Improved vanadium barrier properties of perfluorinated sulfonic acid membranes for vanadium redox flow battery

S S Sha’rani1,2, E Abouzari-Lotf2,3*, M M Nasef2,4, A Ahmad2,3, T M Ting5 and R R Ali1

1Malaysia-Japan International Institute of Technology, International Campus, Universiti Teknologi Malaysia, Jalan Semarak 54100, Kuala Lumpur, Malaysia.
2Advanced Materials Research Group, Center of Hydrogen Energy, Universiti Teknologi Malaysia, Jalan Semarak 54100, Kuala Lumpur, Malaysia.
3Department of Chemical Engineering, Univeristi Teknologi Malaysia, 81310 Johor Bahru, Malaysia.
4Chemical Engineering Department, Universiti Teknologi Petronas, 32610 Seri Iskandar, Perak, Malaysia.
5Nuclear Agency (Nuclear Malaysia) Bangi, 43000 Kajang, Selangor, Malaysia.

*ebrahim@utm.my

Abstract. The search for highly vanadium selective membrane for vanadium redox flow battery (VRFB) is fast growing to accelerate the commercialization of VRFB. Currently, VRFB is challenged by high vanadium permeability through the membranes lowering the battery performance. In this paper, a simple and effective strategy for improving the vanadium barrier permeability of the membranes, without altering the desired proton conductivity, was reported by applying layer(s) of polyelectrolytes. A commercial perfluorinated sulfonic acid membrane, GN115 was modified by layer of positively charged poly(diallyldimethylammonium chloride) (PDDA) or consecutive layers of PDDA and negatively charged poly(sodium styrene sulfonate) (PSS). Upon surface modification, the membranes exhibited a reduced vanadium permeability with a slight decreased in proton conductivity values compared with the pristine GN115 and N117. As a result, higher coulombic efficiency was obtained in VRFB single cell with the modified membranes. This confirms that the addition of the polyelectrolyte layers can suppress the vanadium permeability of the membranes.

1. Introduction
The vanadium redox flow battery (VRFB) is one of the best energy storage techniques that is appealing for promoting of renewable energy. Particularly, VRFB offers various attractive benefits, which meet the grid storage market demands such as long life cycle, deep discharge capacity, low environmental effect and low cost [1]. In VRFB, ion exchange membrane (IEM) plays an imperative role in deciding the battery performance. IEM is a polymer separator in which the positive and negative electrolytes of the cell are separated. IEM also serves as a transport medium for protons to complete the circuit during the passage of the current [2, 3]. To date, most of the IEMs employed in VRFB did not meet most of the requirements to prompt the commercialization of this battery. An ideal membrane for VRFB must have not only low vanadium permeability, high conductivity, small area
resistance, excellent chemical and mechanical stability in the vanadium electrolyte medium but also low cost [4, 5].

There are various types of commercial polymeric membranes that were applied in VRFB applications. Such membranes involve a wide range of polymers ranging from perfluorinated sulfonic acids (PFSA)s [6-8] to hydrocarbon-based ones [9]. PFSA membranes such as Nafion from DuPont, have been widely used in VRFB and demonstrated a good performance. However, this membrane was found to be prone to high vanadium ion crossover leading to continuous capacity decay and lower efficiency of VRFB [10]. Thus, various research efforts have been exerted to solve the permeability issue by employing innovative IEMs or modifying the available PFSA membranes [11-13]. Applying polyelectrolyte layer(s) of opposite charge on the surfaces of PFSA was reported to directly reduce the vanadium permeability without altering desired ion conductivity [14]. This could be due to the Donnan exclusion phenomenon as the positive force in the surface repulse the vanadium ions. Such modifications were applied on various types of membranes including commercial PFSA. However, the modification was not considered widely since adding more cost to expensive PFSA. Therefore, applying of polyelectrolyte layers on low-cost PFSA could be considered as a commercially viable alternative for VRFB application.

In this work, a strategy for improving the performance of VRFB by applying layer(s) of polyelectrolytes on new alternative cheaper commercial PFSA membrane named as GN115 is proposed. The GN115 membrane was modified by applying layer of polycation or two layers of positively charged poly(diallyldimethylammonium chloride) (PDDA) and negatively charged poly(sodium styrene sulfonate) (PSS) polyelectrolytes consecutively. The vanadium permeability and proton conductivity of the modified membranes were evaluated in comparison with Nafion 117 membrane. The performance of the modified membranes was preliminarily tested in a VRFB single cell.

2. Methodology
2.1. Preparation of surface modified membranes
Two different surface modified composite membranes were prepared in this study. The PFSA modified with polycation was prepared by immersing the GN115 in the poly(diallyldimethylammonium chloride) (PDDA, 35 wt. % in H2O, Mw <100,000) for 10 minutes at room temperature. To remove unbounded PDDA, surface modified membranes with polycation (GN115-(PDDA)) was rinsed thoroughly in a deionized water and dried in a vacuum oven. Second type of surface modified membrane was prepared by applying polyanion layer onto surface of GN115-(PDDA). Poly(sodium styrene sulfonate) (PSS, 25 wt. % in H2O, Mw ~ 1,00,000) was added by immersing of the GN115-(PDDA) for 10 minutes at room temperature followed by washing with deionized water and drying. The developed membrane was denoted as GN115-(PDDA/PSS).

2.2 Characterization and analysis
To investigate the existence of the PDDA and PSS on the composite membranes, the infrared (IR) absorption spectra were recorded on a FTIR spectrophotometer (Perkin Elmer, USA) in the region of 600 - 4000 cm⁻¹. To evaluate the effectiveness of the modified membranes, proton conductivities and the vanadium permeability of the membranes were measured. The through-plane (σ) and in-plane (σ) conductivity of the membranes was measured by using a homemade cell with two disc stainless steel electrodes that were polished frequently and four-point probe of Bekk Tech conductivity cells (BT-112), respectively. A DC conductivity tester (Kickstart SMU 2400) was used to measure the conductivity of the membranes. The conductivity (σ) of the membrane was calculated using equation (1) [9]:

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

where, R is the resistance obtained from the slope of voltage versus current plot, L is the distance between the two inner probes and S is the area of the membranes. The denominator of the equation
represents the area of resistance, \( AR \). Anisotropic conductivity ratio was calculated from in-plane and through-plane conductivity values following equation (2) [9]:

\[
\sigma_{\parallel}/\sigma \parallel = \left( \frac{\sigma_{\parallel}}{\sigma \parallel} \right)
\]

The vanadium permeability of the membranes was measured using the same method described in ref. [8]. The membrane with an effective area of 1.72 cm\(^2\) was clamped between the two half-diffusion cell (Perme Gear, Inc.) having two reservoirs. The left reservoir of was filled with 1.0 M VOSO\(_4\) + 2.5 M H\(_2\)SO\(_4\) and the right one was filled with 1.0 M Na\(_2\)SO\(_4\) + 2.5 M H\(_2\)SO\(_4\). The samples were collected from the right reservoir at pre-determined time intervals. The concentration of V(IV), \( C_{V(IV)} \) was measured using UV-Vis spectrophotometer (UV-1800 Shimadzu) and was calculated using equation (3) [9]:

\[
C_{V(IV)} = \frac{SP}{VT} \cdot C_L (t - t_0)
\]

where, \( V_R \) is the volume of the reservoir, \( C_L \) is the concentration of vanadium ion in the left reservoir of the cell, \( P \) is the permeability, \( T \) is the thickness of the membrane, \( S \) is the effective area of the membrane and \( t \) is the diffusion time.

A single cell test was carried out to compare the performance of the surface modified membranes with N117. Carbon felt was activated prior to setup the single cell system as described elsewhere [15]. The VRFB single cell was assembled by clamping the membrane with two carbon felts (C200 AvCarb) (3 cm x 3 cm), two PVC plates and two rubber sheets to provide the necessary pressure. A solution of 1.5 M V\(^{3+}/V^{4+}\) in 3.0 M H\(_2\)SO\(_4\) was used as electrolytes feeding the positive and negative tanks of the cell at 10 mL min\(^{-1}\) (Thermo Scientific FH100). The experiment was carried with a battery analyser (BST8-CDS, MTI Corp.) at room temperature. A schematic view of the VRFB single cell is shown in Figure 1.

Figure 1. The schematic representation for the VRFB single cell

The coulombic efficiency (CE), voltage efficiency (VE), energy efficiency (EE) for each complete cycles were determined from equations 4, 5 and 6, respectively [5].

\[
CE = \frac{I_{\text{constant discharge}}}{I_{\text{constant charge}}} \times 100\% \quad (4)
\]

\[
VE = \frac{V_{\text{discharge}}}{V_{\text{charge}}} \times 100\% \quad (5)
\]

\[
EE = CE \times VE \quad (6)
\]
3. Results and discussion

Two types of PFSA membranes were obtained by surface modification with monolayer of PDDA and two consecutive layers of polycation and polyanion following the scheme presented in Figure 2. The modified membranes are denoted as GN115-PDDA and GN115-PDDA/PSS, respectively.

![Figure 2. Pathway for the preparation of surface modified membranes](image)

FTIR spectra of the developed membranes together with pristine GN115, PDDA and PSS are shown in Figure 3. A typical PFSA membrane, the C-F bonds stretching can usually be seen at around 1000 to 1360 cm\(^{-1}\). Meanwhile, the peaks that correspond to C-O-C and S-O groups can be observed at 976 cm\(^{-1}\) and 1060 cm\(^{-1}\), respectively [16-18]. The peak of C-H bond in the case of PFSA type membrane could hardly be seen since the structure is usually fluorinated [19]. Upon modification, a visible difference can be obviously seen in the modified membranes. The PDDA show some peaks at 2938 and 2865 cm\(^{-1}\) correspond to the stretching vibrations of methyl groups [20]. Meanwhile, PSS spectra shows some stretching vibrations of −CH and −CH\(_2\) groups at 2925 and 2853 cm\(^{-1}\) respectively [21]. The corresponding peaks of \(^{+}\text{NR}_4\) (1644 cm\(^{-1}\)) and C=C (1637 cm\(^{-1}\)) is clearly visible in the zoomed region [21, 22]. Therefore, it was confirmed that the PDDA and PSS bilayers were added on the surface of the GN115 membrane upon modification.
Figure 3. FTIR spectra of GN115, PDDA, PSS and resulting modified membranes.

The permeability of the GN115 membranes were measured before and after modification with polyions. It was found that the membranes modified with PDDA and PDDA/PSS of about 23.5x10^{-7} cm² min⁻¹ layers exhibited a lower permeability compared to that of the pristine membrane (26.05x10^{-7} cm² min⁻¹). This is because, the additional PDDA, polycation create a repulsive charge that hindered the vanadium crossover. Such crossover reduction can be also attributed to the more complicated channels that were created by the surface modification with polycation and polyelectrolyte [23].

The proton conductivity and area resistance of the membranes were measured before and after modification and the obtained data is presented in Table 1. As can be seen the proton conductivity of the membranes decreased slightly for about 8 to 8 % with a little increase in the area resistance upon modification with both PDDA and PDDA/PSS. Nonetheless, the values of the area resistance of these modified membranes are still smaller than the reference Nafion117 membrane. Therefore, it is expected that the modified membranes remain suitable for making better performance in VRFB giving a higher voltage efficiency. All membranes showed anisotropic behaviour since different values for through-plane and in-plane conductivity were obtained.

| Membrane     | Thickness, μm | Proton conductivity, \( \sigma \) (mS/cm) | Area Resistance\(^1\) (Ω cm²) |
|--------------|---------------|------------------------------------------|-------------------------------|
|              |               | Through-plane (\( \sigma || \)) | In-plane (\( \sigma _\perp \)) |                               |
| GN115        | 115           | 96.1                                     | 96.0                          | 0.12                          |
| GN115-(PDDA) | 116           | 90.4                                     | 92.2                          | 0.13                          |
| GN115-(PDDA/PSS) | 119        | 89.4                                     | 90.6                          | 0.13                          |
| Nafion 117   | 177           | 88.0                                     | 82.6                          | 0.20                          |

\(^1\) Based on through-plane conductivity
The electrochemical properties of the newly developed membranes were further evaluated by charge-discharge test in the VRFB cell as shown in Figure 4. The experiment was carried out at 40 mA cm\(^{-2}\) current density for 10 cycles under same operating conditions. It was observed that the modified membranes, GN115-PDDA and GN115-PDDA/PSS have higher CE compared to N117 and pristine GN115 membranes. This value reflects the vanadium permeability pattern emphasizing that the permeability decreased upon modification. The VE of GN115 membrane was observed to be higher than Nafion117 membrane since the area resistance of the membrane is 40% higher than that of GN115 membrane. For the modified GN115 membranes, the value of VE is quite close to pristine GN115 and this because there was no apparent difference in the area resistance. The EE of the battery was determined by multiplying the CE and VE and the obtained data showed that the EE of the pristine and modified GN115 membranes at 40 mA cm\(^{-2}\) is higher than the reference Nafion 117 membrane. This remarkable improvement shown by the modified membranes confirm the suppression of vanadium crossover in the cell.

Figure 4. Efficiencies of the N117, GN115, GN115-PDDA, and GN-PDDA/PSS membranes at 40 mA cm\(^{-2}\).

Figure 5 displays the cycling curves and the change of CE, VE and EE of GN115-PDDA and GN115-PDDA/PSS membranes. The preliminary performance of the modified membranes showed a stable performance at 40 mA cm\(^{-2}\) as the cycling curves were almost consistent for 10 cycles. This is due to the extra repulsive forces created between the positively charged PDDA and vanadium ion [23]. Hence, it can be concluded that the incorporated polyelectrolyte layers of the modified membranes are stable in VRFB. Comparing the performance of the modified membranes, the GN115-PDDA/PSS revealed a higher CE with lower VE than the pristine GN115 and N117. This indicates that the vanadium crossover can be reduced by the additional polyanion on the membrane surface.
4. Conclusion
Modification of GN115 membrane was successfully carried out using PDDA polycation and PSS polyanion to enhance the barrier properties against vanadium crossover in VRFB. The monolayer and bilayer modified membranes showed lower vanadium permeability and reasonable area resistance compared to Nafion 117 membranes. The cycling performance test showed that better efficiencies with PDDA and PDDA/PSS modified membranes compared to N117 and the pristine GN115. The negatively charged PSS further reduce the vanadium crossover through the membrane by Donnan effect. The modified membranes also exhibit a good stability in VRFB environment. It can be concluded that the adopted strategy was effective in improving the resistance to vanadium crossover of the commercial PFS GN115 membrane.

Acknowledgment
The research was primarily supported by Universiti Teknologi Malaysia and ministry of higher education under Fundamental Grants (vote no. #4F878) and joint partnership research program of Innovative Research Universities of Australia and Malaysia Research University Network (IRU-MRUN) (vote no. #00M84). The authors wish to thank General Energy Co., Ltd (China) for providing the samples.

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