, air oxidation of the V(II) electrolyte was reduced by sealing the reservoir with flexible polyethylene sheet. The use of the flexible polyethylene sheet was to prevent any pressure build-up when the volume in the reservoirs fluctuated.

Initially, the cell was charged to an OCV of above 1.65 V to ensure that the cell was above 99 % SOC. The power supplied to the cell was terminated prior to the commencement of the experiment. During the course of the experiment, the pumps which circulated the electrolytes through the cell were running continuously. The solution volume in the reservoir as well as the cell voltage were recorded periodically.

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# 7.2.5 Volumetric crossover monitoring of electrolytes across the membrane during charging/discharging.

The redox flow test cell used is described in Section 4.3.3.b. and the experimental setup is illustrated in Figure 7.2. The solution reservoirs were made from conical flasks with a 250 mm length graduated glass tube (ID = 10 mm) connected in a vertical position to the mouth of each. For this experiment, the solutions exited the cell via a flexible polyethylene tube and flowed to the reservoir through the glass tube. During charge and discharge cycling, the level of the solutions in both of the reservoirs fluctuated along the length of the glass tubing. The polyethylene tubing which conveyed the solutions exiting the cell, could be adjusted along the length of the glass tube to the level of the solutions in the reservoirs, hence, reducing the error in the level reading. The volume of solutions in the reservoirs could be accurately read from the solution level on the graduated glass tubing. This design also ensured all the solutions in the reservoirs were circulated through the cell. It was important also to ensure no air was trapped in the polyethylene tubing or the reservoirs.

Before commencing the experiment, the cell was subjected to a few charge/discharge cycles to allow the system to achieve a 'steady state'. The experiment commenced when the cell was fully discharged and was switched over to charging mode by the automatic controller. The level of the solutions in the glass tubes as well as the cell voltage were recorded periodically during the full charge and discharge cycle.



Figure 7.2 Experimental setup for studying volumetric crossover monitoring of electrolytes during charging/discharging.

### 7.3 Results and discussion

### 7.3.1 Measurement of diffusivity of V(II), V(III), V(IV) and V(V) ions.

The U.V visible spectrographs for 0.04 M solutions of V(II), V(III), V(IV) and V(V) are shown in Figure 7.2 to 7.4 respectively. In the diffusion experiments, measurement of very low vanadium levels was involved, hence, the wavelengths corresponding to the peak maxima for the 0.04 M solutions were selected for absorbance measurements. For the various vanadium species, the respective wavelengths for the absorbance measurements were used: V(II)  $\lambda$ =566 nm, V(III)  $\lambda$ =566 nm, V(III)  $\lambda$ =760 nm and V(V)  $\lambda$ =360 nm.



Figure 7.3 Plot of absorbance versus wavelength (visible region) for: a) V(II) solution, b) V(III) solution.



Figure 7.4 Plot of absorbance versus wavelength (visible region) for: a) V(IV) solution, b) V(V) solution.

The diffusivity values of the various vanadium species tested with different membranes are summarised in Table 7.1. Generally, for all the different types of membranes investigated, the diffusivities of the V(IV) and V(V) species across the membranes were much higher than the V(II) and the V(III) species. The most pronounced difference was seen with the AMV membrane. The higher diffusivities of V(IV) and V(V) species could be attributed to their ion pairing with the SO<sub>4</sub><sup>2-</sup> ions, both negative and positive ion complexes having been reported (Section 3.1.1). Complex formation of this kind thus reduces the efficiency of Donnan exclusion of the electrolyte, while for the V(II) and V(III) ions, no such complex formation has been reported to date. Especially for the anion-exchange membrane, therefore, the presence of negatively charged complex species would enable these species to enter the membrane with relative ease.

 Table 7.1
 Diffusivity (cm min<sup>-1</sup>) of the vanadium ions across the different membranes.

	Diffusivity (cm min <sup>-1</sup> )			
Membrane	V(II)	V(III)	V(IV)	V(V)
AMV	2.01x10 <sup>-6</sup>	1.11x10 <sup>-6</sup>	3.17x10 <sup>-5</sup>	5.67x10 <sup>-5</sup>
CMV	1.01x10 <sup>-5</sup>	1.34x10 <sup>-5</sup>	2.65x10 <sup>-5</sup>	2.14x10 <sup>-4</sup>
Nafion <sup>*</sup> 117	4.63x10 <sup>-5</sup>	4.24x10 <sup>-5</sup>	1.94x10 <sup>-4</sup>	1.41x10 <sup>-4</sup>
Daramic <sup>*</sup>	6.21x10 <sup>-4</sup>	7.09x10 <sup>-4</sup>	1.46x10 <sup>-3</sup>	>1x10 <sup>-2</sup>
Composite	1.26x10 <sup>-4</sup>	1.34x10 <sup>-4</sup>	3.64x10 <sup>-4</sup>	2.92x10 <sup>-3</sup>

Daramic<sup>\*</sup> (0.15mm), Composite membrane (0.23 mm)

Experimental observations suggested that the negatively charged V(V) sulfate complex ( $VO_2SO_4$ ) may associate or form ion-pairs with the fixed ionic groups of the AMV membrane. This membrane when equilibrated in V(V) solution showed a reddish stain suggesting association or ion-pairing between the V(V) ions and the quaternary ammonium ions of the membrane. This association could localise the V(V) ions in the ion-exchanger and could thus reduce the Donnan potential and the efficiency of electrolyte exclusion. The diffusivity of V(V) ions was thus the highest among all the other vanadium species as shown in Table 7.1.

From the coulombic efficiencies obtained in the charge/discharge tests (Table 5.3) and the diffusivity values shown in Table 7.1, the anion-exchange membranes were also shown to be less permeable to the positively charged vanadium ions than the cation-exchange membrane. This could be due to both the Donnan potential of the anion-exchange membrane which excludes the positively charged vanadium species from entering and the sieving effect on the hydrate vanadium species. However, negatively charged species such as VO<sub>2</sub>SO<sub>4</sub><sup>-</sup> may still permeate through. In cation-exchange membranes, the counter ions are the positively charged vanadium (i.e V<sup>2+</sup>, V<sup>3+</sup>, VO<sup>2+</sup> and VO<sub>2</sub><sup>+</sup> etc.) and H<sup>+</sup> ions which are not excluded by the Donnan potential so that the diffusivity values given in Table 7.1 are higher than for the anion-exchange membranes. However, the high coulombic efficiencies obtained with cation-exchange membranes shown in Table 5.3 also indicate effective exclusion of the vanadium ions by these membranes. In this respect, therefore, the low diffusivity values for these membranes is attributed to the size of the hydrated vanadium ions which restricts their movement through the membranes, with the higher cross-linked

membranes being more effective. In the case of Nafion<sup>\*</sup> 117, the swelling of the membrane was greatly reduced in the high ionic strength solution and this could also help in restricting the passage of vanadium ions. In Table 7.1, the Daramic<sup>\*</sup> membrane has the highest diffusivity values for all the different vanadium ions while the composite membrane (treated Daramic<sup>\*</sup>) shows a decrease in the diffusivity values. It is interesting to note that in the case of the untreated Daramic<sup>\*</sup> membrane, the diffusivity of V(V) ions is almost two orders of magnitude higher than that for V(II) and V(III) ions in spite of the fact that this membrane is microporous and non-selective. This phenomenon cannot be explained without further study which unfortunately is beyond the scope of the present work.

From the diffusivity values shown in Table 7.1, it would be expected that in the vanadium redox cell, the net flux of the vanadium ions would be toward the negative half-cell. However, only the anion-exchange membrane exhibited this kind of behaviour. Also, in the vanadium redox cell, the predominant species present in the membrane separating the two half-cell solutions are V(III) and V(IV). Any V(II) or V(V) entering the membrane phase would react to form either of the V(IV) or V(III) species, but because of the higher diffusivity of V(V) compared to V(II) species, the concentration ratio of V(IV) species would be higher than the V(III) species. This would inevitably favour the net diffusional flux of vanadium species toward the negative half-cell.

In spite of the large differences in diffusivity values (apart from the untreated Daramic<sup>\*</sup> which gave very low efficiencies), the coulombic efficiencies (Table 5.4)

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obtained in the vanadium redox cell with each of the membranes tested in Table 7.1, were almost the same except for the AMV membrane which was marginally higher. This indicates that the diffusional flux of these membranes is much lower compared to the transport by electro-migration and convection. Hence, the coulombic efficiency of the battery is not appreciably affected by the differences in diffusivities of the vanadium ions through the membrane. The overall net transport of vanadium ions is greater however, if the direction of transport by the other two processes is the same as the diffusional process and lower if they are in opposite directions. The latter situation would be more beneficial with regard to reducing the capacity loss in the vanadium redox battery.

# 7.3.2 Measurement of water transfer for the vanadium electrolytes with different membranes.

The osmotic pressure in dilute solutions is given by the relation:

$$\Pi = \operatorname{RT} \Sigma C_{1} \tag{7.1}$$

where  $C_1$  is the volume concentration of each solute, R is the gas constant and T is the temperature. The use of equation 7.1 for estimating the osmotic pressure of solutions is limited however to infinite dilution and for more concentrated solutions, activity instead of concentration should be used, activity being a function of the total ionic strength. For the vanadium redox cell electrolytes, a number of different species might be present as a result of ion-pairing (ref. Section 3.1.1.). In principle, if all the equilibrium constants for complexation at a given temperature for a given system are known, the amounts of each species and hence, the osmotic pressure differences between the two solutions can be calculated. However, much of the equilibrium and speciation of vanadium of the different oxidation states is still poorly understood, and since activities cannot be theoretically calculated in solutions of such high ionic strengths, the osmotic pressure of the solutions cannot be theoretically determined.

The experimental measurements of water transfer for the various membranes - AMV, DMV, CMV, Nafion<sup>\*</sup> 117, Flemion<sup>\*</sup>, DOW<sup>\*</sup> XUS13204.10, Daramic<sup>\*</sup> and treated Daramic<sup>\*</sup>, are presented in Figure 7.5 to 7.17 respectively.

In these figures, the positive side solution and the negative side solution refer to the solutions used for the positive half-cell and negative half-cell in the vanadium redox cell. Water transfer measurements were usually terminated when the solutions in the tubes attained the maximum heights. However, for some cases, it was observed that the direction of the solution transfer was reversed after reaching a maximum. The small discrepancies observed in the heights attained in each arm of the osmotic cell shown in Figure 7.5 to 7.19 were due to the expansion of solutions with variation in ambient temperature and changes in electrolyte density with decreases in SOC during the experiment.

In Figure 7.5, water was initially transferred from the negative to the positive halfcell for 100 % SOC solutions separated by AMV and DMV membranes. The direction of the water transfer was reversed at around the 12th hour. When solutions at 50 % initial SOC (Figure 7.6) were used, water is being transferred from the positive to negative half-cell. For the initially 0 % SOC solutions, water is being

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transferred from the negative to the positive half-cell (Figure 7.7).

The direction of water transfer for the CMV (Figure 7.8 to Figure 7.10), Nafion<sup>\*</sup> 117 and Flemion<sup>\*</sup> membranes (Figure 7.11 to Figure 7.13), which are all cation-exchange type, show similar trends at their corresponding SOC's. For these membranes, water was transferred from the negative to the positive half-cell the rate decreasing as the initial SOC of the solutions used decreases. For the Flemion<sup>\*</sup> membrane, a reversal in the direction of the water transfer was observed after the 70th hour when a 0 % initial SOC solution was used. For the treated Daramic<sup>\*</sup> and DOW<sup>\*</sup> membranes, as shown respectively in Figure 7.8 to 7.10 and Figure 7.14 to 7.16, an initial transfer of water to the positive half-cell, then going through a maximum and reversing in its direction, was also observed. Due to the high rate of cross mixing of the two half-cell solutions, the untreated Daramic<sup>\*</sup> (Figure 7.14 and Figure 7.16) did not show any effect. As mentioned earlier, because of the diffusion of vanadium ions across the membrane, self-discharge of the electrolytes leads to a decrease in SOC during the experiments so that the trends observed reflect the dynamic relationship between changes in osmotic pressure and net water transfer.

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Figure 7.5 Water transfer measurement across different types of membranes for the various vanadium ions: AMV and DMV membranes at 100 % initial SOC.



Figure 7.6 Water transfer measurement across different types of membranes for the various vanadium ions: AMV and DMV membranes at 50 % initial SOC.



Figure 7.7 Water transfer measurement across different types of membranes for the various vanadium ions: AMV and DMV membranes at 0% initial SOC.



Figure 7.8 Water transfer measurement across different types of membranes for the various vanadium ions: CMV and Treated Daramic<sup>\*</sup> membranes at 100 % initial SOC.



Figure 7.9 Water transfer measurement across different types of membranes for the various vanadium ions: CMV and Treated Daramic<sup>\*</sup> membranes at 50 % initial SOC.



Figure 7.10 Water transfer measurement across different types of membranes for the various vanadium ions: CMV and Treated Daramic<sup>\*</sup> membranes at 0 % initial SOC.


Figure 7.11 Water transfer measurement across different types of membranes for the various vanadium ions: Nafion<sup>\*</sup> 117 and Flemion<sup>\*</sup> membranes at 100 % initial SOC.



Figure 7.12 Water transfer measurement across different types of membranes for the various vanadium ions: Nafion<sup>\*</sup> 117 and Flemion<sup>\*</sup> membranes at 50 % initial SOC.



Figure 7.13 Water transfer measurement across different types of membranes for the various vanadium ions: Nafion<sup>\*</sup> 117 and Flemion<sup>\*</sup> membranes at 0 % initial SOC.



Figure 7.14 Water transfer measurement across different types of membranes for the various vanadium ions: DOW<sup>\*</sup> and untreated Daramic<sup>\*</sup> (0.22 mm) membranes at 100 % initial SOC.



Figure 7.15 Water transfer measurement across different types of membranes for the various vanadium ions: DOW<sup>\*</sup> and untreated Daramic<sup>\*</sup> (0.22 mm) membranes at 50 % initial SOC.



Figure 7.16 Water transfer measurement across different types of membranes for the various vanadium ions: DOW<sup>\*</sup> and untreated Daramic<sup>\*</sup> (0.22 mm) membranes at 0 % initial SOC.

Because of the complexity of the vanadium-sulphuric acid electrolytes which makes it impossible to theoretically calculate ionic strengths, it was decided to conduct a series of experiments with electrolytes containing only sulphuric acid, the concentrations used being the same as those in the fully charged vanadium electrolytes, i.e 2 M and 4 M  $H_2SO_4$ . Ionic strength of the solution is related to its concentration (C,) and ion charge (Z<sub>i</sub>) as [10]:

$$I = 0.5 \sum C_{1} Z_{1}^{2}$$
 (7.1a)

The ionic strengths of the 2 M and 4 M  $H_2SO_4$  solutions is calculated as 2 M and 4 M respectively. Based on this, osmotic water transfer would be expected to occur from the 2 M to 4 M  $H_2SO_4$  solutions.

The water transfer measured across the AMV and DMV membranes for different concentrations of  $H_2SO_4$  in each half-cell is presented in Figures 7.17 and 7.18, respectively. Interestingly, only a small transfer of water from the diluted to the concentrated side was initially observed for different concentrations of  $H_2SO_4$  used for the two half-cells. When the experiment was extended to longer periods for both membranes, that is after 70 hours for DMV and 90 hours for AMV membranes, the direction of water transfer was from the concentrated side to the dilute side, reflecting transfer of water against its concentration gradient. The observed direction of water transfer is the same as in the case of the fully charged vanadium electrolytes. For the CMV membrane, however, the larger the difference in the concentration of  $H_2SO_4$  in the two half-cells, the greater was the flux of water being transferred from less concentrated side to more concentrated side as shown in Figure 7.19. Comparing Figures 7.8 and 7.19.b, therefore, the direction of water transfer

observed is again the same as that observed with the corresponding vanadium electrolytes.

From the results shown in Figures 7.5 to 7.19, it can be seen that there are many competing phenomena which produce the net volumetric water transfer across the membrane.

Normal osmosis behaviour is exhibited by membranes which are nonionic or completely impermeable to the solute. In this case, the solvent flux is from the dilute to the concentrated solution and is proportional to the osmotic pressure difference between the two solutions. Osmosis makes the level in the capillary rise on the concentrated solution side, until the hydrostatic pressure balances the osmotic pressure difference [178]. The concentration gradient of about 1 M across the membrane in the case of this osmotic water flow study would create an osmotic pressure of about 2.4 MPa while the measured height difference of the two half-cell solutions (Figures 7.15 to 7.19) was in the order of 1 kPa. This could indicate the diminishing effect of osmotic pressure in the highly concentrate solutions. On the other hand, for a concentration difference of 1 M H<sub>4</sub>SO<sub>4</sub> across the membrane and assuming the dissociated H<sup>+</sup> carries one H<sub>2</sub>O and HSO<sub>4</sub><sup>-</sup> carries 6 H<sub>2</sub>O, then the amount of water transferred to equalize the concentration of solutions on each side of the membrane would be about 4.1 ml. This magnitude of the water flow more closely reflects the data shown in Figures 7.5 to 7.19, indicating that the flow of water across the membrane associated with the hydrated ions is significant compared to the net volumetric water transfer.



Figure 7.17 Water transfer measurement across AMV membrane with different  $H_2SO_4$  concentration: 4 M and 2 M.



Figure 7.18 Water transfer measurement across DMV membrane with different  $H_2SO_4$  concentration: 4 M and 2 M.



Figure 7.19 Water transfer measurement across CMV membrane with different  $H_2SO_4$  concentration: a) 4 M and 3.5 M, b) 4 M and 3 M, c) 4 M and 2.5 M, d) 4 M and 2 M.





Using the simple case of  $H_2SO_4$  solutions of different concentrations separated by an ion-exchange membrane (Figures 7.17 to 7.19), there are two main competing water fluxes in opposite directions to produce the observed water transfer, these being the water transfer due to the osmotic pressure gradient and the diffusion of hydrated H<sup>+</sup> and  $HSO_4^-$  ions under the concentration gradient. Where a pH gradient exists, an anion-exchange membrane exhibits a higher acid permeation rate than does a cation-exchange membrane.

For the CMV membrane shown in Figure 7.19, the observed water transfer is from lower to higher concentration. This indicates that the water flux due to the pressure gradient is higher than competing flux arises from the diffusion of the hydrated ions. In the case of cation-exchange membrane, the movement of hydrated  $H^+$  ions is not restricted through the membrane, whereas hydrated  $HSO_4^-$  ions are. On the other hand, for the AMV and DMV membrane (Figures 7.17 and 7.18), the initial water transfer is from lower  $H_2SO_4$  concentration to higher  $H_2SO_4$  concentration but the direction of the net water fluxes is reversed after 80 and 60 hours for the respective membrane. For these membranes, the initial water flux arises from the diffusion of the hydrated  $HSO_4^-$  and  $H^+$  ions is lower than those due to pressure gradient. After 80 and 60 hours for the respective AMV and DMV membrane, the water flux due to the diffusion of hydrated  $HSO_4^-$  and  $H^+$  ions is higher than that caused by the pressure gradient.

#### 7.3.3 Measurement of transport numbers for vanadium, bisulphate and hydrogen ions.

The transport numbers of vanadium, bisulphate and hydrogen ions for some commercial membranes were measured by electrolysis. The transference number,  $t_i$  of a species i is defined as the number of moles of the species transferred by 1 faraday of electricity through a stationary cross section in the direction of positive current. The transference numbers of anions are negative since there are transferred in the direction opposite to that of the positive current. The transport number ( $T_i$  where  $T_i = z_i t_i$  and  $z_i = 1$  for hydrogen ion, 1 for vanadium ion and -1 for bisulphate ion) of a species is defined as the fraction of the electric current carried by the species. The transport numbers by definition are all positive for ions [66]. The sum over all transport numbers is equal to unity represented by equation 7.2.

$$\Sigma_{i} T_{i} = \Sigma_{i} z_{i} t_{i} = 1 \tag{7.2}$$

The experimental set-up employed for measurement of transport numbers is described in Section 7.2.3. In the case of the V(IV) ion, a solution of 0.1 M V(IV) in 0.1 M  $H_2SO_4$  was employed while the other half-cell solution was 0.2 M  $H_2SO_4$ . During electrolysis, at the anode, V(IV) was oxidized to V(V) whereas at the cathode, hydrogen evolution occurred. The current flowed from the anode to the cathode and induced convection in the pores of the membrane. Graphite felt bonded to conductive plastic, was used at the anode to provide a high surface area for the reaction and to ensure no side reactions occurred during electrolysis. After the experiment, the polarity of the electrodes was reversed to remove any V(V) species residing in the graphite felt and fresh V(IV) was used for the next run. Because oxygen evolution at a graphite felt electrode would lead to oxidation of the carbon and mechanical disintegration of the electrode, lead was used as the cathode during electrolysis. On reversal of polarity, when serving as an anode, lead would be more stable than graphite.

In this experiment, low concentrations of vanadium ions and sulphuric acid were used to reduce the error in diluting the samples for ICP analysis. For a typical 2 M vanadium sulphate solution, the dilution required for 0.2 ml samples is 2500 times and errors of up to 5 % are usually encountered. By employing 0.1 M solution however, only a 125 times dilution is required and thus reducing the errors considerably. The period for the electrolysis was kept to less than 90 minutes to ensure that there was no appreciable diffusion of ions nor transfer of solvent due to osmosis. The ionic flux across the membrane was thus solely due to electromigration.

The transport numbers for vanadium, bisulphate and hydrogen ions, obtained for some commercial membranes are presented in Table 7.2. The values shown in this table are associated with the positive half-cell reaction during charging of the vanadium redox cell and the current flows from the positive to the negative side.

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Membrane type	Transport number					
	T <sub>Bisulphate</sub>	T <sub>Vanadium</sub>	T <sub>Hydrogen</sub>			
CMV	0.05	0.07	0.88			
AMV	0.40	0.00	0.60			
Nafion <sup>*</sup> 117	0.10	0.13	0.77			
Flemion*	0.03	0.01	0.96			
Treated Daramic*	0.09	0.03	0.88			

Table 7.2Membrane transport numbers of vanadium, bisulphate and hydrogenions.

For the AMV membrane, the current is carried by both H<sup>+</sup> and HSO<sub>4</sub><sup>-</sup> ions, the HSO<sub>4</sub><sup>-</sup> ions carrying a significant portion of the current (40 %). Vanadium ions do not carry any appreciable current, this being confirmed by the high coulombic efficiency achieved when employing this membrane in the vanadium redox cell (Table 5.4). These results also imply that, in the preparation of vanadium electrolyte by electrolysis using an anion-exchange membrane as the separator for the cell, the transfer of HSO<sub>4</sub><sup>-</sup> ions out of the negative half-cell would mean that the HSO<sub>4</sub><sup>-</sup> ion concentration in the vanadium electrolyte produced could be different from that prepared by using a cation-exchange membrane. The H<sub>2</sub>SO<sub>4</sub> concentration used in the actual vanadium redox battery or vanadium electrolysis cell is above 2 M, therefore, the T<sub>Bissuphate</sub> in these cases could be lower and probably in the order of 0.1.

The  $H^+$  ions are the major current carrying ion for the cation-exchange membrane, however, the selectivity of these membranes toward  $H^+$  ions is poorer compared to the AMV membrane which does not show any leakage of vanadium ions. The vanadium transport numbers for CMV and Nafion<sup>\*</sup> 117 membranes are considerably high, in contrast to what is being observed when these membranes are employed in the vanadium redox cell where coulombic efficiency of 95 % are achieved. However, in the vanadium redox cell, the high concentration of sulphuric acid would increase the transport of hydrogen ions and furthermore, with the higher ionic strength solution used, the swelling of the membranes (especially Nafion<sup>\*</sup> 117) is effectively reduced. One might expect the much tighter structure to effect 'sieving' action on the large hydrated vanadium ions, selectively allowing the H<sup>+</sup> ions to pass through. As the concentration of the solutions increases, the effectiveness of Donnan exclusion the of co-ions (HSO<sub>4</sub><sup>-</sup> ions) should also decrease.

The transport numbers of vanadium and bisulphate obtained for the Flemion<sup>\*</sup> membrane are low and this also suggest that it is the most suitable membrane for use in the electrolysis cell for the preparation of vanadium electrolyte. The vanadium transport number is also low for the treated Daramic<sup>\*</sup>.

## 7.3.4 Self-discharge currents of vanadium redox cell for different types of membranes.

When the vanadium redox cell is on stand-by with the pumps off, the self-discharge of the battery is confined to the solutions present in the battery stack which are usually less than 10 % of the total capacity of the battery. The design of the battery system can be varied depending on the type of application. If the height of the battery stack is level with the height of the reservoir, then the battery stack will not drain and all the capacity of the battery stack can be self-discharged. Self-discharge occurs in any battery system, but for the vanadium redox battery, since the energy required to run the pumps is tapped off from the battery, it is essential to design the battery with the lowest self-discharge rate to eliminate the need for external power to start the pumps. Generally, commercial membranes which have low diffusivity also possess high electrical resistance. However, for certain types of applications, it is more desirable to select membranes with lower resistance and acceptable diffusivity value for a higher voltage output. The self-discharge rate or self-discharge current of various commercial membranes has been evaluated to aid in the design and the selection of the membrane for the vanadium redox battery with respect to specific applications.

The self-discharge voltage versus time plots for a fully charged vanadium redox test cell using different types of membranes are illustrated in Figures 7.20 to 7.26 together with the volume of solution transferred across the membranes during self-discharge. During the measurement of self-discharge, the total volume of the solution

in the reservoirs is circulated through the cell (i.e pumps were ON throughout the experiment). The self-discharge of the cell is indicated by the drop in cell potential with respect to time. As expected, the rate of self-discharge of all the membranes investigated is not constant, being higher at high SOC, when the active vanadium ion concentration is the highest.

From the data shown in Figures 7.20 to 7.26, the self-discharge currents at different SOC's and the average self-discharge current over a period of time were calculated for each membrane and are presented in Tables 7.3 and 7.4 respectively. In calculating the self-discharge current at a particular SOC, the gradient of the curve (cell voltage versus time in Figures 7.20 to 7.26) is measured and this is proportional to the rate of capacity loss, since the cell open circuit voltage (OCV) is related to SOC as shown in Figure 3.1. Using equation 3.20, the self-discharge current can be calculated. As already mentioned, these experiments were conducted with the pumps ON, so that the measured discharge currents will be higher than the situation where the batteries are on stand-by with pumps OFF. In calculating the average self-discharge current, the loss in battery capacity over the time period was used.



Figure 7.20 Self discharge of fully charged vanadium redox cell with AMV membrane: (area 138 cm<sup>2</sup>), volume of electrolytes on each side = 250 ml: a) volume variation b) cell potential profile with respect to time.



Figure 7.21 Self discharge of fully charged vanadium redox cell with DMV membrane: (area 138 cm<sup>2</sup>), volume of electrolytes on each side = 250 ml: a) volume variation b) cell potential profile with respect to time.



Figure 7.22 Self discharge of fully charged vanadium redox cell with Nafion<sup>\*</sup> 117 membrane: (area 138 cm<sup>2</sup>), volume of electrolytes on each side = 250 ml: a) volume variation b) cell potential profile with respect to time.



Figure 7.23 Self discharge of fully charged vanadium redox cell with Flemion<sup>\*</sup> membrane (area 138 cm<sup>2</sup>) and volume of electrolytes on each side = 250 ml: a) volume variation b) cell potential profile with respect to time.



Figure 7.24 Self discharge of fully charged vanadium redox cell with treated Daramic<sup>\*</sup> membrane (area 138 cm<sup>2</sup>) and volume of electrolytes on each side = 250 ml: a) volume variation b) cell potential profile with respect to time.



Figure 7.25 Self discharge of fully charged vanadium redox cell with DOW<sup>\*</sup> membrane (area 138 cm<sup>2</sup>) and volume of electrolytes on each side = 250 ml: a) volume variation b) cell potential profile with respect to time.



Figure 7.26 Self discharge of fully charged vanadium redox cell with CMV membrane (area 138 cm<sup>2</sup>) and volume of electrolytes on each side = 250 ml: a) volume variation b) cell potential profile with respect to time.

	Self-discharge current density (i <sub>sd</sub> , mA cm <sup>-2</sup> ) at different SOC						
Membrane type	SOC	i <sub>sd</sub>	SOC	i <sub>sd</sub>	SOC	i <sub>sd</sub>	
AMV	>99.5	8.1	98	0.29	85	0.17	
DMV	>99.5	18.7	98	3.03	90	0.71	
CMV	>99.5	30.6	98	4.57	70	1.21	
Nafion <sup>*</sup> 117	>99.5	32.0	98	5.60	95	1.23	
Flemion <sup>*</sup>	>99.5	30.6	98	1.16	97	0.95	
DOW*	>99.0	75.0	96	40.0	-	-	
Treated Daramic <sup>*</sup>	>99.5	35.1	95	6.0	70	2.14	

Table 7.3Self-discharge current density of the vanadium redox cell at different

SOC's	for	various	commercial	membranes.	

#### Table 7.4 Average self-discharge current density of the vanadium redox cell

using various commercial membranes.

Membrane type	Initial SOC	Period (hr)	Final SOC	Average self-discharge current density (mA cm <sup>-2</sup> )
AMV	99.5	375	83	0.38
DMV	99.5	130	88	0.90
CMV	99.5	140	72	1.27
Nafion <sup>*</sup> 117	99.5	124	80	1.58
Flemion*	99.5	46	95	0.98
DOW*	99.0	22	16	38.0
Treated Daramic*	99.5	74	71	3.73

As illustrated in Table 7.3, the self-discharge current densities for all of the membranes investigated are high when the SOC of the cell is above 99 %, but they decrease rapidly with a slight decrease in the SOC. Below 95 % SOC, the self-discharge currents remain relatively constant. This also suggests that it is unnecessary to charge the vanadium redox battery to above 95 % SOC since the extra capacity will be lost rapidly. The average self-discharge currents for the different membranes tested, as indicated in Table 7.4, although measured over different times, are consistent with the observed coulombic efficiencies obtained with the vanadium redox cell.

In Figures 7.20 and 7.21, the net solution fluxes (H<sub>2</sub>O and hydrated ions) across the membranes at SOC's above 99 % are seen to be low for the AMV and DMV membranes. This is contrary to the behaviour of CMV, Nafion<sup>\*</sup> 117, Flemion<sup>\*</sup> and DOW<sup>\*</sup> membranes which show maximum fluxes (Figures 7.22, 7.23, 7.25 and 7.26) at the highest SOC decreasing with a decrease in SOC. It should be noted that only the vanadium species crossing the membrane could cause the self-discharge and not the H<sup>+</sup> and the HSO<sub>4</sub><sup>-</sup> ions. These observations indicate that the self-discharge for the AMV and DMV membranes at SOC > 99 % is predominantly caused by the diffusion of hydrated vanadium species across the membrane. (In the water transfer measurement for AMV membrane shown in Figure 7.5, the initial water flux seems quite high and the direction of the water flux reversed at about 12th hours. However, as shown in Figure 7.20, the total change in volume in the two half-cell solutions is almost negligible during the first 30 hours.) The solution flux across AMV and DMV membranes (Figure 7.20 and 7.21) increases with a decrease in the SOC of the

solutions, and the direction of the flux is opposite to that observed for the Nafion<sup>\*</sup> 117, Flemion<sup>\*</sup>, CMV and DOW<sup>\*</sup> membranes. Moreover, the water transfer for AMV and DMV membranes at SOC < 95 % could in fact counteract the diffusional flux of vanadium ions, thus decreasing the self-discharge.

For the Nafion<sup>\*</sup> 117, Flemion<sup>\*</sup>, CMV and DOW<sup>\*</sup> membranes, the convective transport of vanadium species (ions carried along by the water flow due to osmotic pressure gradient) at SOC's above 99 % is the predominant factor causing the self-discharge. As the SOC of the solution decreases, the water transfer across the membrane decreases, thus reducing the convective transport of vanadium species and the selfdischarge rate. The diffusional flux of vanadium species is the predominant factor causing the self-discharge at lower SOC's (i.e SOC < 95 % or cell voltage < 1.48 V from Figures 7.22, 7.26 and 7.26) for these membranes.

Besides the DOW<sup>\*</sup> membrane, the treated Daramic<sup>\*</sup> shows the highest rate of selfdischarge compared to the commercial membranes tested, as indicated in Figure 7.25. The direction of solution transfer across the membrane is similar to that observed for the anion-exchange membranes.

The self-discharge of the vanadium redox test cell from the fully charged to fully discharged state was also conducted with the CMV membrane. During the course of the experiment, 0.2 ml samples of each half-cell solutions were periodically taken and diluted for analysis of the vanadium and sulphate concentration by ICP technique. The volume of solution transferred over the time period and the cell

potential profile, are shown in Figure 7.27.a and Figure 7.27.b, respectively, while the total vanadium and sulphate content of each of the half-cell solution is shown in Figure 7.27.c.



Figure 7.27 Self discharge of a fully charged vanadium redox cell with CMV membrane: (area 138 cm<sup>2</sup>), volume of electrolytes on each side = 200 ml: a) volume variation. b) cell potential profile with respect to time. c) total vanadium ion and sulphate content of the half-cell reservoirs.







As indicated in Figure 7.27.c, the total vanadium and sulphate content of the positive half-cell solution increased rapidly during the first 20 hours and then levelled off. With the SOC of the solutions above 95 %, therefore, the self-discharge is due to the combined effects of diffusion and convective transport across the membrane, from the negative to the positive half-cell. Below 95 % SOC, the convective transport subsides and the self-discharge remains relatively constant.

## 7.3.5 Volumetric crossover monitoring of electrolytes across the membrane during charge/discharge of vanadium redox cell.

As already mentioned, during the charge/discharge cycling of the vanadium redox cell, there is a preferential volumetric transfer of solution across the membrane. For a cell employing an anion-exchange membrane, it was observed that the net volumetric transfer is toward the negative half-cell whereas for the cation-exchange membrane, the opposite is true. The accumulation of solution during long term cycling causes not only the reduction in the cell capacity but in severe cases, flooding of the solution reservoir. Furthermore, the unequal vanadium ions fluxes through the membrane also lead to concentration of the solution in one half-cell while diluting the solution in the other. The change in concentration could result in thermal precipitation of V(V) ions on the positive side (Figure 3.4) or V(III) precipitation on the negative side with extremes in temperature (Figure 3.3.b). It was thus essential to remix the two half-cell solutions periodically to restore the cell capacity as well as to normalise the concentration of the vanadium and sulphate ions in the two half-cell solutions.

The transport of water (which could also carry the ionic fluxes) across different types of membranes in the vanadium redox cell during charging/discharging is presented in Figures 7.28 to 7.34 and the cell efficiencies during charging and discharging, computed from this data are summarised in Tables 7.5 and 7.6, respectively.

For a particular membrane, the transport number of water  $(T_{\rm H20})$  is defined as moles of water transported by electro-osmosis through the membrane per Faraday of electricity passed. The moles of water transported is obtained from the volume changes in the half-cell solution reservoirs and the amount of electricity passed is the product of current supply (4.14 A) x time (which can be obtained from Figures 7.28 to 7.34). The transport number of water term is applicable to the water transferred by electro-osmosis (which includes hydrated charge balancing ions and electroconvection) across the membrane under the influence of an applied electric field. In electrochemical processes, water transport number could vary as the anolyte and catholyte concentration is changed, hence, water transport numbers are usually quoted for the specified anolyte and catholyte concentration. Usually, the measurement of water transport number is conducted over a short period of time (< 1 hour) where the contribution from osmotic effects (hydration water of ions and hydraulic flow) is insignificant. In this study, the period for the measurement of transport numbers was about 3 hours, hence the osmotic water flux could complement or reduce the electroosmosis water flux. In addition to this, water is consumed by the charge/discharge reaction at the positive electrode according to :  $VO_2^{+} + H_2O \Rightarrow VO_2^{+} + 2 H^{+} + e$ , leading to small density changes in the solutions during cycling. Therefore the values of water transport presented in Table 7.5 are actually a measure of the net water

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transported (or transport of water,  $T'_{H2O}$ ) due to both electro-osmosis and osmotic effects per Faraday of electricity passed and they are the average values for the full charging or discharging cycle. As mentioned above however, the effect of slight density changes in the solutions during cycling has not been included, however, this effect should be the same for all membranes. For the present system therefore, it is not possible to calculate the transport number of water, however, it is still of interest to compare the net transfer of water during charge and discharge for the different types of membrane used in this study.



Figure 7.28 Transport of water during charge/discharge of a vanadium redox cell using AMV membrane.



Figure 7.29 Transport of water during charge/discharge of a vanadium redox cell using DMV membrane.



Figure 7.30 Transport of water during charge/discharge of a vanadium redox cell using CMV membrane.



Figure 7.31 Transport of water during charge/discharge of a vanadium redox cell using Nafion<sup>\*</sup> 117 membrane.



Figure 7.32 Transport of water during charge/discharge of a vanadium redox cell using Flemion<sup>\*</sup> membrane.



Figure 7.33 Transport of water during charge/discharge of a vanadium redox cell using Treated Daramic<sup>\*</sup> membrane: negative half-cell charged first.



Figure 7.34 Transport of water during charge/discharge of a vanadium redox cell using Treated Daramic<sup>\*</sup> membrane: positive half-cell charged first.

# Table 7.5Water flux per Faraday of electricity passed ( $T_{H20}$ ) during charge/discharge of the vanadium redox cell employing different membranesat constant charging/discharging current density of 30 mA cm<sup>-2</sup>.

Membrane type	T <sup>'<sub>H2O</sub> during charge</sup>	T <sub>H20</sub> during discharge	Observed net volumetric transfer of solution in a complete cycle (cm <sup>3</sup> )
AMV	0.28	0.19	0.18 from the +ve to the -ve side
DMV	0.20	0.10	0.45 from the +ve to the -ve side
CMV	0.48	1.10	4.50 from the -ve to the +ve side
Nafion <sup>*</sup> 117	0.95	1.04	0.40 from the -ve to the +ve side
Flemion*	1.02	1.20	1.00 from the -ve to the +ve side
Treated (1) Daramic <sup>*</sup> (2) (0.23 mm)	0.48 0.40	0.38 0.38	1.10 from the +ve to the -ve side 0.20 from the +ve to the -ve side

#### Table 7.6 Cell efficiencies and capacities obtained during transport of water

measurements of Table 7.5.

Membrane	Cell capacity		Efficiency (%)		
type	Ahr.in	Ahr.out	Coulombic	Voltage	Energy
AMV	9.59	9.11	95	80	76
DMV	13.46	13.32	99	82	81
CMV	11.04	10.35	94	81	76
Nafion <sup>*</sup> 117	14.49	13.80	95	85	80
Flemion*	13.11	12.77	97	86	83
Treated (1) Daramic <sup>*</sup> (2) (0.23 mm)	12.21 11.87	10.97 11.73	90 99	80 81	72 80

(1) Situation when negative half-cell solution charged up first.

(2) Situation when positive half-cell solution charged up first.

During charging, the overall solution fluxes are toward the negative half-cell and they reverse in direction during discharging as illustrated in Figures 7.28 to 7.34. The change in volumes on the two half-cells do not however, correspond during charging or discharging because of the effect of hydrogen evolution at the negative electrode. As was observed on the cyclic voltammogram of a graphite felt bonded to conductive plastic electrode in a VOSO<sub>4</sub> solution in  $H_2SO_4$ , the potential for the V(III) reduction reaction is very close to that for hydrogen evolution [168,p138]. The hydrogen gas produced during charging adheres to the surface of the felt electrode and thus, displaces some of the solution in the cell cavity. As the SOC of the cell increases, the rate of hydrogen evolution increases too, giving rise to the formation of more hydrogen gas bubbles which grow in size until they coalesce. When the larger gas bubbles have sufficient buoyancy to dislodge themselves from the felt surface, hydrogen gas can be observed exiting the outlet port. This is usually observed when the cell is above 70 % SOC. During discharging, the solution starts displacing the remaining hydrogen gas trapped in the felt or the cell cavity. It is observed that when the cell is fully discharged, an insignificant volume of hydrogen gas is still trapped in the cell cavity irrespective of the discharge period.

For the graphite felt electrodes used, the hydrogen reaction proceeds slowly even when the cell is at a very low SOC. On the other hand, oxygen evolution does not occur until the positive half-cell solution is overcharged (when the cell potential exceeds 2.0 V). The moles of water transported per Faraday of electricity,  $T'_{H20}$ , shown in Table 7.5 was thus calculated from the volume change in the positive halfcell. The values of  $T'_{H20}$  differed slightly for charging and discharging. The anion-

exchange membranes (AMV and DMV) and the treated Daramic\* have low values of  $T'_{H20}$  while the cation-exchange membranes (Nafion<sup>\*</sup> 117, Flemion<sup>\*</sup> and CMV) have higher values. With the anion-exchange membrane, the bisulphate ions could carry a portion of the current while the balance is provided by the hydrogen ions. Thus, although the bulk of the current is carried by H<sup>+</sup> ions, only 0.28 moles of H<sub>2</sub>O are transferred per faraday of electricity passed. This could be due to the fact that HSO<sub>4</sub> ions are carrying water in the opposite direction. The low values of  $T'_{\rm H2O}$  for these membranes could also indicate that even though the balance of the current carrying ions are the H<sup>+</sup> ions, the transport of these H<sup>+</sup> ions across the anion-exchange membrane does not carry all the bound water molecules. Some of the H<sup>+</sup> ion transport across anion-exchange membranes follows the Grotthuss type mechanism [176] where the  $H_2O$  molecules form bridges for the  $H^+$  ions to leap across the membrane. In cation-exchange membranes, the H<sup>+</sup> ions carry the bulk of current, however, the H<sup>+</sup> ions also carry the water molecules along with them. From the measurements of the  $T'_{H20}$  for these membranes, it can be concluded that each H<sup>+</sup> ion carries one water molecule with it. The treated Daramic\* possesses a low anionexchange capacity and exhibits behaviour similar to the anion-exchange membrane.

The transport of water across the membrane during charge/discharge also provides the convective transport of vanadium and sulphate ions. Differences in the water transport during charging and discharging causes the accumulation of solution in one of the half-cells during cycling. As shown in Table 7.5, the values of  $T'_{H20}$  for AMV and DMV membranes are higher during charging than discharging and the opposite is true for CMV, Nafion<sup>\*</sup> 117 and Flemion<sup>\*</sup> membranes. However, for the treated
Daramic<sup>\*</sup>, the preferential accumulation of solution depends on which half-cell solution reaches the fully charged state first. It was observed with this membrane that the net transfer of solution shifts toward the half-cell solution with the lower SOC.

The interplay of different types of transport phenomena occurring simultaneously during charge/discharge in the vanadium redox cell is quite complicated. To quantify the individual contribution to the ionic fluxes is not possible. However, based on the different aspects of transport studies conducted, a qualitative interpretation of the transport phenomena occurring across the membrane is provided. The direction of water and ionic fluxes due to diffusion, electro-migration and convection during charge/discharge are shown in Figure 7.1 a,b, for the respective cation and anion exchange membranes.

The measurement of solution flux (hydrated ions and free water) for charging and discharging as shown in Figures 7.28 to 7.32 was conducted over a period of 2.5 to 3.0 hours for the different types of membranes tested. The volumetric flux values (solution transfer) measured during the charging period for the respective membranes: AMV, DMV, CMV, Nafion<sup>\*</sup> 117 and Flemion<sup>\*</sup>, with an area 138 cm<sup>2</sup> in Figures 7.28 to 7.32 were about 4.8, 5.8, 7.0, 15.0 and 15.0 cm<sup>3</sup>. The estimated solution flux values (hydrated ions and free water) across the same membranes of area 138 cm<sup>2</sup>, based on the results of Figures 7.5 to 7.13 in the absence of any applied electric field (osmotic water transfer) at different initial SOC's are summarised in the Table 7.6a.

Total Membrane	solutic 100	on flux ± 0.1 (c % SOC	cm <sup>3</sup> /hr) 50 %	in absence of e SOC	lectric 0 %	field, at initial SOC
AMV	1.9 (•	ve to +ve side)	<0.2	(+ve to -ve side)	<0.2	(+ve to -ve side)
DMV	0.7	(as above)	<0.2	(as above)	<0.2	(as above)
CMV	2.3	(as above)	1.2 (-	ve to + ve side)	1.7 (	ve to +ve side)
Nafion <sup>*</sup> 117	4.1	(as above)	3.2	(as above)	1.5	(as above)
Flemion <sup>*</sup>	3.7	(as above)	2.3	(as above)	1.2	(as above)

 Table 7.6a
 Osmotic solution flux at different initial SOC's.

The contribution of solution flux due to osmosis (hydrated ions and water transfer due to the pressure gradient) is also significant compared to that being transported by electro-osmosis. (The electro-osmosis flow of water through a membrane is the algebraic sum of that transported by the solvation shells of the charge balancing ions and electro-convection.) However, because of the longer periods (about 2.5 to 3 hours) used for the water transport measurements during charging or discharging, the  $T'_{H20}$  values presented in Table 7.5 are affected by the competing or complementary solution flux due to osmosis. The difference in the solution fluxes during charging and discharging causes the net accumulation of water/solution in one half-cell after a complete cycle.

Based on experimental observations from charging/discharging tests as presented in Figures 7.30 to 7.32 and data presented in Table 7.6a, the rate of solution transfer at the end of the charging process is always lower than during the early part of the process for both cation and anion-exchange membrane. The overall solution fluxes

for both cases is still in the direction of the current flow (from +ve to -ve side). This seems to indicate that solution flux due to the osmotic water transfer (from -ve to + ve side), which are a maximum at the end of charging for both cation and anion-exchange membrane, are still less than the electro-osmotic transfer of solution (from +ve to -ve side).

With the anion-exchange membrane such as AMV and DMV, during charging, the current flows toward the negative electrode. Under electro-migration, water is being transferred by electro-osmosis  $(H_3O^+ \text{ moving towards the negative electrode or})$ solvated  $HSO_4^-$  ions in the opposite direction). From the data presented in Table 7.6a for AMV and DMV membranes, without the influence of an applied electric field, osmotic water transfer from the competing fluxes due to the diffusion of hydrated ions and pressure gradient at initial 0 and 50 % SOC's, is from the positive to the negative half-cell. Therefore, both effects (electro-osmosis and osmotic effects) complement each other and cause the transport of solution towards the negative halfcell. However, at the latter part of the charging process (SOC>50 %), the solution transferred by electro-osmosis is counteracts by osmotic transfer and causes a lower overall solution flux towards the negative half-cell. During the discharge cycle, the current flow is reversed and the transport of solution due to electro-osmosis follows the direction of the current (from negative to the positive half-cell). When the solution SOC>50 %, the osmotic solution flux complements the transport of solution due to electro-osmosis. When the solution SOC<50 %, the osmotic solution flux counteracts the electro-osmosis solution flux. Therefore, the difference in the T'<sub>H20</sub> values during charging and discharging causes the net accumulation of solution in the

negative half-cell for the anion-exchange membrane in a complete charge and discharge cycle. Moreover, the solution fluxes across the anion-exchange membrane are also lower than those observed for the cation-exchange membrane as shown in Table 7.5. This is due to the fact that water is also transported by the solvated  $HSO_4^-$  ion which carries the current in the opposite direction to the H<sup>+</sup> ion.

A similar interplay of transport phenomena is present across the cation-exchange membrane during charge/discharge. During charging, solution flux is toward the negative half-cell under electro-osmosis and the solution flux due to osmotic effects (water transport by the solvated ions and pressure gradient) is toward the positive half-cell. In the discharge cycle, both the electro-osmosis and osmotic solution fluxes are both toward the positive half-cell. Therefore, there is an accumulation of solution on the positive half-cell during a complete charge and discharge cycle.

The transport of water at various charging and discharging current densities was investigated using the Nafion<sup>\*</sup> 117 membrane and the values of  $T'_{H20}$  as well as the cell efficiencies obtained are presented in Table 7.7 and Table 7.8 respectively. Nafion<sup>\*</sup> 117 membrane was chosen for these experiments because other membranes tended to deteriorate with extended use and their properties would also change. From the range of current densities investigated (Table 7.7), the  $T'_{H20}$  values did not vary appreciably except at 50 mA cm<sup>-2</sup>, at which it is slightly higher. The volume of solution in the reservoirs of the vanadium redox cell employing the Nafion<sup>\*</sup> 117 membrane was monitored during the long term charge/discharge cycling and the results obtained are presented in Figure 7.35 a-c.

Table 7.7Water flux per Faraday of electricity passed in the vanadium redox cell<br/>employing Nafion\* 117 membrane at various constant charging/<br/>discharging current densities.

Current density (mA cm <sup>-2</sup> )	T' <sub>H2O</sub> during charging	T' <sub>H20</sub> during discharging	Observed net volumetric transfer of solution in a complete cycle (cm <sup>3</sup> )
20	0.94	1.03	0.2 from the -ve to the +ve side
30	0.95	1.04	0.4 from the -ve to the +ve side
40	0.96	1.10	0.6 from the -ve to the +ve side
50	1.08	1.13	0.4 from the -ve to the +ve side

Table 7.8	Cell efficiencies	and capacity	obtained	with the	water f	flux

measurement.

Current density (mA cm <sup>-2</sup> )	Cell ca	apacity	Efficiency (%)		
	Ahr.in	Ahr.out	Coulombic	Voltage	Energy
20	14.31	13.34	93	88	82
30	14.49	13.80	95	85	80
40	14.35	13.98	97	83	80
50	13.65	13.54	99	80	79



Figure 7.35 Volumetric crossover monitoring for vanadium redox cell with Nafion<sup>\*</sup> 117 membrane during long term charge/discharge cycling: a) cell efficiencies and capacity, b) volume change in reservoirs, c) total contents in each reservoir.



Figure 7.35.a, shows the cell efficiencies and the capacity obtained at the current density of 30 mA cm<sup>-2</sup>. The change in the volume of solutions in the positive half-cell and the negative half-cell reservoirs with respect to cycle number as well as time are shown in Figure 7.35.b. Figure 7.35.c, shows the variation of total vanadium and sulphate content in each of the reservoirs with respect to cycle number and time. The concentration of vanadium and sulphate were analysed by ICP technique after dilution of the samples taken.

The cell efficiencies remained relatively constant throughout the testing period as shown in Figure 7.35.a, indicating that the properties of the Nafion<sup>\*</sup> 117 membrane were maintained. This membrane had also been used in other studies for a total of 3600 hours. Initially, the cell capacity rose slightly and fell off at a fairly constant rate. There is no significant difference in the shape of the curves on the plot of cell capacity with respect to cycle number or time.

In Figure 7.35.b, the positive half-cell solution was charged up first during the first 20 cycles. There was a slight volumetric transfer of solution from the positive half-cell to the negative half-cell of about 2 ml which would be equivalent to about 0.004 moles of vanadium. The measured increase in cell capacity however, was about 1.5 Ahr, corresponding to 0.55 moles of vanadium as shown in Figure 7.35.a. Therefore, the vanadium ion fluxes across the membrane to the positive half-cell were greater than the volume of solution transferred. The increase in the cell capacity was mainly due to the fact that the negative half-cell solution was not fully utilized. During the charging cycle, when the upper cell voltage of 1.75 V was reached, the cell was

switched to discharge. Therefore, even when the positive half-cell solution was fully charged, the negative half-cell solution was way below full charge. The transport of V(II) and V(III) ions to the positive side reduced the SOC of the positive half-cell solution, thus bringing the SOC of the solutions to a more 'balanced' state. After the 20th cycle, the negative half-cell was charged up first, and the direction of the net volumetric crossover was reversed, from the negative half-cell to the positive halfcell. Therefore, the capacity of the cell was governed by the negative half-cell solution. As more of vanadium ions were transported to the positive half-cell, the capacity of the cell decreased further after every successive cycle. The volumetric crossover during each successive cycle was relatively constant. The drop in the capacity of the cell during the 200 cycle period corresponded to a 40% decrease, whereas, the percentage reduction in the volume of the negative half-cell solution was 30%. In Figure 7.35.c, the total number of moles of vanadium/bisulphate during the long term cycle charge/discharge show a net transfer of both vanadium and sulphate ions from the negative half-cell to the positive half-cell. The rate of transfer at the beginning (for the first 30 cycles) was slightly higher than for the rest of the test and also remained relatively constant.

### 7.4 Conclusion

The diffusivity of vanadium ions in different oxidation states was found to be different for different membranes tested. V(V) species had the highest diffusivity value followed by V(IV), V(II) and V(III) in descending order. Generally, anion-exchange membranes have diffusivity values an order of magnitude lower than the cation-exchange membranes. The diffusional flux across the membranes was found to be very much smaller than the transport due to electro-migration and convection during the charge/discharge of the vanadium redox cell.

The net water transfer rate across the membrane in the vanadium redox battery in the absence of any applied electric field varies for solutions of different initial SOC. A maximum water transfer from the negative to the positive half-cell was observed for the cation-exchange membrane when the two half-cell solutions were at 100 % initial SOC and decreased as the initial SOC decreased. For the anion-exchange membranes, the water flux from negative to the positive half-cell was high at initial 100 % SOC but the direction of the water flux reversed as the SOC decreased. The self-discharge of the vanadium redox battery was highest when it was fully charged but decreased quite significantly when the SOC decreased. Below 95 % SOC, the self-discharge current was relatively constant.

In the vanadium redox cell, the major current carrying ions were found to be the hydrogen ions with the cation-exchange membrane whereas, sulphate/bisulpahte ions also carry a portion of the current when an anion-exchange membrane was used. Highly cross-linked ion-exchange membranes were found to possess low values of net water transport per Faraday of electricity passed ( $T'_{H20}$  about 0.2 to 0.3) and the PTFE-based ionomer had a  $T'_{H20}$  value of about 1.  $T'_{H20}$  values were different during charge and discharge, being higher during charging in anion-exchange membranes and during discharging in the cation-exchange membranes.

During charge/discharge cycling of the vanadium redox battery, a volumetric transfer of solution across the membrane was observed. A net accumulation of solution occurred in one of the reservoirs, this being due to the difference in the solution fluxes across the membrane during charging and discharging. For the anionexchanges membrane, the preferential accumulation was in the negative half-cell, whilst cation-exchange membranes showed the opposite trend.

### **CHAPTER 8**

### OPTIMIZATION OF PERFORMANCE OF VANADIUM REDOX FLOW CELL

### 8.1 Introduction

Various aspects of the transport phenomena occurring across the membrane associated with the performance of the vanadium redox cell were investigated in Chapter 7. As the vanadium redox cell cycles through charge and discharge, the volume of one reservoir steadily increases. This causes the cell capacity to decrease from cycle to cycle and the direction of the flow of electrolytes depends on the type of membrane used as the separator. For the anion-exchange type of membrane, it has been shown that the electrolytes are preferentially transferred from the positive half-cell to the negative half-cell side of the cell, whereas the reverse is true for the cation-exchange membranes (ref. Section 7.35).

Since the design of the vanadium redox battery is symmetrical and the electrodes are the same for the two half-cells, the polarity of the battery can be reversed without any effect on its performance. If there is an appreciable transfer of solution to one side of the reservoir, reversing the polarity of the battery will gradually transfer the solution back again with cycling. However, the recovery in battery capacity is not immediate, but eventually maximum capacity can be achieved before it starts to decline again. The usual techniques used to recover the battery capacity are discussed in Section 5.3.3.

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The preferential transfer of the electrolytes through the membrane from one half-cell to the other side was also observed in NASA's Fe/Cr redox flow cell system [39]. The volume of the reactant solution containing chromium had been observed to steadily increase over a period of time. Various techniques employed by NASA's researchers to reduce or eliminate the flow were not very successful and, furthermore the reproducibility of the results was poor.

This preferential transfer of electrolytes across the membrane during cycling of the cell is caused by several factors. The predominant factors are the difference in the osmotic water transfer across the membrane (due to the difference in ionic strength of the anolyte and the catholyte) and the type of membrane used as the separator for the two half-cells. For the vanadium redox cell, the flow of water due to osmotic pressure across the membrane also causes convective transport of vanadium,  $H_2SO_4$  and H<sup>+</sup> ions. However, the transport current carrying ions (solvated H<sup>+</sup> and/or  $SO_4^{2^-}$ ) across the membrane due to electro-migration should remain relatively constant for both charging and discharging, since the applied current are the same in both instances.

It was shown in Figure 7.19, the osmotic water transfer across the cation-exchange membrane is mainly due to the difference in  $H_2SO_4$  concentration on opposite sides of the membrane. However, for an anion-exchange membranes as shown in Figures 7.17 and 7.18, the difference in  $H_2SO_4$  concentration across the membrane produced less osmotic water transfer in the opposite direction to that being observed with cation-exchange membrane. For the vanadium redox cell electrolytes, the vanadium

and sulphate ion concentrations are the same at the different SOC's, but not the  $H^+$  ion concentration (see Section 3.1.2.). The difference in  $H^+$  ion concentration at different SOC's is the main factor contributing to the variation in osmotic water transfer between the two half-cell solutions with the Nafion<sup>\*</sup> 117 membrane. The different vanadium species have very little effect.

In this part of the study, two techniques were employed to reduce if not eliminate, the capacity loss of the vanadium redox cell. The first technique involved using different  $H_2SO_4$  concentrations for the two half-cell solutions. In the second technique, both cation and anion-exchange membranes were employed in alternate cell in a multi-cell stack.

### 8.2 Experimental

## 8.2.1 To investigate the effects of different $H_2SO_4$ concentration on the net transfer of vanadium electrolytes during charge/discharging cycling.

The experimental set-up and the procedures used were similar to those described in Section 5.2.3. Nafion<sup>\*</sup> 117 membrane was chosen for the test as other types of membranes had been shown to be chemically unstable during the long term cycling in the vanadium redox cell leading to a variation in the properties of the membrane during the test period. The area of the membrane for the cell design was 160 cm<sup>2</sup>. The vanadium solutions were prepared by the electrolysis as discussed in Section 4.3.7. The prepared solutions were 2 M vanadium ions with varying H<sub>2</sub>SO<sub>4</sub>

concentration. Since, for the Nafion<sup>\*</sup> 117 membrane the solution is preferentially transferred to the positive half-cell, the concentration of  $H_2SO_4$  used in the negative half-cell solution was increased. Initial tests of the volumetric transfer of solution were conducted by using the negative half-cell solution consisting of 2 M V(III) in 2 M  $H_2SO_4$  while the positive half-cell solution was 2 M V(IV) in 3 M  $H_2SO_4$  (these are the solutions presently used in the vanadium redox cell). The  $H_2SO_4$  concentration on the negative half-cell was then varied from 2.5 M to 3 M in the subsequent experiments. Higher concentration of  $H_2SO_4$  was not tested as crystallization of V(III) species starts to occur at concentrations above 3 M. The volumes of the electrolytes in positive and negative half-cell reservoirs were recorded periodically.

## 8.2.2 Investigation of the net volumetric transfer of electrolytes using different membranes for alternate cells in the battery stack.

In this experiment, cation and anion-exchange membranes were arranged in alternate cells in the multi-cell stack. The setup of the experiment was similar to that discussed in Section 5.2.3. A bi-polar electrode consisting of graphite felt bonded on both sides of the conductive plastic, were used in the multi-cell assembly. Flemion<sup>\*</sup> and AMV membranes were selected for the study. AMV membrane was used since it was the most stable anion-exchange membrane available. The study was to demonstrate that the use of cation and anion-exchange membranes in multi-cell assemblies is capable of reducing the capacity loss. If this could be confirmed by experiment, then careful selection of membranes used in the battery could eliminate its capacity loss during

continuous cycling.

### 8.3 Results and discussion

# 8.3.1 Investigation of the effects of different $H_2SO_4$ concentration on the net transfer of vanadium electrolytes during charge/discharging cycling.

The use of different concentrations of  $H_2SO_4$  in the two half-cell solutions does not affect the efficiency of the battery as shown in Figure 8.1.a and Figure 8.2.a. A summary of the results obtained with different acid concentrations is presented in Table 8.1.



Figure 8.1 Charge/discharge cycling of the vanadium redox cell employing Nafion<sup>\*</sup> 117 membrane with different  $H_2SO_4$  concentration for the two half-cell electrolytes - positive half-cell solution 3.0 M  $H_2SO_4$  and negative half-cell solution 2.5 M  $H_2SO_4$ .



Figure 8.2 Charge/discharge cycling of the vanadium redox cell employing Nafion<sup>\*</sup> 117 membrane with different  $H_2SO_4$  concentration for the two half-cell electrolytes - positive half-cell solution 3.0 M  $H_2SO_4$  and negative half-cell solution 3.0 M  $H_2SO_4$ .

Table 8.1 Summary of the volumetric transfer of solution using different  $H_2SO_4$ 

concentrations for each half-cell solution.

Concentration of		Average drop in cell capacity (Ahr)			
$H_2SO_4$ in negative half-cell solution (M)	No. of cycle (or hours)	per cycle	per hour		
3.0	58 (260)	0.0406	0.0087		
Volumetric transfer of solution from negative to positive side. From cycle 1 to $20 = 1 \text{ ml} (0.05 \text{ ml per cycle})$ 20  to  41 = 3  ml (0.14  ml per cycle) 41  to  52 = 6  ml (0.55  ml per cycle)					
2.5	80 (350)	0.0345	0.0081		
Volumetric transfer of solution from negative to positive side. From cycle 1 to $18 = 0$ ml 18 to $50 = 6$ ml (0.19 ml per cycle) 50 to $80 = 17$ ml (0.57 ml per cycle)					
2.0 Cycle 1 to 190 Cycle 220 to 410	190 (966) 190 (918)	0.0158 0.0290	0.0031 0.0060		
Volumetric transfer of solution from negative to positive side. From cycle 220 to $250 = 0$ ml 250 to $320 = 40.0$ ml (0.57 ml per cycle) 360 to $405 = 14.5$ ml (0.32 ml per cycle)					

The average capacity loss per cycle shown in Table 8.1 was obtained from the linear portion of the graphs of Figure 8.1.b, 8.2.b and Figure (5.7.b). In all of these three figures, the cell capacities increased in the first 20 to 30 cycles by about 10 to 12 %, to reach the maximum values, after which they start to decrease. The loss in cell capacity is quite constant. As shown in Figure 5.7.b, the rate of capacity loss changes every time when the cell is rebalanced. The initial increase in cell capacity is due to the imbalance in the SOC of the two half-cell solutions. The positive half-cell

solution was initially at a higher SOC than the negative half-cell solution. The transport of V(III) or V(II) species to the positive half-cell reduces its SOC and maximum cell capacity is attained when the SOC's of the two half-cell solutions are the same. The initial increase in cell capacity is not accompanied by much water being transfer to the positive side, as shown in Table 8.1. However, the rate of water transferred increases after the maximum cell capacity is achieved.

From the results in Table 8.1, increasing the  $H_2SO_4$  concentration over the range of 2 M to 3 M in the negative half-cell solution, does not affect the net volumetric transfer during charge/discharge cycling. In fact, the average capacity loss per cycle actually increases with the increase in  $H_2SO_4$  concentration in the negative half-cell. Therefore, the use  $H_2SO_4$  to reduce the osmotic water transfer across the cell with Nafion<sup>\*</sup> 117 membrane has not been successful in reducing the capacity loss within the concentration range used. The results obtained for the Nafion<sup>\*</sup> 117 membrane do not however imply that all other cation-exchange membranes would exhibit similar behaviour. As discussed in Section 3.3.2.2, the transport properties of Nafion<sup>\*</sup> membrane are very different from the conventional cross-linked ion-exchange membrane. Moreover, with Nafion<sup>\*</sup> 117 membrane, the transport of water is 2 to 3 times higher than for the cross-linked ion-exchange membranes tested during charging and discharging in the vanadium redox cell.

### 8.3.2 Investigation of the net volumetric transfer of electrolytes using different membranes for alternate cells in battery stack.

The cell capacity during long term charge/discharge cycling of a cell employing AMV or Flemion<sup>\*</sup> membranes are shown in Figures 5.4 and 5.8 respectively. Battery efficiencies and capacities obtained when employing both AMV and Flemion<sup>\*</sup> membranes in a two cell stack are shown in Figure 8.3 while Figure 8.4 shows the battery efficiencies and capacities obtained when a pair of AMV and a Flemion<sup>\*</sup> membrane were employed in a three cell stack.



Figure 8.3 Charge/discharge cycling of the vanadium redox battery employing an AMV and a Flemion<sup>\*</sup> membrane in a 2-cell stack.



Figure 8.4 Charge/discharge cycling of the vanadium redox battery employing two AMV and one Flemion<sup>\*</sup> membrane in a 3-cell stack.

The numbers shown on the curves indicate times when the battery was rebalanced. The battery capacity shown in these figures is divided by the number of cells in the battery so that the results obtained could be directly compared with a single cell. A summary of the results shown in Figures 5.4, 5.8, 8.3 and 8.4 is presented in Table 8.2.

Table 8.2Summary of results showing average capacity loss the multi-cells<br/>employing AMV and Flemion\* membranes.

Membrane type	Number of cycles (or hours)	Average drop in cell capacity (Ahr)		
		per cycle	per hour	
AMV	10 (126)	0.0277	0.0060	
Flemion*	68 (320)	0.084	0.0178	
2 cells with AMV and Flemion <sup>*</sup>	57 (265)	0.020	0.0043	
3 cells with 2 AMV and 1 Flemion <sup>*</sup>				
Cycle 13 to 85 100 to 200 240 to 468 470 to 558 560 to 675 676 to 721 723 to 762	72 (356) 100 (489) 228 (930) 88 (298) 115 (423) 45 (153) 39 (147)	0.023 0.017 0.015 0.033 0.043 0.071 0.122	0.0047 0.0034 0.0036 0.0097 0.0117 0.0210 0.0323	
3 cells with 2 AMV and 1 Flemion <sup>*</sup> (*)	173 (797)	0.017	0.0038	

(\*)System where a glass tubing was connected to the negative half-cell reservoir.

In Table 8.2, the average drop in capacity for the different systems indicates that the battery employing a combination of anion and cation-exchange types of membranes

shows a reduction in the net transfer of vanadium ions to one of the reservoirs during charge/discharge cycling. The capacity loss of the battery using a combination of cation and anion-exchange membranes was less than that observed for the individual membrane. For the 2-cell battery using an AMV and a Flemion<sup>\*</sup> membrane, there was only a slight net volumetric transfer of solution toward the positive half-cell. For the 3-cell battery employing a pair of AMV and one Flemion<sup>\*</sup> membrane, the net volumetric transfer of solution for the first 200 cycles was towards the positive halfcell, after which there was no 'apparent' accumulation of solution on any specific half-cell for the next 150 cycles (Figure 8.4). There was however, a slight fluctuation of the volume recorded for both of the reservoirs during these periods. This was due to gases trapped in the graphite felt electrode, hence there were occasions when both of the reservoirs actually registered an increase in volume, but usually less than 1 cm<sup>3</sup>. After the 350 cycles, the net volumetric transfer of the solution was toward the negative half-cell. This was also represented by the increase in the rate of capacity loss after each successive cycle during this period (Table 8.2). It should be noted that during the later stage of the cycling test, the AMV membranes started to deteriorate, at which time any slight difference in the hydraulic pressure across the membrane due to unequal pumping rates, caused an appreciable transfer of solution.

For the 3-cell battery, the capacity loss was quite substantial after cycling for more than 700 cycles. A test was conducted to investigate whether the increased rate in capacity loss of the battery could be reduced. A glass tube was connected to the top of the negative half-cell reservoir. As the volumetric transfer of the solution to the negative half-cell reservoir caused the solution to rise up the glass tubing, this would in turn increase the static pressure head to the pump. Since the flow of the solution for each half-cell was in a closed loop, the static head from the negative half-cell reservoir created an additional back pressure on the negative side of the membranes in the cells. This way, any imbalance in the pressure across the membrane would be corrected. It was shown that the maximum height attained by the solution in the glass tubing was less than 30 cm above the level on the positive half-cell reservoir.



Figure 8.5 Setup of charge/discharge experiment which shows the incorporation of glass tubes to the reservoirs.

The battery efficiencies and the capacities obtained for this system is shown in Figure 8.6 and the results are summarised in Table 8.2.



Figure 8.6 Charge/discharge cycling of the vanadium redox battery employing two AMV and one Flemion<sup>\*</sup> membrane, with modified reservoir for the negative side.

The system investigated was capable of resuscitating and restoring the performance of the battery. Even though the loss in the capacity of the battery was greatly reduced, the efficiency obtained was slightly lower compared to the initial cycling test which is due to the slight deterioration of the AMV membrane during the period of usage.

This principle could thus be applied to the vanadium redox battery to prevent flooding of the reservoir caused by excessive solution being transferred across the membrane during operation by allowing the static head from the solution in the tube to balance the pressure across the membrane.

### 8.4 Vanadium redox battery - Design considerations.

In the design of the vanadium redox battery, fluctuation of the solution volumes in the reservoirs, self-discharge characteristics and temperature variations of the electrolytes have to be taken into account.

### 8.4.1 Volume fluctuation in reservoirs.

In designing the vanadium redox battery, emphasis should be placed upon the transport processes associated with the membrane. In Chapter 7, transport of vanadium solutions across the membrane, causing volumetric fluctuation in the reservoirs are investigated. A few aspects of these findings which are relevant to the design of the vanadium redox battery system are discussed here.

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The major causes of volumetric fluctuation of solution, beside minor contributions from density and temperature variation, during cycling are:

- a) Transport of water across the membrane during charge/discharge.
- b) Osmotic water transfer across the membrane when the battery is not in operation ( i.e no power is drained or supplied to the battery).
- Displacement of solution in the graphite felt electrode by the gas generated during charging.

In the designs of the reservoirs, allowance has to be provided for 'normal' fluctuation in the level on the two reservoirs due to the transport of solution moving back and forth during charging and discharging respectively. The volume of solution being transferred depends on the type of membrane used. PTFE-based ionomers (such as Nafion<sup>\*</sup> 117 and Flemion<sup>\*</sup>) generally have higher water transport than conventional cross-linked membranes like Selemion<sup>\*</sup>-AMV, DMV, and CMV.

The osmotic water transfer across the membrane could cause quite significant transfer of solution when the battery is not in operation. Maximum volumetric transfer of solution would occur when the battery is fully charged when a cation-exchange membrane is employed while the opposite is true for the anion-exchange membrane.

Besides the transfer of solution across the membrane which causes fluctuation in reservoirs levels, hydrogen gas evolution during charging which displaces some of the solution in the battery stack could also have a similar effect.

Usually in the design, an 'overflow' tube is installed at the top sides of the two reservoirs to prevent flooding if significant transfer of solution occurs. The design of the overflow tube should also ensure that it does not form a complete circuit for the solutions in the two reservoirs, since it would self-discharge the battery due to the migration of the active vanadium ions from one reservoir to the other.

#### 8.4.2. Self-discharge

Self-discharge is generally limited to the solutions residing in the battery, usually 10 to 20 % depending on the cavity of the flow frame and the total Amphour capacity of the system. The cavity of the flow frame selected is dependent on the battery applications. Generally for applications where space is not the limiting factor, a thicker flow frame and graphite felt electrodes can be employed, whereas mobile application, thinner flow frames and electrodes are sought.

It is preferred to design the battery system in which the reservoirs and the cells stack are at the same level. Elevating the battery above the reservoir is not desirable since if the solution is completely drained from the battery, precipitation could occur on the felt as well as dehydration of the membrane. Moreover, an external power source would be required to start the pumps in this case.

### 8.4.3 Temperature variation

During the operation of the 1 kW vanadium redox battery, it is observed that the temperature of the solution fluctuates. Figure 8.7 shows a typical temperature versus time profile obtained from measurements of the reservoir solutions when AMV membrane is utilized in the cell stack.



Figure 8.7 A typical temperature versus time profile of the reservoir solutions in a battery stack which employed AMV membrane.

Some heat energy is generated from the IR losses in the system and from the selfdischarge of the two half-cell solutions. Surprisingly, the temperature decreases linearly during charging and increases in the same fashion during discharge. When AMV membrane is employed in the battery, the volumetric crossover of electrolytes across the membrane during charge is less than during discharge (Section 7.3.5), hence, there is less heat generated due to self-discharge in the charging. Moreover, the battery resistance (IR losses) during charge is also less than for the discharge cycle (Figure 5.14). The cooling rate observed during the charging cycle cannot however be fully accounted for by these processes and is believed to be also affected by the heat of dilution associated with the change in the H<sup>+</sup> ion concentration during charge and discharge (see Section 3.1.2.). A maximum temperature is thus recorded when the battery is fully discharged in a complete cycle (assuming constant ambient temperature), the temperature in both reservoirs being the same. This is because of the high surface area of the membrane which transfers the heat generated in one halfcell to the cooler side. If the ambient temperature fluctuates greatly during daytime and at night, there is a possibility of thermal precipitation of V(V) solution if the temperature goes above 50 °C. This would occur only if the battery is fully charged and also, the V(V) concentration is over 1.8 M.

Besides the possibility of thermal precipitation occurring with increased temperature, the selectivity of the membrane decreases also, causing a higher rate of self-discharge and generating more heat.

Since the 'ideal membrane' is presently not available, a compromise is needed in

selecting an appropriate membrane, taking into consideration the type of application destined for the battery.

### 8.5 Conclusion

The use of different  $H_2SO_4$  concentration to reduce the osmotic water transfer across Nafion<sup>\*</sup> 117 membrane in the two half-cell electrolytes of the vanadium redox cell was incapable of eliminating or reducing the rate of preferential transfer of solution to the positive half-cell over the concentration range studied. However, this does not implied that other types of membranes would exhibit similar behaviour.

In the battery stack employing cation and anion-exchange membranes arranged in alternate cell fashion, the rate of preferential transfer of solution to one half-cell was greatly reduced and so does the capacity losses during cycling. By selecting appropriate types cation and anion-exchange membranes, it is possible to eliminate the solution transfer and the losses in capacity during cycling.

#### **CHAPTER 9**

### CONCLUSIONS

In the vanadium redox battery, or any redox flow battery, the functions of the separator/membrane is to separate the positive and the negative half-cell electrolytes and the electrodes whilst still permitting the transport of charge balancing ions of the supporting electrolyte. Ideally, the separator should exhibit very low resistance and high selectivity to achieve high energy efficiency for the redox flow battery. However, equal emphasis has to be placed upon other properties of the membrane which are not related to the battery performance such as its chemical and dimensional stability.

In this studies, evaluation of commercially available membranes were conducted to identify suitable membranes for the vanadium redox battery applications. Modification or treatment to improve the selectivity of an otherwise non-selective microporous separator, Daramic<sup>\*</sup>, was also conducted. Transport properties of different types of membranes are also evaluated to provide an understanding of the different processes occurring across the membrane in the vanadium redox flow battery.

Evaluation of the commercial membranes AMV, DMV, CMV, CMS, DSV, ASS, Nafion<sup>\*</sup> 117, Nafion<sup>\*</sup> 324, DOW<sup>\*</sup> XUS1 3204.10, RAI 1010, RAI 4010 and K142 showed acceptable area resistance values and high selectivity, with the exception of the DOW<sup>\*</sup> membrane. Energy efficiencies above 85 % were achieved when these

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membranes were employed in the vanadium redox battery. Generally, anion-exchange membranes gave marginally higher coulombic efficiencies than the cation-exchange membranes, but the gain was offset by the lower voltage efficiency obtained.

For all the commercial membranes evaluated, most gave acceptable performance in the short term, less than 6 months, after which the performance of the battery dropped off rapidly. One exception was the Nafion<sup>\*</sup> 117 membrane, which offered consistent performance for more than 18 months of accelerate cycle testing and showed no sign of impairment in performance. The Flemion<sup>\*</sup> membrane also exhibited excellent stability in the cycling tests.

The CMV membrane, although an excellence membrane for the vanadium redox battery application in terms of performance showed very poor stability. Various treatments applied to this membrane failed to appreciably improve the stability and moreover, the resistance of the membrane after treatment also increased significantly, making it unsuitable for redox cell applications. The most promising membrane to date, however, is a second type of 'New' Selemion<sup>\*</sup> membrane recently developed by Asahi Glass Co. (Japan), for the Kashima-Kita Power Corporation vanadium battery development program. Recent discussions with these workers have revealed that excellent stability and area resistance values of less than 1  $\Omega$  cm<sup>2</sup> have been achieved with this new membrane which also promises to have an acceptable cost (~\$200/kW) for most energy storage applications.

For larger scale load levelling applications, a membrane cost of less than \$100/kW is
essential if battery storage is to compete with other forms of energy storage. The development of a low cost, stable membrane for such applications was also conducted. The approach taken was by applying a suitable treatment to the low cost non-selective microporous separator, Daramic<sup>\*</sup>, thereby improving its selectivity. Various methods of incorporating ion-selective capability to improve the selectivity of the microporous separator, Daramic\* were investigated. The adsorption of the polyelectrolyte/ion-exchange resin on the Daramic\* separator greatly reduced its hydraulic permeability  $(K_h)$  and only a slight decrease in the diffusivity of the membrane was observed. The treated Daramic<sup>\*</sup> with the highest selectivity and area resistance of less than 3  $\Omega$ .cm<sup>2</sup>, was obtained by treatment with Amberlite CG400 and further cross-linking using divinyl benzene (DVB). A coulombic efficiency of greater than 90% was achieved during charge/discharge cycling of a vanadium redox test cell using this membrane, compared with about 77% for the original material. This membrane has been tested for over 8000 hours or 1650 cycles in a vanadium redox cell with no sign of deterioration. Long term exposure to the V(V) solution has also confirmed the excellent stability of the treated membrane for this application.

Transport studies were conducted to study the phenomena occurring in the vanadium redox cell during charge/discharge cycling. The diffusivity of the membranes tested for vanadium ions in different oxidation states was found to be different. V(V) species had the highest diffusivity value followed by V(IV), V(II) and V(III) in descending order. Generally, anion-exchange membranes tested have diffusivity values an order of magnitude lower than the cation-exchange membranes. The diffusional flux across the membrane was found to be very much smaller than the

transport due to electro-migration and convection during the charge/discharge of the vanadium redox cell.

Both cation and anion-exchange membranes possess low water ( $T^*<0.5$ ) transport compared with PTFE-based membranes which have a value of about 1. For the cation-exchange and PTFE-based membranes, the hydrogen ions were the major current carrying ions whereas for the anion-exchange membrane, a portion of the current was carried by the sulphate/bisulphate ions.

The osmotic water transfer fluxes across the membrane in the vanadium redox battery varies from 0 to 100 % SOC. A maximum water flux was observed for the cation-exchange membrane when the two half-cell solutions were at 100 % SOC and decreased as the SOC decreased. For the anion-exchange membranes, the opposite behaviour was observed.

The self-discharge of the vanadium redox battery was highest when it was fully charged but decreased quite significantly when the SOC decreased. Below 95 % SOC, the self-discharge current was quite constant.

During charge/discharge cycling of the vanadium redox battery, a volumetric transfer of solution across the membrane was observed. A net accumulation of solution occurred in one of the reservoirs, this being due to the difference in the solution fluxes across the membrane during charging and discharging. For the anion-exchange membrane, the preferential accumulation was in the negative half-cell, whilst cationexchange membranes showed the opposite trend.

The use of different  $H_2SO_4$  concentrations to reduce the osmotic water transfer across Nafion<sup>\*</sup> 117 membrane in the two half-cell electrolytes of the vanadium redox cell was incapable of eliminating or reducing the rate of preferential transfer of solution to the positive half-cell over the concentration range studied. However, this does not imply that other types of membranes would exhibit similar behaviour.

In the battery stack employing cation and anion-exchange membranes arranged in alternate cells, the rate of preferential transfer of solution to one half-cell was greatly reduced as so did the capacity losses during cycling. By selecting appropriate types of cation and anion-exchange membranes, it is thus possible to eliminate the solution transfer and the losses in capacity during cycling.

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## APPENDIX I

Mathematical derivation of pore size (diameter, d) for membrane with parallel and cylindrical pore. In the pore size determination using the mercury intrusion technique, the pores are assumed to be parallel and cylindrical.

Assume a cylindrical pore of height, h and radius, r;

Volume of cylinder (V) =  $\pi r^2 h$ 

Surface area of cylinder (A) =  $2 \pi r h$ 

Therefore, V/A = r/2

r = 2V/A

d = 4V/A