

## STABILITY AND PERFORMANCE EVALUATION OF ION-EXCHANGE MEMBRANES FOR VANADIUM REDOX FLOW BATTERY

Saidatul Sophia Sha'rani<sup>a</sup>, Ebrahim Abouzari Lottf<sup>b\*</sup>, Arshad Ahmad<sup>b</sup>, Wan Atika Wan Ibrahim<sup>a</sup>, Mohamed Mahmoud El-sayed Nasef<sup>a,b</sup>, Roshafima Rasit Ali<sup>a</sup>

<sup>a</sup>Malaysia–Japan International Institute of Technology, International Campus, Univeristi Teknologi Malaysia, 54100 Kuala Lumpur, Malaysia

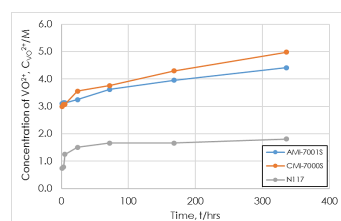
<sup>b</sup>Advanced Materials Research Group, Center of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, 54100, Kuala Lumpur, Malaysia

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\*Corresponding author  
ebrahim@utm.my

### Graphical abstract



### Abstract

The performance of vanadium redox flow battery (VRFB) is highly dependent on the efficiency of the membrane. Generally, anion exchange membranes and cation exchange membranes can be applied in the VRFB. In this paperwork, AMI-7001S anion exchange membrane and CMI-7000S cation exchange membranes were tested for their suitability in the VRFB application. Both of the membranes were originally used for electrocoat and water treatment system. In order to study the behavior of the membranes in the VRFB, several tests were performed. This includes  $\text{VO}_2^+$  ion permeability, ionic conductivity, ion selectivity, chemical stability and single cell performance. The results obtained were compared to Nafion 117 which is a proton exchange membrane. This membrane is one of the most established membranes for VRFB. From the experiment, it can be summarized that the membranes are unsuitable to be used in VRFB. This is due to the low ion selectivity, poor chemical stability and high resistance.

**Keywords:** Permeability, anion exchange membrane, cation exchange membrane, vanadium redox flow battery, stability test, single cell performance

### Abstrak

Prestasi bateri vanadium aliran redoks (VRFB) adalah sangat bergantung kepada kecekapan membran. Secara umumnya, membran pertukaran anion) dan membran pertukaran kation boleh digunakan dalam applikasi VRFB. Dalam kertas kerja ini, membran pertukaran anion AMI-7001 dan membran pertukaran kation CMI-7000 telah diuji kesesuaiannya dalam penggunaan VRFB. Kedua-dua membran pada asalnya digunakan untuk sistem lapisan elektro dan rawatan air. Dalam usaha untuk mengkaji tingkah laku membran dalam penggunaan VRFB, beberapa ujian telah dijalankan. Ini termasuk ujian kebolehtelapan  $\text{VO}_2^+$  ion, proton kekonduksian, pemilihan ion, kestabilan kimia dan prestasi sel tunggal. Keputusan yang diperolehi dibandingkan dengan membran Nafion 117 (N117) yang merupakan membran pertukaran proton. Membran ini adalah salah satu daripada membran yang paling baik untuk penggunaan VRFB. Darpada eksperimen yang dijalankan, dapat dirumuskan bahawa kedua-dua membran ini tidak sesuai untuk digunakan dalam VRFB. Ini adalah kerana pemilihan yang rendah ion, kestabilan kimia yang lemah dan rintangan yang tinggi.

**Kata kunci:** Kebolehtelapan, membran pertukaran anion, membran pertukaran kation, bateri vanadium aliran redoks, ujian kestabilan kimia, prestasi sel tunggal.

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## 1.0 INTRODUCTION

Vanadium redox flow battery (VRFB) is a type of rechargeable flow battery that uses vanadium ions as its electroactive elements in the electrolyte to store energy. This battery has been extensively studied by many researchers as it offers many great advantages compared to the another commercialized flow battery such as Zinc-Bromide flow battery (ZNBR) and Iron-Chromium flow battery (ICB). The advantages of this battery include long lifespan, fast response time, high energy efficiency, the absence of electrolytes contamination, deep charge and discharge capacity, low cost, low environmental effect, flexible design and relatively large power and low energy ratings [1-4].

There are many factors that could affect the performance of the VRFB. One of the most significant factor is the efficiency of the ion exchange membrane (IEM) employed. In VRFB, the membrane acts as a separator to prevent cross-mixing of the vanadium ions in positive and negative electrolytes while at the same time allowing the transfer of other supporting ions during the passage of current [5]. In order to get an excellent performance of the battery, the membrane should possess these following characteristics; low vanadium ions permeability, high proton conductivity, high ion selectivity and good chemical stability under acidic and oxidative conditions as well as low cost [6,7].

It is well known that both anion exchange membrane (AEM) and cation exchange membrane (CEM) can be considered under VRFB operating conditions [7]. There are many types of membranes that could be used in the VRFB. Traditionally, the membrane used in the VRFB is a series of Nafion which is a type of proton exchange membrane from DuPont [6]. This membrane is usually chosen due to its unique properties such as high proton conductivity and high chemical stability. Despite its good properties, the membrane however, is extremely expensive and it has low ion selectivity which means it has high vanadium ions crossover [8]. High in vanadium cross over would decrease the VRFB performance as it will lead the cell to be self-discharged [6]. Other than Nafion, Selemion CMV from Asahi Glass was also used in the VRFB [9,10]. This membrane, however, did not work very well in the VRFB as it can be easily degraded by the formation of  $VO_2^+$  ion when charging process of the battery takes place [9]. Therefore, more and more works are currently developing to find more suitable membranes for the VRFB application.

It has been reported that the performance of the VRFB with CEM could give high conductivity and high energy efficiency but usually suffers from severe permeation of vanadium ions [11]. Unlike CEM, AEM could give a better performance of the VRFB in terms of exhibiting low vanadium ion permeation albeit it gives lower conductivity. This membrane phenomenon is due to the effect of Donnan exclusion [11-14].

In this work, two different types of polystyrene based ion exchange membranes were evaluated for possible application in VRFB; anion exchange membrane (AMI-7001S) and cation exchange membrane (CMI-7000S). Both of these membranes are cross-linked with divinylbenzene and were commercialized for electrocoat systems and water treatment industries [15]. These membranes were chosen due to their low cost and no report with regards to their VRFB application. It is however, as reported by Biljana S. *et al.* both of the membranes can be used in direct borohydride fuel cells (DBFC) [16]. The suitability of these membranes was tested in the VRFB by conducting several tests. This includes vanadium ion permeability, ionic conductivity, and ion selectivity. Other than that, chemical stability of the membranes in the VRFB electrolyte was investigated. Finally, the performance of the single cell of the VRFB was studied in detail by using these membranes. Table 1 shows the basic properties of the studied membranes.

**Table 1** Relevant properties for AMI-7001 and CMI-7000 membranes

Properties	AMI-7001S	CMI-7000S
Membrane type	Strong base anion exchange membrane	Strong acid cation exchange membrane
Polymer structure	Gel polystyrene cross-linked with divinylbenzene	
Functional group	Quaternary Ammonium	Sulphonic Acid
Thickness (mm)	0.45	0.45

## 2.0 METHODOLOGY

### 2.1 Materials and Membrane Pre-Treatment

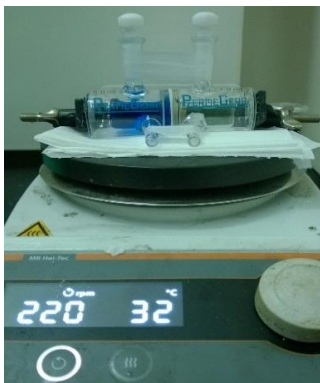
Both of the membranes AEM (AMI-7001S) and CEM (CMI-7000S) used in this study were supplied by Membranes International Inc. (Ringwood, NJ, USA) as a single sheet.  $VOSO_4 \cdot xH_2O$  (97%) was purchased from Sigma Aldrich, Germany. Other reagents used in this paperwork, such as  $H_2SO_4$  and  $Na_2SO_4$  were purchased from Mallinckrodt Baker, Mexico and used as received without further purification. Prior to the experiment, both of the membranes were pre-treated differently depending on the type of membrane. The AEM was immersed in 1.0 M KOH at room temperature for 24 hours while the CEM was immersed in 0.2 M  $H_2SO_4$  at room temperature. This pre-treatment step is to allow membrane hydration and expansion. The membranes were left in deionized water when not in used.

## 2.2 VO<sup>2+</sup> Permeability Test

The permeability of the vanadium ions in this work was tested by using two half diffusion cell (PermeGear, Inc.) of 5.0 mL as shown in Figure 1. The membrane with an effective area of 1.76 cm<sup>2</sup> was sandwiched between the two half diffusion cells and a pair of gasket. The left compartment of the cell was filled with 1.5 M VOSO<sub>4</sub> in 2.5 M H<sub>2</sub>SO<sub>4</sub> and the right compartment of the cell was filled with 1.5 M Na<sub>2</sub>SO<sub>4</sub> in 2.5 M H<sub>2</sub>SO<sub>4</sub>. Na<sub>2</sub>SO<sub>4</sub> was used to reduce the osmotic pressure effect and to equalize ionic strength of the solutions. The solutions in the cells were left at room temperature and were magnetically stirred at 220 RPM to prevent the concentration polarization. 0.2 mL of the solutions from the right compartment were extracted at selected time intervals and the concentration of VO<sup>2+</sup> ions was determined by using UV Vis spectroscopy (UV-1800 Shimadzu). Prior to the experiment, a standard curve of VO<sup>2+</sup> solutions of different concentrations was prepared. The peak absorbance of VO<sup>2+</sup> ion was established at 760 nm and act as a reference. The permeability of the membranes was calculated by applying the Fick's diffusion law as shown in equation 1.

$$V \frac{dC_R}{dt} = S \frac{P}{T} [C_L - C_R] \quad (1)$$

V is the initial volume of the solution in both compartments of the cell. C<sub>L</sub> and C<sub>R</sub> are the concentration of the VO<sup>2+</sup> ion in the left and right compartment of the cells, respectively. P is the vanadium ion permeability, T is the thickness of the membrane and S is the surface area of the membrane that is being exposed to the solutions.



**Figure 1** Photograph of the membrane - separated diffusion cell

## 2.3 Ionic Conductivity and Selectivity

The procedure applied in measuring the ionic conductivity in this study was demonstrated in previous works [17-19]. The in-plane conductivity of

the membranes was determined by using a four-point probe of Bekk Tech conductivity cells (BT-112). The resistance of the membranes was measured by using a DC conductivity testing system (Keithley 2400 sourcemeter). The current was measured by using a potentiostat. The potentiostat was set to provide a specific voltage between the two inner probes. The resistance (R) and conductivity ( $\sigma$ ) were calculated by using following equation.

$$\sigma(S/cm) = \frac{L(cm)}{R(\Omega) \times S(cm^2)} \quad (2)$$

L is the distance in the direction of ion flow between voltage measurement probes whereas S is the area of the membrane. The denominator represents the area resistance area. The ion selectivity was calculated as the ratio of ionic conductivity to vanadium ion permeability as reported by other paperwork [20].

## 2.4 Chemical Stability Test

The chemical stability test for both membranes was evaluated by an immersion in low and high concentration of the VO<sub>2</sub><sup>+</sup> solution. The low concentration solution used was 0.5 M VO<sub>2</sub><sup>+</sup> in 3.0 M H<sub>2</sub>SO<sub>4</sub> and the high concentration solution used was 1.5 M VO<sub>2</sub><sup>+</sup> in 3.0 M H<sub>2</sub>SO<sub>4</sub>. The high concentration of the solution mimics the real operations of VRFB. The experiment was done in 14 days where both of the membranes were immersed in sealed vials at room temperature. 0.4 mL of the samples were taken at predetermined time intervals and the concentration of the VO<sub>2</sub><sup>+</sup> formed were analyzed by using UV Vis Spectroscopy, indicating the oxidative degree of the membranes.

## 2.5 Single Cell Performance Test

The AEM and CEM membranes were further evaluated by performing the single cell performance test as illustrated in

Figure 2. The VRFB was assembled by sandwiching the membranes in between two carbon felts with an effective reaction surface of 9.0 cm<sup>2</sup> and two carbon plates as the current collector. The initial electrolyte used for positive and negative sides was 1.5 M V<sup>3.5+</sup> in 3.0 M H<sub>2</sub>SO<sub>4</sub>. The volume of the electrolyte in each side was 23 mL and both of the electrolytes were cyclically pumped from the storage tank into respective half-cells. The charge-discharged test was done where all of the operating conditions were kept constant. The flow rate applied was 80 L/min throughout the experiment and the initial current density applied was 18 mA/cm<sup>2</sup> at room temperature. The cut-off voltages were set at 1.72 V and 0.8 V, respectively. During the experiment, N<sub>2</sub> gas was supplied at the negative side of the cell to prevent the oxidation by the air.



Figure 2 Photograph of VRFB single cell

### 3.0 RESULTS AND DISCUSSION

As summarized in Table 1, both of the membranes are heterogeneous membranes which are based on polystyrene gel cross-linked with divinylbenzene. These membranes are differentiated by their functional groups. The AMI-7001S is an anion exchange membrane with quaternary ammonium functional groups whereas the CMI-7000S is a cation exchange membrane with sulfonic acid groups. It is well known that membranes are charged selective, the AMI-7001S membrane will usually allow the movement of anions and CMI-7000S membrane will allow the movement of cations. Not only that, both of the membranes have different appearance since the AMI-7000S membrane is yellow in color and CMI-7001S membrane is brown in color. Figure 3 shows the photograph of the membranes.

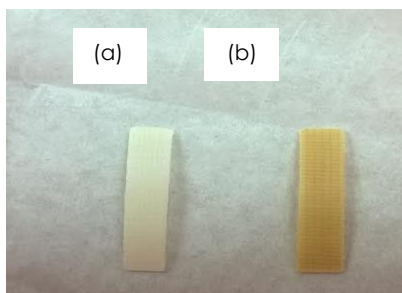


Figure 3 Photographs of the membranes: (a) AMI-7001 anion exchange membrane (b) CMI-7000 cation exchange membrane

The properties of the membranes were studied by carrying out  $\text{VO}_2^+$  ion permeability test, proton conductivity test, ion selectivity, chemical stability test and single cell vanadium redox battery performance test.

In order to achieve durable and high performance of the vanadium redox flow battery, the membrane should possess low vanadium ion permeability. This property is essential as high vanadium ion permeability will lead to the reduction of coulombic efficiency and energy efficiency of the VRFB. For this work, only  $\text{VO}_2^+$  ion permeability was measured across the membranes. Prior to the experiment, a

standard curve for the concentration of  $\text{VO}_2^+$  ion was prepared as a reference for the permeate  $\text{VO}_2^+$ . The standard curve was prepared by using UV-Vis technique and the main peak absorbance of the  $\text{VO}_2^+$  ion was observed to be 760 nm.  $\text{VO}_2^+$  ion permeability, ionic conductivity and ion selectivity values of both of the membranes were measured and the data are presented in Table 2. All of the data obtained were compared with a proton exchange membrane used from our previous work which is Nafion 117.

The  $\text{VO}_2^+$  ion permeability of AMI-7001S is lower than CMI-7000S and N117. This result agreed with the theory that has been explained previously. The degree of permeation of  $\text{VO}_2^+$  ion in AMI-7001 is lower due to the Donnan exclusion effect as the membrane has quaternary ammonium cation. Another factor that lead the reduction value of permeability in both membranes is their thickness. Theoretically, the time taken for the  $\text{VO}_2^+$  ions to travel from left side to right side of the half-cell will increase as the thickness of the membrane increases. Therefore, since CMI-7000 has greater thickness compared to N117, CMI-7000 exhibit greater value of  $\text{VO}_2^+$  ion permeability.

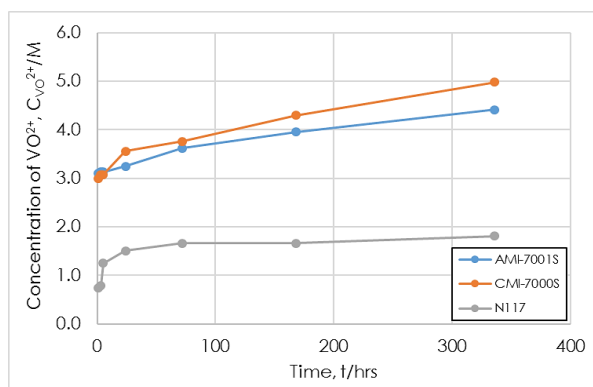
Ionic conductivity is another important key in determining the efficiency of the membranes as it is responsible for low ohmic resistance [10]. From the measurement, it should be noted that the proton conductivity for both membranes is lower compared to the Nafion 117 under similar conditions [17-19]. Ion selectivity was taken as another parameter in order to determine the suitability of the membranes for the VRFB. Ion selectivity is the ratio of conductivity to  $\text{VO}_2^+$  ion permeability, hence, high ion selectivity means high ionic conductivity and low  $\text{VO}_2^+$  ion permeability. In this paper, both of the membranes showed very low ion selectivity compared to N117.

Table 2  $\text{VO}_2^+$  ion permeability, ionic conductivity and ion selectivity

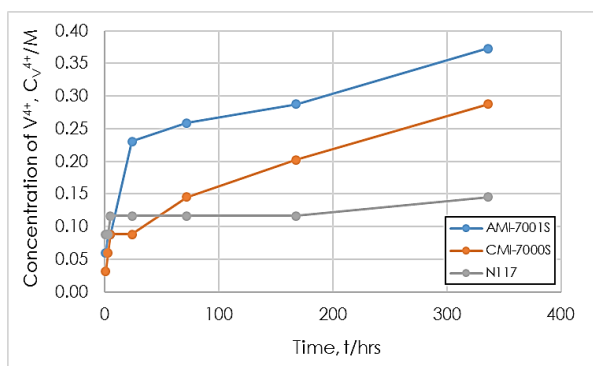
Membrane	$\text{VO}_2^+$ ion permeability ( $10^{-7} \text{ cm}^2/\text{min}$ )	ionic conductivity* (mS/cm)	Ion selectivity ( $10^4 \text{ S min cm}^{-3}$ )
AMI-7001	13.8	8.9	0.65
CMI-7000	37.3	23.6	0.63
N117	15.2	36.4	2.39

\*Measured at 100% relative humidity and room temperature (25 °C)

Chemical stability test of the membranes was carried out by immersing the membranes in the high and low concentration of  $\text{VO}_2^+$  solution. Figure 4 and 5 show the concentration of  $\text{VO}_2^+$  formed for all the membranes during the 14 days of immersion in high and low concentration of the  $\text{VO}_2^+$  solution. From the figures, it can be seen that both of the membranes have poor stability compared to N117 since the concentration of  $\text{VO}_2^+$  is higher in both high and low concentration of the  $\text{VO}_2^+$  solution.



**Figure 4** Concentration of  $\text{VO}_2^+$  formed in 1.5 M  $\text{VO}_2^+$  in 3.0 M  $\text{H}_2\text{SO}_4$



**Figure 5** Concentration of  $\text{VO}_2^+$  formed in 0.5 M  $\text{VO}_2^+$  in 3.0 M  $\text{H}_2\text{SO}_4$

The single cell performance test was conducted for both membranes under the same operating conditions. The test was started by applying 18  $\text{mA}/\text{cm}^2$  current density and reduced to 15  $\text{mA}/\text{cm}^2$  and 10  $\text{mA}/\text{cm}^2$ . For both membranes, initial observation showed a good performance of the battery where the color of the positive electrolyte changed from blue to yellow. It is however, the current values during the experiment was unstable making the reading of the experiment interrupted and no data were able to be recorded. This phenomenon may be attributed by the exceeded limit of the current density applied during the test.

#### 4.0 CONCLUSION

In summary, we have investigated the possibility of low-cost commercially anion exchange membrane (AMI-7001S) and cation exchange membrane (CMI-7000S) under the VRFB operating conditions for the first time. From the study, the results showed that the membranes are unsuitable to be used in VRFB. This is because, the  $\text{VO}_2^+$  ion permeability of the membranes is higher than  $\text{VO}_2^+$  ion permeability of NI17 which is the most conventional membranes for VRFB. In addition, the value of the ionic conductivity of the membranes are also lower compared to NI17.

As a result, the ion selectivity of the membranes is low. Comparing the chemical stability of the membranes with NI17, the membranes have poorer stability since the concentration of the  $\text{VO}_2^+$  formed is higher. The single cell performance test for both membranes did not show promising results as no data were able to be recorded. This shows that the membranes exhibit high resistance since none of the cell cycling were able to be performed with the set voltage limits.

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