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Sulfonated poly (ether ether ketone) based proton exchange membranes for vanadium redox battery applications

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ABSTRACT

Low cost sulfonated poly (ether ether ketone) membranes have been successfully prepared and optimized at various sulfonation conditions by casting method for vanadium redox battery applications. The optimized SPEEK membrane was initially tested in the G1 Vanadium Redox Battery (VRB) before being evaluated in the G2 Vanadium Bromide Redox Flow Battery (V/Br), and the performance was compared to that of Nafion 117. From the G1 VRB performance tests, the energy efficiency of the membrane was found to be 77%, slightly higher than Nafion 117 which gave 73% at current density 40 mA/cm². For the first time, the SPEEK membrane was evaluated in the G2 V/Br at two different ratios of bromine complexing agents and the performance was assessed from the measured cell efficiencies. At 4 mA/cm², the optimum energy efficiency was 76% using SPEEK in the presence of 0.19 M MEM and 0.56 M MEP, when compared to 75% obtained with Nafion 117. Similar to Nafion 117, SPEEK also exhibits excellent chemical stability in the highly oxidizing electrolytes. The SPEEK membrane thus appears to be a promising candidate for both G1 and G2 VRB applications.

Keywords: Vanadium redox battery; Sulfonated polymer; Ion exchange membrane.

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1. Introduction

The detrimental effects of fossil fuel consumption on the environment and earth climate has led to rapid development of renewable energy sources for sustainable development. However, renewable energy sources are intermittent in nature and thus require energy storage systems. Among the many types of energy storage technologies such as pumped hydro, compressed air, fly-wheel, capacitors, etc., the redox battery is considered the best option for medium to large scale storage due to its excellent combination of energy efficiency, capital and life cycle costs without specific site requirement [1].

Among the redox batteries developed, the first generation vanadium redox battery (G1 VRB) pioneered by Maria Skyllas-Kazacos and co-workers at the University of New South Wales [2-5] attracts the most interest due to its excellent energy efficiency of over 80% and long cycle life over 200,000 cycles in large installations [6-8]. The G1 VRB consists of two electrolytes tanks containing active species of vanadium in different valence states in sulfuric acid medium, namely the V(IV)/V(V) redox couple in the positive tank and V(II)/V(III) redox couple in the negative tank. Further development of vanadium-based flow batteries has led to the second generation (G2) V/Br that employs a vanadium bromide/chloride mixed electrolyte in both positive and negative tanks. This is more promising because of its ability to generate energy density two times higher than G1 VRB [9-11]. The main concern of the G2 V/Br however, is the possibility of bromine gas evolution during charging. Bromine complexing agents, such as *N*-methyl-*N*-ethyl morpholinium bromide (MEM) and *N*-methyl-*N*-ethyl pyrrolidinium bromide (MEP) have been studied in G2 V/Br and have been shown to effectively reduce bromine vapors [4]. Their use in the V/Br electrolyte however has been found to give rise to membrane fouling when perfluorinated cation exchange membranes have been used. For further development of the

G2 V/Br cell, therefore, a chemically stable low cost membrane is needed that is not subject to fouling by the organic layer produced by the bromine complex in solution during charging.

The ion exchange membrane plays an important role in all redox flow batteries, allowing the transport of protons during the charge-discharge reactions in order to achieve electrical balance [12]. While proprietary anion exchange membranes have been used in most of the large-scale demonstrations and field trials of the G1 VRB by Sumitomo and Kashima-Kita Electric Power Corporation, Japan, to date [2], anion exchange membranes have been found to be unsuitable for the G2 V/Br since they cannot prevent the transfer of the negatively charged Br_3^- species from the positive half-cell [4]. A good proton exchange membrane is thus required. Such a membrane should have high ion exchange capacity (IEC), good proton conductivity, and possess good chemical stability [13, 14]. The perfluorosulfonic acid Nafion[®] membrane produced by DuPont has commonly been used as a proton exchange membrane in many laboratory scale VRB studies due to its good proton conductivity and excellent chemical stability in acidic vanadium electrolytes [15-18]. However, the high cost of Nafion limits its use in commercial applications.

Since the early 2000s, sulfonated aromatic polymeric membranes have received broad attention for G1 VRB applications due to their low cost, excellent chemical resistance and high ion selectivity [13, 14]. Sulfonated poly(ether ether ketone) (SPEEK) [19-21], sulfonated poly(sulfone) [22, 23], sulfonated poly(fluorenyl ether ketone) [24, 25], sulfonated poly(tetramethyldiphenyl ether ether ketone) [26], sulfonated poly(arylene ether sulfone) [27], and sulfonated poly(arylene thioether) [28] have been tested as proton exchange membranes in G1 VRB. Poly(ether ether ketone) (PEEK) is the most thoroughly studied, because it could easily

be sulfonated into SPEEK and the desired level of sulfonation can be controlled by varying the time and temperature of the reaction [29, 30].

Several research groups have prepared SPEEK membranes at different degrees of sulfonation and evaluated them in the G1 VRB [19-21, 31]. However, most of the evaluation performance did not include chemical stability tests in the highly oxidizing V(V) solution of the fully charged positive half-cell electrolyte. Furthermore, no one has as yet tested and reported the application and performance of SPEEK membrane in the G2 V/Br. This paper reports the performance evaluation of the in-house synthesized SPEEK membrane for G1 VRB application including the chemical stability test. Moreover, for the first time, this article also presents the performance evaluation of SPEEK membrane and compares it with Nafion membrane in the G2 V/Br in terms of cell efficiencies using a static cell.

2. Experimental

2.1. Sulfonated poly (ether ether ketone) membrane preparation

SPEEK was prepared by sulfonation of industrial grade PEEK (Victrex[®] US, Inc.) in a glass beaker at a constant temperature in air [29]. Typically, 5 g PEEK was dissolved in 100 mL of H₂SO₄ (97 wt. %) and stirred at 50⁰C for different reaction times. The solution was then cooled to room temperature and poured slowly into ice cooled distilled water under mechanical agitation. The solid samples were washed with distilled water to remove residual acid and were dried in an oven at 60⁰C overnight. A photograph of the as-synthesized SPEEK is shown in **Figure 1**. For the preparation of SPEEK membranes, dried SPEEK was dissolved in *N*-methyl-2-pyrrolidone (NMP) (Merck) to form a 15 wt. % solution. Solutions were cast onto glass plates in a dust-free environment; and dried in air for 1 day followed by treatment in vacuum at 60⁰C for 1

day, respectively. The transparent SPEEK membrane was peeled from the glass plates, rinsed, and kept in distilled water before characterization.

[Figure 1]

2.2. Membrane characterization

Ion exchange capacity (IEC) and sulfonation degree (SD) of the SPEEK membranes were determined by the back titration method as reported by Huang and co-workers [15, 29]. The membranes were immersed in 50 mL of 0.01 M NaOH aqueous solution for 1 day, and the ion exchange capacity of each membrane were determined by the titration with HCl aqueous solution and calculated as follows:

$$IEC = \frac{M_{0,NaOH} - M_{E,NaOH}}{W} \quad (\text{Eq.1})$$

where $M_{0,NaOH}$ is the moles of NaOH in the flask at the start (mol), $M_{E,NaOH}$ is the moles of NaOH after titration (mol), and W is the weight of the wet membrane (g).

$$SD = \frac{FW \cdot IEC}{1 - 80IEC} \quad (\text{Eq.2})$$

where FW is the molar weight of the repeat units of synthesized polymers.

Fourier transform infra red (FTIR) analysis was conducted using a Perkin Elmer (Model Spectrum GX) spectrometer to analyze the chemical structural changes upon sulfonation and soaking test. The spectra were measured in transmittance mode in the wave number range of 4000-500 cm^{-1} .

The morphology was investigated by using a field-emission scanning electron microscopy (FESEM) (JEOL, Model JSM-7600F) operating at 5-20 kV.

Proton conductivity of the membranes was tested by Electrochemical Impedance Spectroscopy (EIS) over a frequency range of 10 mHz-200 kHz at an amplitude of 1 mV, using a Solartron Electrochemical Instrument (Sol-1470E, Solartron (UK)). The fully hydrated membranes were immersed in water for 3 days and 1.0 M H₂SO₄ solution for 2 days and then washed thoroughly with deionized water to remove residual acid. A membrane was placed in an open, temperature controlled cell, where it was clamped between 2 blocking platinum electrodes as electrical contacts with a pressure of about 3 kg/cm². The conductivity (σ) of the membrane in the transverse direction was calculated from the impedance data, using the equation:

$$\sigma = \frac{d}{RS} \quad (\text{Eq.3})$$

where, d and S were the thickness (cm) and face area (cm²) of the membrane respectively, and the resistance R (Ω) was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re(Z) axis. The thickness of the hydrated membranes was measured using a micrometer. The total conductivity measured by this method is the sum of partial conductivities; either electrical or proton conductivity; of the different current carriers. However, often only one type of current carriers (protons) dominates the charge transport, and in many cases, and as approximation, contributions from minority carriers (electrons) are neglected.

Water uptake (WU), swelling ratio (SR), and electrolyte uptake (EU) of the membrane were determined by comparison of weights/lengths of a blotted soaked membrane and vacuum dried one. Membranes were first dried at 60°C for 48 h and weighed. The dried polymer membranes (50 mm x 10 mm) were then immersed in water at room temperature. Water uptake and swelling ratio were then calculated as follows:

$$\text{WU} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (\text{Eq.4})$$

$$SR = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \quad (\text{Eq.5})$$

where W_{wet} and L_{wet} are the weight and lengths of wet membranes, while W_{dry} and L_{dry} are the weight and lengths of dry membranes, respectively.

For the electrolyte uptake, a similar method was applied and the electrolyte used was 1.0 M V(III) + 1.0 M V(IV) (referred to as 2.0 M $V^{3.5+}$) in 4.0 M H_2SO_4 for 24 h.

$$EU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (\text{Eq.6})$$

2.3. G1 and G2 VRB performance

Charge-discharge tests in a G1 VRB were carried out by sandwiching the membrane between two pieces of graphite plates and felts, which served as the electrodes. The felt (Golden Energy Fuel Cell Co., Ltd., China) had a thickness of 5 mm and was placed within a 3 mm thick cell cavity where it made direct electrical contact to the graphite plate electrode substrate. Titanium plates were used as current collectors. The positive electrolyte and negative electrolytes each comprised of 70 mL of 1.7 M $V^{3.5+}$ (*i.e.* 50:50 V(III)/V(IV)) solution in 4.0 M H_2SO_4 . The electrolytes were pumped through the cell at room temperature. The effective area of the electrodes and membrane was 25 cm². The charge-discharge cycling was performed at a current density 40 mA/cm² and at a potential range of 1.6 - 0.5 V.

For G2 V/Br performance, a static cell was constructed of two halves, each with an end plate, a plastic plate, a copper current collector, a graphite plate and a graphite felt (Golden Energy Fuel Cell Co., Ltd., China) stacked on top of one another. Two 5 mm thick felts were soaked in 10 mL of electrolyte containing 2.5 M $V^{3.7+}$ in 8.5 M HBr and 2.0 M HCl solution before placing them inside the half-cell cavity. For the tests with complexing agents, the

electrolyte was mixed with the complexing agents at an appropriate ratio. The complexing agents were added at two different ratios; 0.19 M MEM + 0.56 M MEP and 0.56 M MEM + 0.19 M MEP. A sheet of membrane was placed between the two halves of the cell which were then bolted together. Given the absence of pumps and electrolyte flow in the static cell tests, the charge-discharge cycling was performed at the lower current densities of 4 and 10 mA/cm² and at a potential range of 1.5 - 0.5 V. All the testing was performed at room temperature.

2.4. Chemical stability test

This ex-situ chemical stability testing of membranes in G1 VRB electrolyte has been previously reported [32, 33]. A sample of each membrane (25 mm x 25 mm) was soaked in 25 mL of 0.1 M V(V) in 4.0 M H₂SO₄ obtained by diluting the fully charged positive half-cell electrolyte (1.7 M V(V)). To study the membrane behavior at a higher concentration of V(V), each membrane was also immersed in 25 mL of 1.0 M V(V) in 4.0 M H₂SO₄ solution. Oxidation of the membrane by the yellow V(V) ions leads to the formation of the blue V(IV) species which can be used as an indicator to measure the degree of oxidation of the membrane by V(V) and therefore, the stability of a particular membrane [33]. The concentration of V(IV) ions in the solution was thus determined by using a ultraviolet visible spectrophotometer (Shimadzu, Model UV-2501 PC). The absorbance of each solution was periodically determined to monitor the rate of oxidation by V(V). To standardize the method, mixtures of 0.1 M V(IV) solution and 0.1 M V(V) solution were prepared at different ratios. The absorbance was determined for each mixture using a 0.1 M V(V) solution as reference for all measurements. The absorbance of each mixture was determined at a wavelength of 760 nm.

In order to check the membrane stabilities in G2 V/Br electrolyte, the membranes (20 mm x 20 mm) were also immersed in electrolytes comprising of 2.5 M $V^{3.7+}$ in 8.5 M HBr and 2.0 M HCl solution for 30 days.

3. Results and Discussion

3.1. SPEEK membrane properties

Sulfonated PEEK with different reaction time varying from 12 to 96 hours was synthesized while the reaction temperature and the polymer concentration were kept constant. As expected, ion exchange capacity (IEC) and degree of sulfonation (SD) of the SPEEK membranes increase monotonically with increasing reaction time, as shown in **Figure 2a** and **Figure 2b**, respectively. The increase in IEC and SD is linear from 0 to 48 h and non-linear from 48 to 96 h. From the results, the optimum sulfonation reaction time is found to be 48 hours (SPEEK 48). When the reaction time is increased from 48 to 96 hours, sulfonation significantly affects the backbone of the polymer and these highly sulfonated PEEKs become soluble in water. The IEC and SD in this work are lower than those reported by Chang *et al* [34]. Different experimental conditions may affect the IEC and SD of SPEEK. It has been reported that moisture contamination significantly affects the SD [29].

[Figure 2]

In this work, *N*-methyl-2-pyrrolidone (NMP) was selected as the casting solvent for membrane fabrication instead of other solvents, such as dimethylformamide (DMF) and dimethylacetamide (DMAc) owing to strong interaction between DMF/DMAc and sulfonic acid group of SPEEK. The amide group from both DMF and DMAc interacts with sulfonic acid group from SPEEK via hydrogen bonding, thus decreasing the proton conductivity [35, 36]. It is

well known that the proton conductivity of SPEEK membranes increases with IEC and SD. Also, with increments of both IEC and SD, the polymer becomes hydrophilic and tends to absorb more water, which is beneficial for facilitating the proton transport [37].

The impedance spectroscopy was used to determine the proton conductivity of the membrane. **Figure 3** shows the complex impedance spectra of SPEEK membrane. From the Nyquist plot, the membrane resistance value was taken from the intercept of the X-axis value. The proton conductivity of the SPEEK 48 membrane at room temperature was found to be comparable with Nafion 117, as shown in **Table 1**. The water uptake of sulfonated polymers is known to have a profound effect on proton conductivity. Hence, the high proton conductivity of the SPEEK 48 membrane can be attributed to its high water uptake capacity.

[Table 1]

[Figure 3]

Table 2 shows the water uptake, electrolyte uptake and swelling ratio of SPEEK 48 and Nafion 117. It is found that the water uptake, electrolyte uptake, and swelling ratio of SPEEK 48 are higher than that of Nafion 117 indicating higher water uptake requirement for SPEEK to achieve comparable proton conductivity as Nafion 117 membrane due to the difference in microstructures of Nafion and SPEEK, as already described by Kreuer [38].

[Table 2]

3.2. Fourier Transform Infrared Spectroscopy Analysis (FTIR)

The comparative FT-IR spectra of PEEK and SPEEK membrane are shown in **Figure 4**. In the case of the SPEEK spectra, new peaks have been observed. Upon sulfonation reaction, new peaks appear at 1252, 1080, 1024, 709 cm^{-1} . These new peaks represent asymmetric O=S=O

stretching (1252 cm^{-1}), symmetric O=S=O stretching (1080 cm^{-1}), S=O stretching (1024 cm^{-1}), and S-O stretching (709 cm^{-1}), respectively.

[Figure 4]

3.3. Field Emission Scanning Electron Microscopy Studies (FESEM)

Figure 5 shows the FESEM images of pure PEEK, SPEEK powder, and SPEEK membrane. The average size of SPEEK particles is larger than PEEK and this can be attributed to the aggregation of particles during sulfonation [39]. The morphology of SPEEK membrane is free of large pinhole defects and large surface ripples.

[Figure 5]

3.4. G1 VRB performance

Figure 6a shows the charge-discharge curves of the G1 VRB cell employing SPEEK 48 and Nafion 117 membrane at a current density of 40 mA/cm^2 . The charge-discharge curve of each membrane is taken from the second cycle since the first cycle represents the initial charging from the $\text{V}^{3.5+}$ solutions in each half-cell. As can be seen in **Figure 6a**, the average charge voltage of the cell employing SPEEK 48 is lower than that of Nafion 117. As a result, the higher voltage efficiency obtained with the SPEEK 48 membrane can be attributed to the small IR drop associated with its lower area resistance (**Table 1**). In addition, SPEEK 48 exhibits a higher discharge capacity than Nafion 117, which indicates a higher state-of-charge range over the set voltage limits, again due to the lower voltage losses. **Table 3** provides the average coulombic, voltage and energy efficiencies of both membranes. The cell employing SPEEK 48 membrane shows a coulombic efficiency of 92% and a voltage efficiency of 83%, which are slightly higher

than the corresponding values of 91% and 81% for the cell employing Nafion 117. Also, the energy efficiency of SPEEK 48 (77%) is found to be slightly higher than Nafion 117 (73%) which is partly attributed to the greater thickness of Nafion 117 leading to a higher resistance.

The charge retention of the cell using the SPEEK membrane was also determined by monitoring the open circuit voltage (OCV) of the cell while circulating the electrolyte at room temperature after the cell was charged to 90% state-of-charge. **Figure 6b** shows the change in the OCV value of both membranes with increasing time. The OCV value gradually decreases with time as a result of diffusion of the V^{2+} and $V(V)$ species across the membrane leading to self-discharge reactions. It is found that the OCV drops faster for Nafion 117 than for the SPEEK 48 indicating that the self-discharge of G1 VRB caused by diffusion of the vanadium ions across Nafion 117 is more pronounced. Given that the Nafion membrane used here is thicker than SPEEK 48, the lower permeability of the latter can therefore be ascribed to the different microstructures of the SPEEK and Nafion 117 membranes. The smaller ionic cluster region formed in SPEEK may reduce the migration of vanadium ions [38]. These results are also in agreement with the higher discharge capacity of SPEEK membrane resulting in higher coulombic efficiency due to lower self-discharge of SPEEK 48 than that of Nafion 117.

[Figure 6]

[Table 3]

Figure 7a and Figure 7b depict the performance of SPEEK 48 and Nafion 117 in the G1 VRB flow cell at a constant current density of 40 mA/cm^2 . There is no decrease in energy efficiency after 10 cycles for both membranes indicating acceptable short-term stability for both membranes in the highly acidic electrolytes.

[Figure 7]

3.5. G2 V/Br performance

SPEEK and Nafion membranes were tested in a small static cell employing G2 vanadium bromide electrolyte at room temperature. The performance of the two membranes was studied at different current densities and in the presence of MEM and MEP at two different ratios. Representatively, **Figure 8** shows the typical charge-discharge curves of SPEEK 48 employing 2.5 M $V^{3.7+}$ (in 8.5 M HBr and 2.0 M HCl) solution at a constant current density 10 mA/cm². In the first charging cycle, the clear potential step observed after 5 minutes can be attributed to the oxidation of $V^{3.7+}$ to VO^{2+} . Meanwhile, the minor step occurring after around 12 minutes can be assigned to the reduction of $V^{3.7+}$ to V^{3+} . Theoretically, the reduction of $V^{3.7+}$ to V^{3+} in the negative half-cell will take a much longer time than the oxidation of $V^{3.7+}$ to VO^{2+} in the positive half-cell due to the high V(IV) to V(III) ratio in the solution. Thus, as expected, this leads to two apparent potential steps. During cell discharge, the oxidation of V^{2+} to V^{3+} is the limiting reaction and hence a single potential step is observed. From the second cycle onwards, V^{3+} and Br^- are the reactive redox species. Therefore, only one potential step occurs in subsequent charge and discharge cycles.

[Figure 8]

The charge-discharge curves for the static cell using the SPEEK and Nafion membranes and a G2 V/Br electrolyte with and without complexing agents are presented in **Figure 9**. It is well known that the capacity of a redox battery is a function of the volume of electrolyte used and the amount of active species stored. In the case of the static cell, the precise volume in the cell is difficult to quantify since some electrolyte leaks out when the felt is compressed during

cell assembly. The observed variation of capacity for each cell is therefore possibly due to electrolyte loss during compression of the felt and tightening of the bolts.

As can also be seen in **Figure 9**, there is some capacity loss with increasing cycle number for each cell, although a lower discharge capacity loss is observed in the cells using 0.19 M MEM + 0.56 M MEP compared with that of the cells without MEM and MEP. This is caused by the reduced concentration of neutral Br₂ species in solution that also leads to higher coulombic efficiencies.

All static cell results for SPEEK 48 and Nafion 117 in the V/Br cell employing 2.5 M V^{3.7+} (in 8.5 M HBr and 2.0 M HCl) solution at different ratios of MEM and MEP and different current densities have been summarized in **Table 4**. In the absence of complexing agents, at a current density of 10 mA/cm² the energy efficiency of SPEEK 48 (61%) is slightly lower than that of Nafion 117 (63%) contrasting to the results at 4 mA/cm², at which the energy efficiency of SPEEK 48 (73%) is higher than that of Nafion 117 (70%). For both Nafion and SPEEK, the energy efficiency is found to increase in the presence of 0.19 M MEM + 0.56 M MEP. In the absence of the bromine complexing agent, dissolved neutral Br₂ molecules in solution can readily diffuse through each cation exchange membrane since they are not repelled by the anionic functional groups in the membrane pores.

In the presence of 0.56 M MEM + 0.19 M MEP, however, the energy efficiencies are reduced considerably. This may be due to the higher resistance of the electrolyte containing 0.56 M MEM + 0.19 M MEP compared with that containing 0.19 M MEM + 0.56 M MEP or without MEM and MEP, thus decreasing voltage efficiency [40]. The highest energy efficiency of 76% can be obtained in SPEEK 48 in the presence of 0.19 M MEM + 0.56 M MEP at a current density of 4 mA/cm². Overall, the SPEEK membrane can give comparable performance to

Nafion in the G2 V/Br cell and has good potential to be an alternative membrane for vanadium bromide flow cell applications. The mechanism of membrane/vanadium bromide electrolyte interactions in the presence of MEM and MEP during charging-discharging is still unclear however and further studies are needed.

[Figure 9]

[Table 4]

3.6. Chemical stability test

The chemical stability of the synthesized SPEEK membrane was further studied and evaluated by immersing the membrane in highly oxidizing V(V) electrolytes. It is well known that the chemical degradation of polymeric membranes is related to the oxidation of the membrane backbone material by the V(V) ions. Thus, the oxidation of V(V) ions to V(IV) ions indicates the rate of attack and the stability of the membrane. Previous study by Mohammadi *et al* showed that only Nafion 112 and New Selemin type 2 had excellent chemical stability in 0.1 M V(V) electrolytes [32] and to date no-one has reported the chemical stability of SPEEK membrane in the G1 VRB.

Figure 10 shows the ultraviolet visible (UV-Vis) absorbance of standard solutions containing the mixture of V(V) and V(IV) ions with different ratios (total vanadium concentration is 0.1 M) at 760 nm. As V(IV) concentration ratio increases, the absorbance at 760 nm also increases linearly. This is in agreement with Beer's law. The SPEEK 48 membrane and Nafion 117 were immersed in 0.1 M and 1.0 M V(V) ions and the concentration of V(IV) ions were measured after 1, 3, 5, 7 and 60 days of immersion.

[Figure 10]

The concentration against immersion time plots of membranes immersed in 0.1 M V(V) ions is shown in **Figure 11a**. There is no significant change of V(V) concentration for both SPEEK 48 and Nafion 117 even after 60 days soaking, indicating excellent chemical stability for SPEEK 48 membrane which is comparable to Nafion 117. This result is consistent with the previous study of Nafion in 0.1 M V(V) [32]. Chemical oxidation is observed for both SPEEK 48 and Nafion 117 membranes in 1.0 M V(V) solutions however (**Figure 11b**) with a faster oxidation rate noted for SPEEK 48 membrane. As expected, the reduction of V(V) to V(IV) ions after 60 days of soaking in 1.0 M V(V) solutions is more pronounced than that in 0.1 M V(V) solutions for both SPEEK 48 and Nafion 117 membranes, as shown in **Table 5**. This could potentially be a serious problem for this membrane in the G1 VRB.

[Figure 11]

[Table 5]

To understand the degradation mechanism of the SPEEK 48 membrane, the morphology of the membrane before and after soaking was studied by Field-Emission Scanning Electron Microscopy (FESEM), which is shown in **Figure 12**. Both membranes show uniform morphology without any cracks detected prior to soaking and after soaking in 0.1 M V(V) solutions. No signs of physical deterioration are observed for both membranes after soaking in a low concentration of V(V), which is in agreement with a very small V(IV) concentration measured. Meanwhile, there is a slight deterioration observed for both SPEEK and Nafion after soaking in higher concentration of V(V), which may also correlate to the higher chemical conversion from V(V) to V(IV) of both membranes. However, although V(IV) concentration is detected, no physical breakage is found for both membranes in 1.0 M V(V) solutions as well as in 0.1 M V(V) solutions.

[Figure 12]

In order to further investigate the chemical stability behavior of membranes in V(V) solutions, particularly SPEEK membrane in 1.0 M V(V), FT-IR spectroscopy was used for structural characterization. **Figure 13a** shows the FT-IR spectra of SPEEK membrane before and after 60 days soaking in 1.0 M V(V) solution. The FT-IR spectrum of SPEEK powder has been included for comparison. At region 3200-3600 cm^{-1} , a broad peak is observed for the powder and the soaked membrane, indicating OH vibration from SO_3H groups interacting with molecular water [41]. Meanwhile, a sharper peak is observed for the original membrane, indicating the presence of strong NH_2 antisymmetric and symmetric stretching bands at 3320 and 3245 cm^{-1} respectively. A band at around 3065 cm^{-1} is assigned to the C-H vibration of aromatic stretching in SPEEK backbone. The new absorption band at 2880 cm^{-1} observed in the original membrane has been assigned to the C-H band of the methyl group in the NMP, indicating the presence of the solvent in the membrane. Interestingly, the band disappeared after the soaking process, suggesting the remaining NMP was effectively removed from the membrane by a sulfuric acid in V(V) solution [42]. At lower wavenumber region, as shown in **Figure 13b**, four absorption bands of sulfonic acid groups (SO_3H) from SPEEK backbone, namely at 1252, 1080, 1024, and 709 cm^{-1} are still observed for the soaked membrane, suggesting good chemical stability of the SPEEK membrane.

[Figure 13]

From the SEM observation and FT-IR analysis, it has been suggested that 25% chemical conversion from V(V) to V(IV) of SPEEK membrane might be due to contribution of residual organic compounds that reacts with 1.0 M V(V) solution. The SPEEK membrane thus remains stable after soaking in 1.0 M V(V) after 60 days period. In addition, SPEEK and Nafion 117

membrane also show good chemical stability in 2.5 M $V^{3.7+}$ in 8.5 M HBr and 2.0 M HCl electrolyte after being soaked for 30 days.

4. Conclusions

Sulfonated poly (ether ether ketone) membrane has been successfully prepared and optimized for vanadium redox battery application. The low cost SPEEK membrane had a comparable proton conductivity, lower membrane resistance, and slower rate of self-discharge than Nafion 117, which results in slightly higher voltage efficiency, coulombic efficiency, and energy efficiency. For the first time, the SPEEK was tested and evaluated in the G2 V/Br cell and the performance of the membrane was studied in terms of energy efficiency and compared to Nafion 117. The results show that the SPEEK membrane can deliver comparable performance to Nafion 117 in both the G1 and G2 vanadium redox cell electrolytes. Most importantly, the chemical stability of SPEEK membrane has been studied and has shown excellent stability in highly oxidizing V(V) electrolytes. It has been found that residual organic compounds remained in the SPEEK membrane contributes to the apparent chemical degradation observed from the rate of appearance of the V(IV) reaction product in the V(V) solution. The only unexpected result has been the greater degree of swelling of the SPEEK membrane compared with Nafion, but this problem may be addressed by cross-linking the membrane to enhance its dimensional stability. Further work in this area is required.

Acknowledgement

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Figures



Figure 1. As-synthesized sulfonated poly (ether ether ketone) (SPEEK). (Color online)

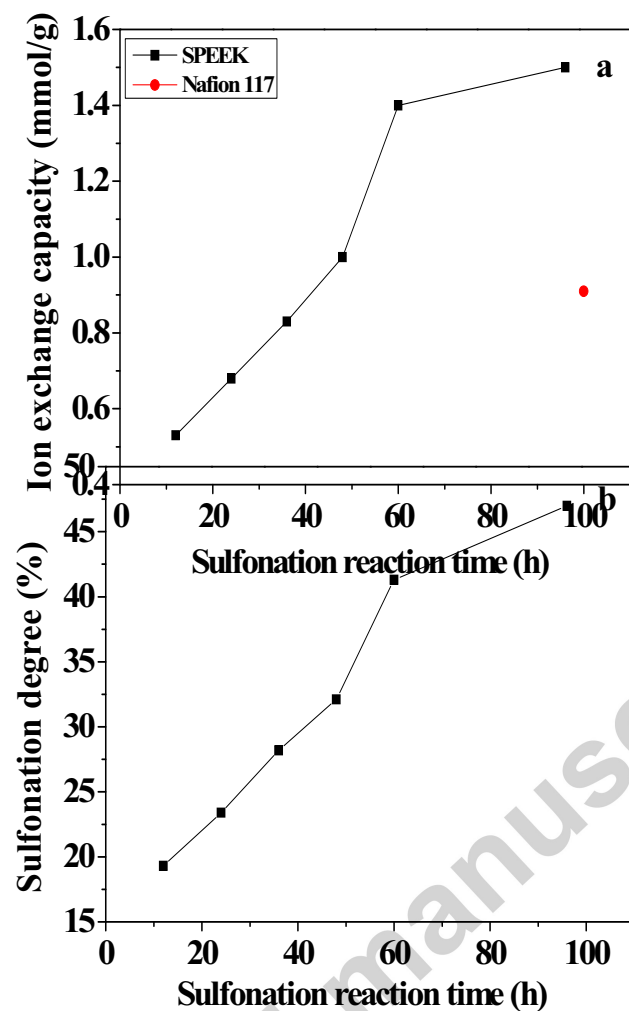


Figure 2. Effect of sulfonation reaction time on **a.** ion exchange capacity (IEC) and, **b.** degree of sulfonation (SD) of SPEEK membranes. (Color online)

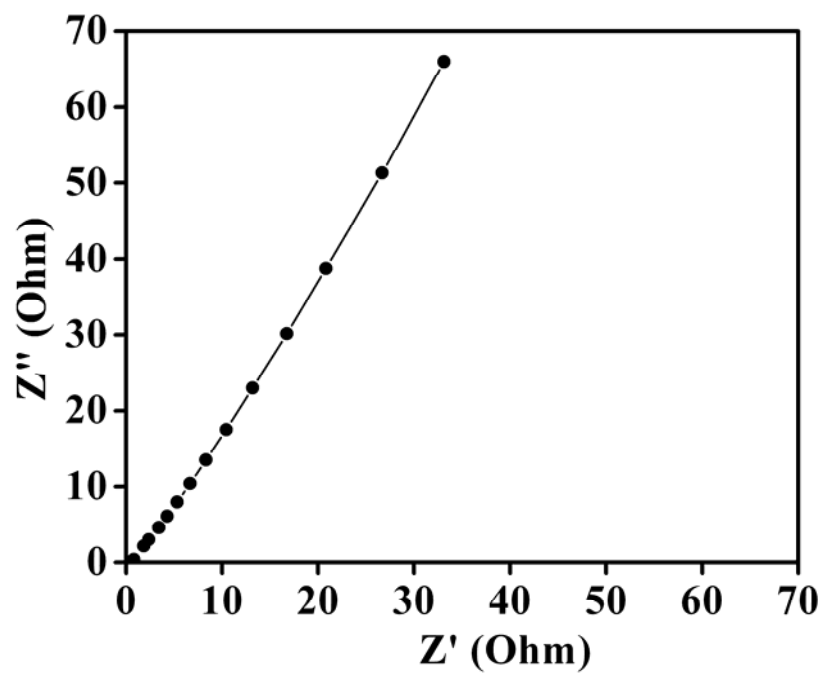


Figure 3. The complex impedance plot of the SPEEK membrane.

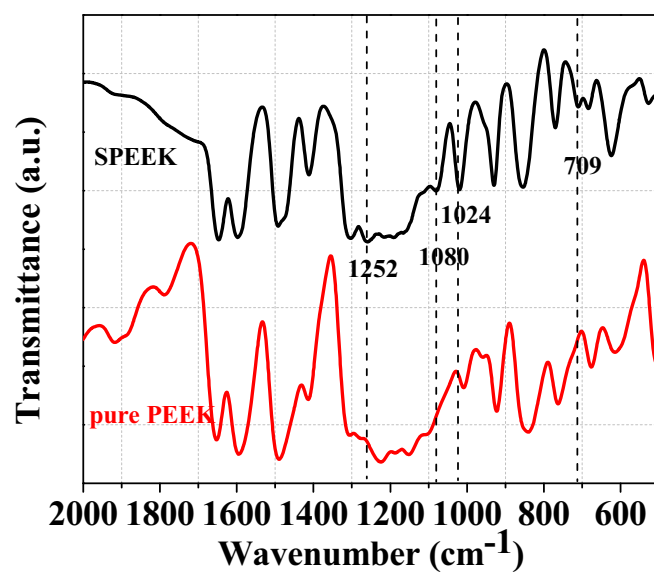


Figure 4. FT-IR spectra of pure PEEK and SPEEK membrane. (Color online)

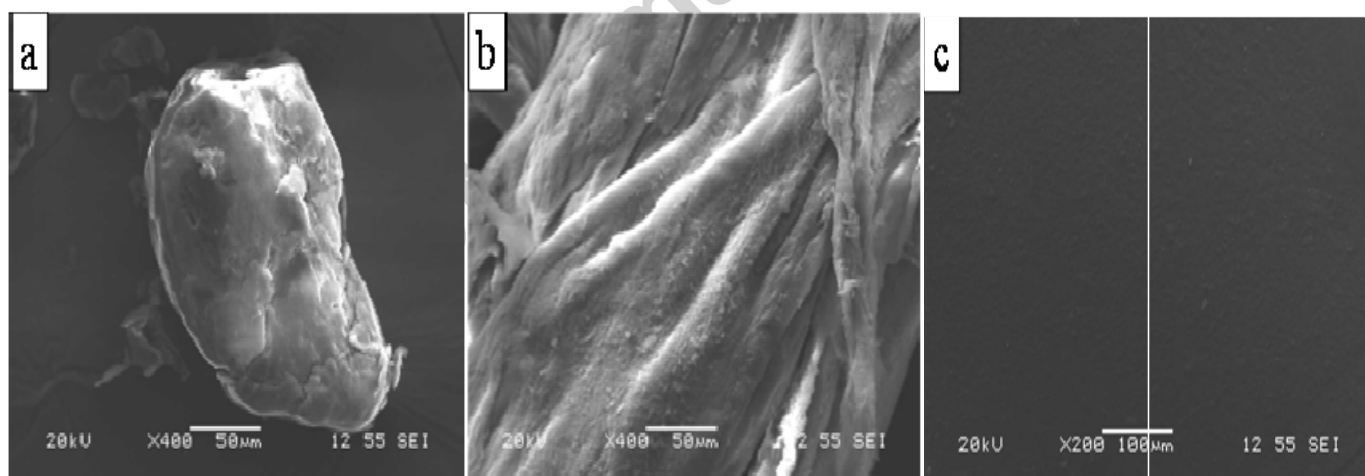


Figure 5. FESEM images of **a.** pure PEEK, **b.** SPEEK powder, and **c.** SPEEK membrane.

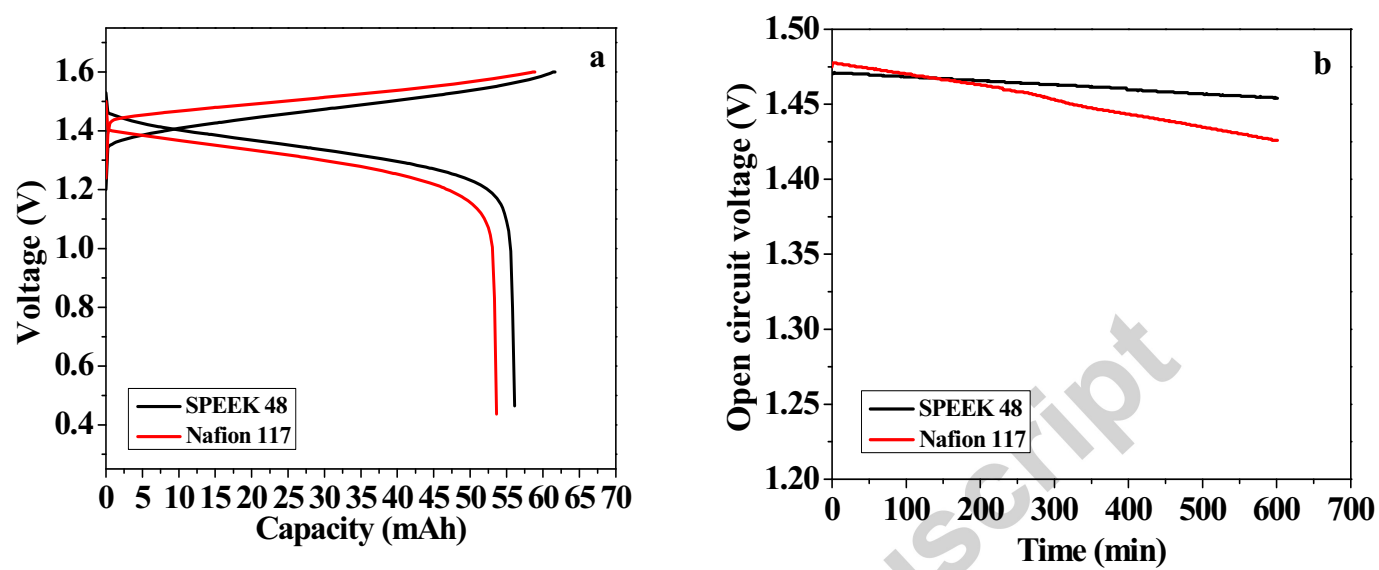


Figure 6.a. Charge-discharge curves of the G1 VRB with SPEEK 48 and Nafion 117 at a current density of 40 mA/cm² and **b.** Self-discharge properties of SPEEK 48 and Nafion 117. (Color online)

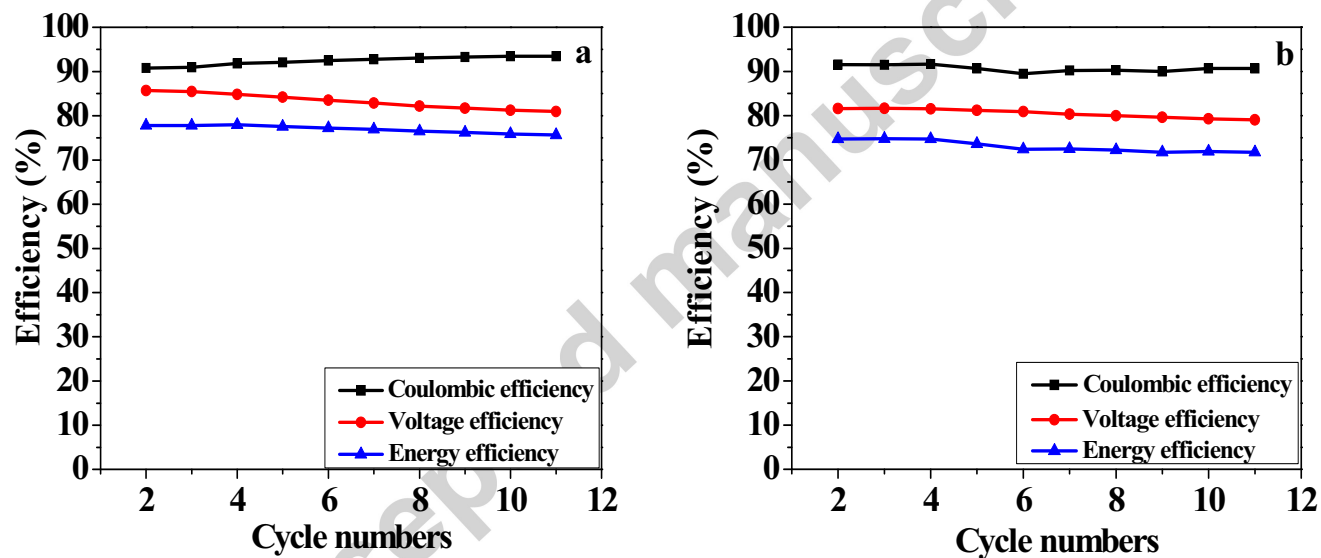


Figure 7.a. Cycle performances of G1 VRB using SPEEK 48 and **b.** Nafion 117 at a current density of 40 mA/cm^2 . (Color online)

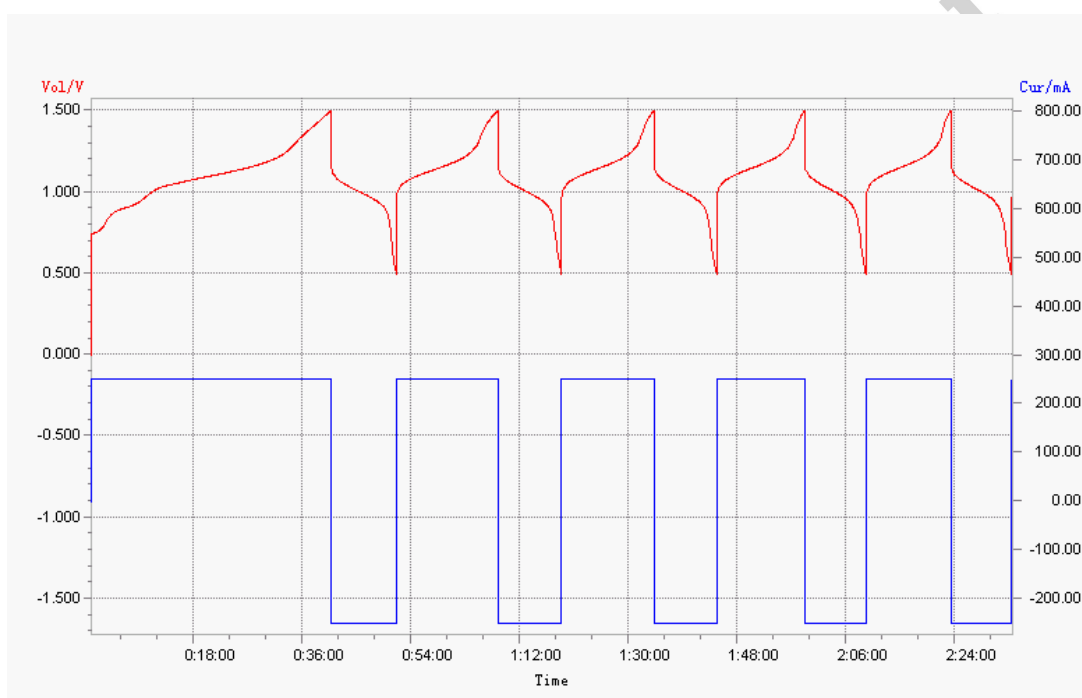


Figure 8. The first five charge-discharge curves of the G2 V/Br using SPEEK 48 membrane at room temperature (25°C) and a current density of 10 mA/cm^2 . (Color online)

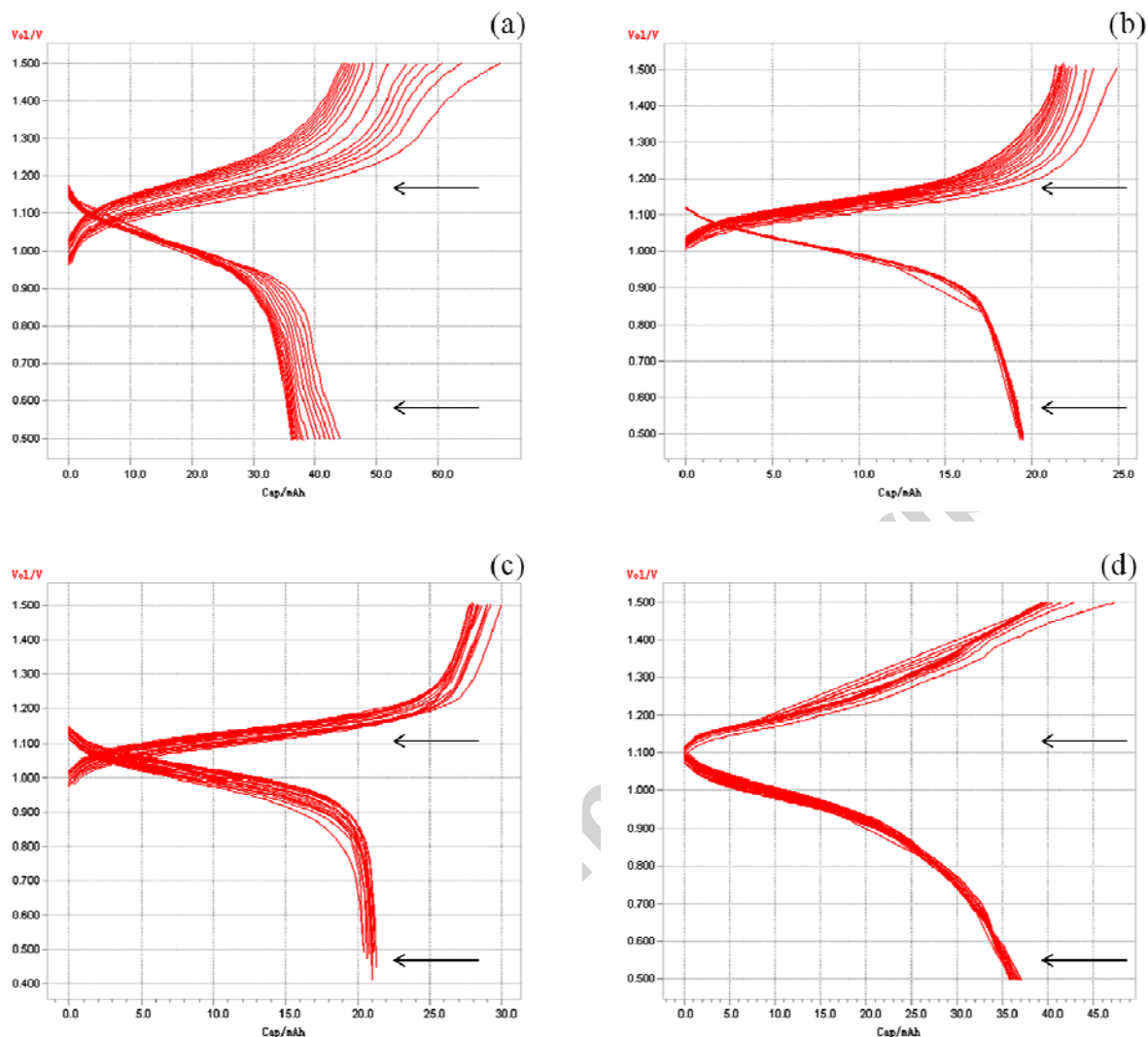


Figure 9. Cell potential vs. capacity curves of the static cell at a current density of $10 \text{ mA}/\text{cm}^2$ using SPEEK 48 membrane: **(a)** without MEM & MEP, and **(b)** with 0.19 M MEM + 0.56 M MEP; Nafion 117: **(c)** without MEM & MEP, and **(d)** with 0.19 M MEM + 0.56 M MEP.

Arrows show increasing cycle number from 2 to 17. (Color online)

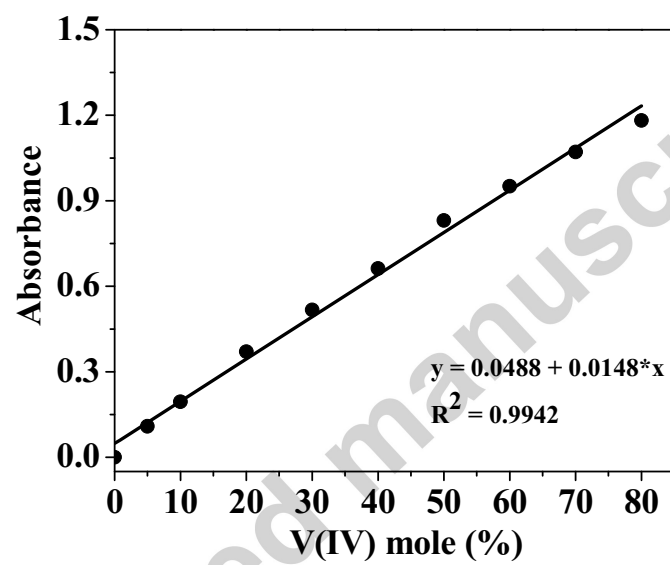
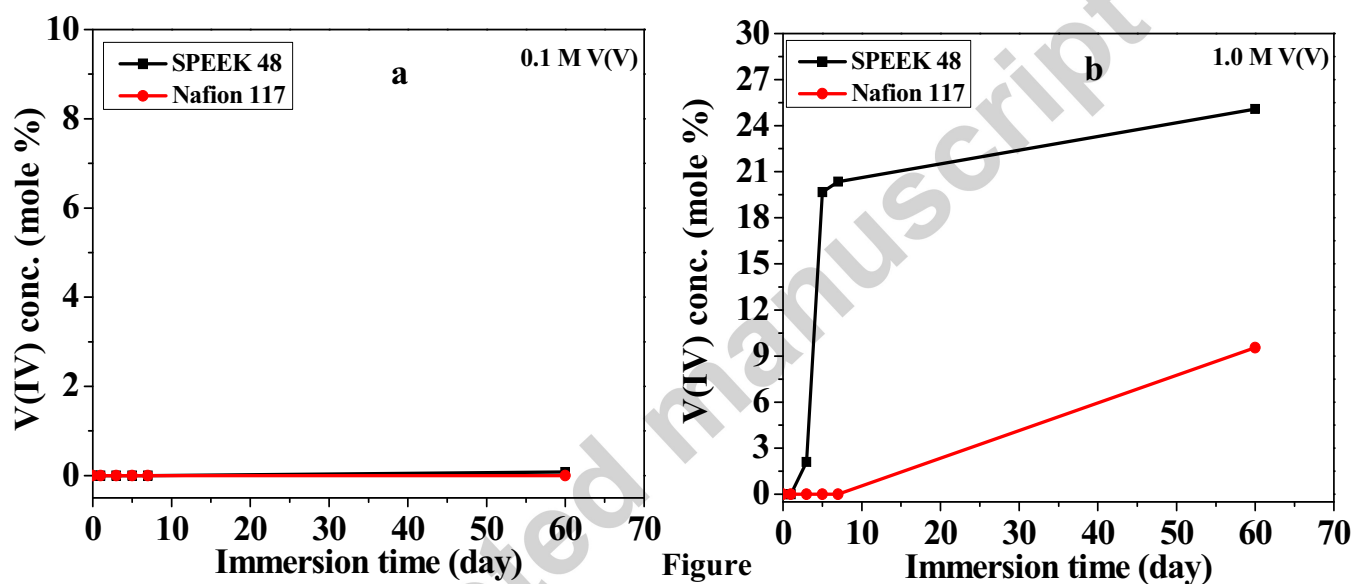


Figure 10. UV-Vis absorbance at 760 nm against V(IV)% for different ratios of V(V) and V(IV) ions (total vanadium concentration = 0.1 M).



11. Chemical stability of SPEEK 48 membrane and Nafion 117 in V(V) solution **a.** 0.1 M and **b.** 1.0 M (Color online)

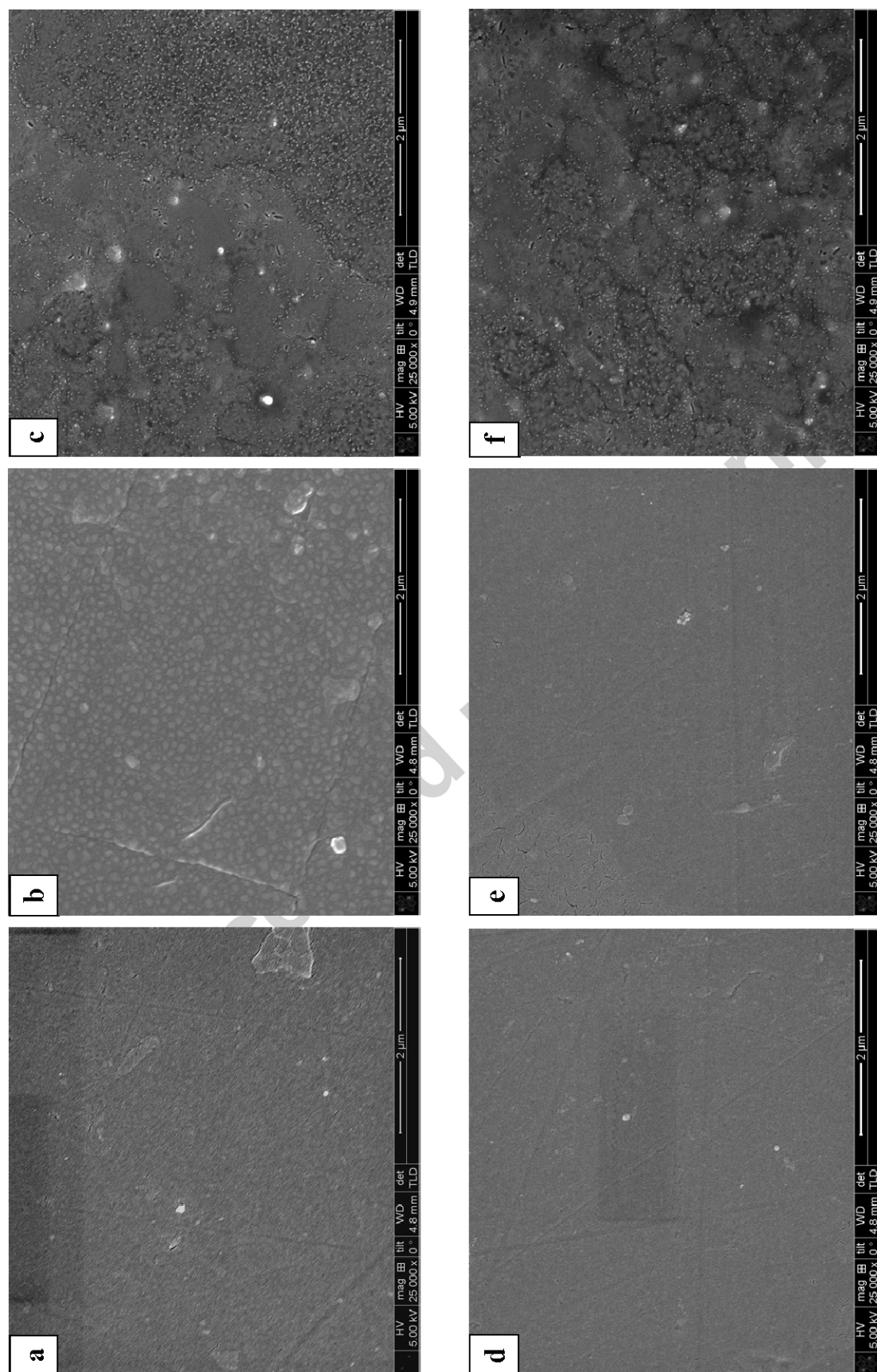


Figure 12. FESEM images of surface of SPEEK 48: **a.** before soaking; **b.** after 60 days soaking in 0.1 M V(V); **c.** after 60 days soaking in 1.0 M V(V); Nafion 117: **d.** before soaking; **e.** after 60 days soaking in 0.1 M V(V); **f.** after 60 days soaking in 1.0 M V(V).

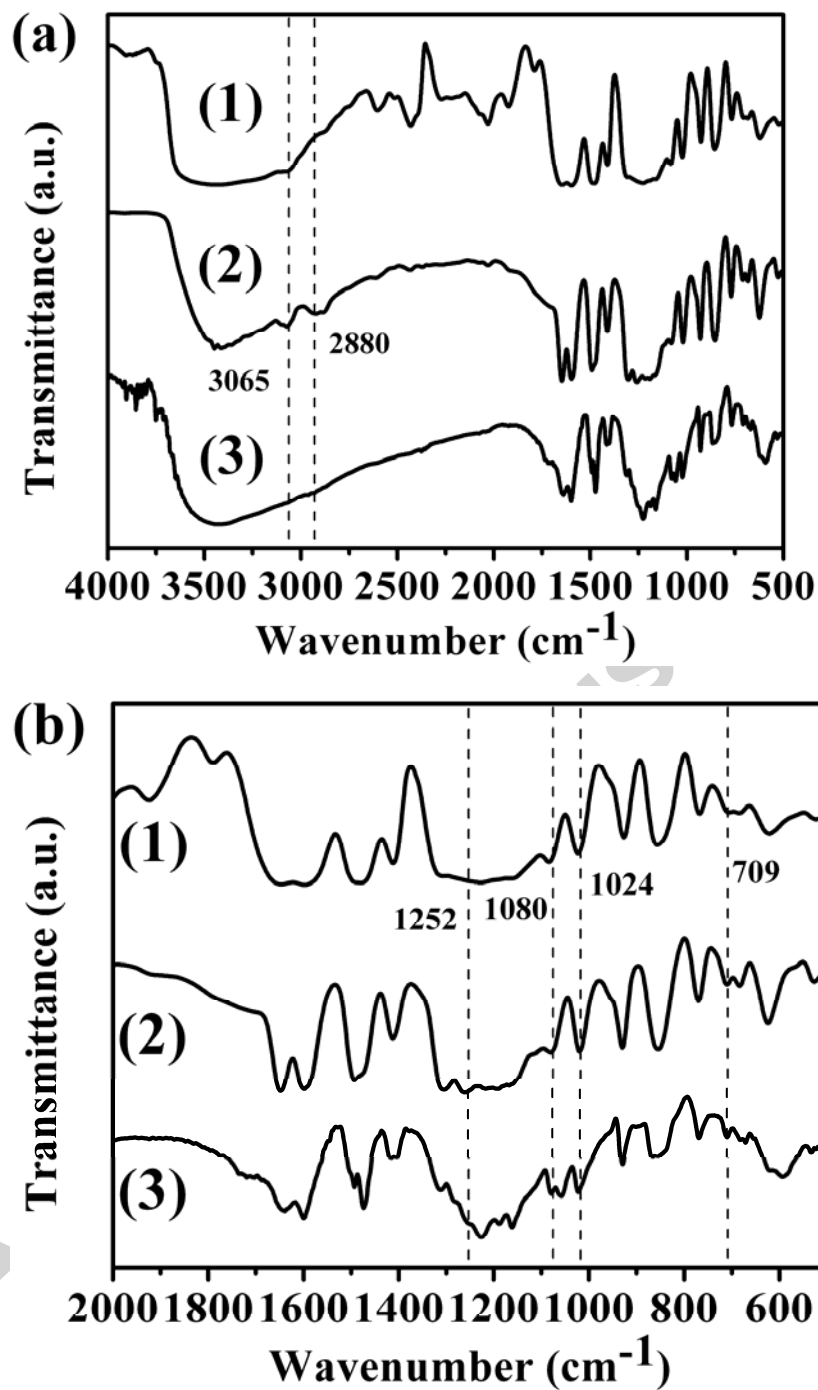


Figure 13. a. FT-IR spectra of (1) SPEEK powder, (2) SPEEK membrane, and (3) SPEEK membrane after 60 days soaking in 1.0 M V(V) solution **b.** FT-IR spectra of both in range 2000-500 cm^{-1} .

Tables

Table 1. Proton conductivity of SPEEK 48 membrane and Nafion 117 at room temperature.

Membrane	Thickness, d (cm)	Resistance, R (Ω)*	Face area, S (cm ²)	Proton conductivity, σ (S/cm)
SPEEK 48	0.0100	0.65	1.44	10.67×10^{-3}
Nafion 117	0.0175	1.02	1.44	11.92×10^{-3}

* The resistance was determined from the average value of two measurement results

Table 2. Comparison of water uptake, electrolyte uptake, and swelling ratio of SPEEK 48 with Nafion 117.

Membrane	Water uptake (%) ^{*a}	Electrolyte uptake (%) ^{*b}	Swelling ratio (%) ^{*a}	IEC (mmol/g)	Proton conductivity, σ (S/cm)
SPEEK 48	41 \pm 5	14 \pm 2	21 \pm 5	1.00	10.67 $\times 10^{-3}$
Nafion 117	14 \pm 1	11 \pm 0	11 \pm 2	0.91	11.92 $\times 10^{-3}$

* Absolute error estimation from minimum 5 experimental points

^a All membranes were immersed in distilled water at room temperature for 24 h.

^b All membranes were soaked in 1.0 M V(III) + 1.0 M V(IV) (2.0 M V^{3.5+}) in 4.0 M H₂SO₄ for 24 h.

Table 3. The average Coulombic efficiency, voltage efficiency, and energy efficiency of SPEEK 48 and Nafion 117 in G1 VRB.*

Membrane	Coulombic efficiency (%)	Voltage efficiency (%)	Energy efficiency (%)
SPEEK 48	92	83	77
Nafion 117	91	81	73

* Each average data was taken from 10 charge-discharge cycles and repeated twice.

Table 4. Average Coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) at different current densities and at different ratios of MEM & MEP using a static cell with SPEEK 48 and Nafion 117 membrane in 2.5 M $V^{3.7+}$ G2 V/Br electrolyte at room temperature.*

Membrane sample	At 10 mA/cm ²			At 4 mA/cm ²		
	CE (%)	VE (%)	EE (%)	CE (%)	VE (%)	EE (%)
SPEEK; without MEM & MEP	76	80	61	97	75	73
Nafion; without MEM & MEP	74	86	63	78	90	70
SPEEK; 0.19 M MEM + 0.56 M MEP	88	83	73	94	80	76
Nafion; 0.19 M MEM + 0.56 M MEP	90	70	63	85	88	75
SPEEK; 0.56 M MEM + 0.19 M MEP	41	76	31	88	73	65
Nafion; 0.56 M MEM + 0.19 M MEP	89	64	57	82	82	68

* Each average data was taken from 16 charge-discharge cycles and repeated twice.

Table 5. The chemical stability of SPEEK 48 and Nafion 117 in G1 VRB electrolyte (V(V) in 4.0 M H₂SO₄) solution after 60 days soaking.

Membrane	Reduction of V(V) to V(IV) in 0.1 M V(V) after 60 days soaking (%) [*]	Reduction of V(V) to V(IV) in 1.0 M V(V) after 60 days soaking (%) [*]
SPEEK 48	0.08	25.08
Nafion 117	0.05	9.54

^{*} The average data was taken from two different set of samples.

Highlights:

- Synthesized and tested SPEEK membrane for vanadium bromide redox battery.
- Bromine complexing agents were used to suppressing bromine vapour during charging.
- Cell performance efficiency in SPEEK membranes was slightly higher than Nafion 117.
- The SPEEK membrane was found to be chemically stable in vanadium electrolytes.