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The use of polybenzimidazole membranes in vanadium redox flow batteries leading to increased coulombic efficiency and cycling performance

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An issue with conventional vanadium redox flow batteries (VRFB) with Nafion membranes is the crossover of vanadium ions, resulting in low coulombic efficiency and rapid decay in capacity. In this work, a VRFB with a polybenzimidazole (PBI) membrane is tested and compared with the Nafion system. Results show that the PBI-based VRFB exhibits a substantially higher coulombic efficiency of up to 99% at current densities ranging from 20 mA cm^{-2} to 80 mA cm^{-2}. More importantly, it is demonstrated that the PBI-based VRFB has a capacity decay rate of as low as 0.3% per cycle, which is four times lower than that of the Nafion system (1.3% per cycle). The improved coulombic efficiency and cycling performance are attributed to the low crossover of vanadium ions through the PBI membrane.

1. Introduction

Pressing concerns on the environmental impacts of burning fossil fuels and their limited reserves have led to a growing global usage of renewable energy, such as wind and solar energy. The wide deployment of renewables is, however, hindered by a viable energy storage technology. Among a wide range of energy storage technologies, flow batteries offer several unique advantages, including the system scalability, long cycle life, and high energy efficiency [1–4]. In particular, the all-vanadium redox flow battery (VRFB) has been regarded as one of the most promising technologies, primarily because it uses the same element in both half-cells, which avoids the problem of cross-contamination between the two half-cell electrolytes [5,6].

A typical VRFB consists of two porous electrodes and two circulating electrolyte solutions separated by a membrane, as shown in Fig. 1. The membrane acts as a key component, not only separating the positive electrolytes and negative electrolytes, but also providing an ionic conduction pathway between the two electrolytes during the charge and discharge process. To date, the most widely used membranes in VRFBs system are perfluorosulfonic cation exchange membranes (typically Nafion) due to their high ionic conductivity and decent chemical stability. However, Nafion membranes suffer from a high crossover rate of vanadium ions, which results in a decrease in the coulombic efficiency and capacity fading after prolonged cycling. Previous studies reported two main reasons for the high vanadium crossover with Nafion membranes. First, the chemical structure of currently employed Nafion consists of hydrophilic sulfonic acid groups and a hydrophobic Teflon backbone. Once hydrated, the microphase separation between hydrophilic sulfonic acid groups and the hydrophobic Teflon backbone forms water channels, which create unwanted ion transport pathways. These water channels are typically 4.0 nm in diameter [7], which is much larger than the size of hydrated vanadium ions (typically 0.6 nm [8]), allowing free movement of vanadium ions through Nafion membranes. Second, the negatively charged functional groups from Nafion membranes facilitate the adsorption and diffusion of positively charged vanadium ions in the membrane due to electrostatic attraction. In order to improve VRFB's performance, efforts have been made to reduce vanadium crossover [9–16]. For example, inorganic particles like SiO_2, TiO_2 and zirconium phosphate have been introduced into Nafion membranes in an attempt to reduce the size of water channels, thereby decreasing vanadium permeability [9–11]. Some alternative CEMs such as SPEEK membranes, which possess more rigid structures and narrower water channels, have proven to exhibit a lower vanadium permeability, but have not completely eliminated the problem [12–15]. Further reduction in the vanadium permeability of CEMs is limited by the negatively charged functional groups.

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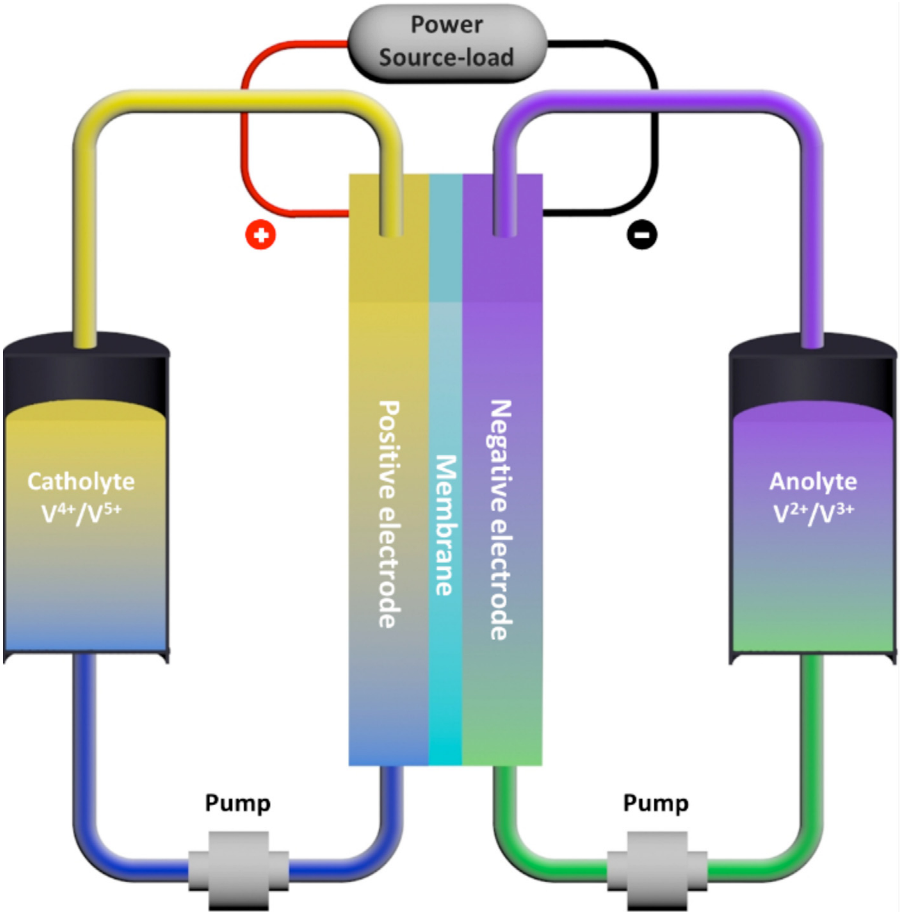

Fig. 1. Schematic of vanadium redox flow batteries.

Xu *et al.* [17] recently demonstrated a zeolite membrane for flow batteries, suggesting that effective separation of protons from vanadium ions can be achieved by using porous membranes with small pore sizes due to the size exclusion effect. Considering the fact that the Stokes radius of hydrated vanadium ions is much larger than that of H_3O^+, it is possible to separate protons from vanadium ions by using a porous separator [18]. A porous separator may be a likely solution to eliminating vanadium crossover, since it contains no functional groups, but the brittleness of zeolite membranes is a serious limiting factor in practical applications. Therefore, a porous polymer membrane with small pore sizes that offers better mechanical properties is highly desired.

The PBI membrane has been widely investigated for nanofiltration [19,20] and high-temperature proton exchange membrane fuel cells [21–26]. The chemical structure is illustrated in Fig. 2. PBI has a highly chemically stable polymer backbone, making it especially suitable for VRFBs, which has a strong acidic and oxidizing environment. Previous studies show that the pore size of PBI membranes should range from 0.5 nm to 2.0 nm [19,20] (much smaller in comparison to that of Nafion membranes and other alternative ion exchange membranes at typically 2–4 nm in diameter), which helps to reduce vanadium ion crossover significantly. The objective of this work is to employ the PBI membrane as a porous separator for a VRFB system and conduct a comparison study with the Nafion-based system through investigating conductivity, vanadium ion permeability and cell performance. It is demonstrated that the vanadium permeability of a PBI membrane is two orders of magnitude lower than that of the Nafion system, indicating that effective separation of protons from vanadium ions is achieved. A PBI-based VRFB demonstrates a coulombic efficiency of up to 99% at current densities ranging from 20 mA cm^{-2} to 80 mA cm^{-2}, as opposed to a coulombic efficiency of 82% to 94% seen in a Nafion-based VRFB.

2. Experimental

2.1. Membrane preparation

A PBI membrane, 30 μm in thickness, was provided by Yick-Vic. It should be noted that the ionic conductivity of a pure PBI membrane is extremely low, i.e. 10^{-12} S cm^{-1} [27] and have nearly no pores. Thus, the PBI membrane was pretreated by immersion in 4 M H_2SO_4 for 7 days to form the porous membrane. The PBI membrane was then thoroughly washed in DI water to remove excess sulfuric acid. Nafion ® 211 (thickness: 25 μm) was examined as a benchmark under the same conditions.

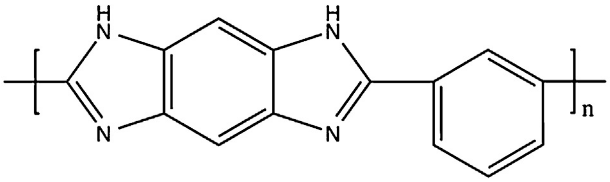

Fig. 2. Chemical structure of PBI.

2.2. Membrane characterization

2.2.1. Area resistance and proton conductivity

The area resistance (ASR) of the membranes was detected with a method described in the literature [16]. Two half cells containing 1 M $VOSO_4$ + 4 M H_2SO_4 were separated by the membrane. The effective area of the cell was designed at 3.14 cm^2. R_1 and R_2, which represent the electric resistances of the cell with and without a membrane respectively, were determined by electrochemical impedance spectroscopy (EIS) over a frequency range from 1 kHz to 1 MHz. The area resistance *R* was calculated by

$$R = (R_1 - R_2) \times S \tag{1}$$

Where S is the effective area of the cell.

Both membranes were immersed in 1 M VOSO4 and 4 M H_2SO_4 solution for 24 hours before measurements were taken.

2.2.2. Permeability of VO^{2+}

The permeability of vanadium (IV) through the membrane was tested using an in-house dialysis cell, which is similar to the conductivity cell mentioned in Section 2.2.1. The cell was separated into two compartments by a membrane with an effective area of 3.14 cm^2. One compartment was filled with 80 ml of 1.0 M $VOSO_4$ (ZhongTian Chemical Ltd. China) in 4.0 M H_2SO_4, while the other compartment was filled with 80 ml of 1.0 M $MgSO_4$ (Fluka, USA) in 4.0 M H_2SO_4. The purpose of $MgSO_4$ is to reduce the osmosis effect of anions by incorporating sulfate anions (SO_4^{2-}) in the deficiency side. In this experiment, we assumed that the change in vanadium ion concentration in the vanadium enrichment compartment is negligible and a pseudo-steady state condition is used in the membrane. At a regular time interval (8 hours), samples in the magnesium sulfate compartment were taken and analyzed for vanadium ion concentration using inductively coupled plasma mass spectrometry (ICP-MS).

2.2.3. VRFB single cell performance characterization

A VRFB single cell was charge–discharge cycled using a computer controlled battery test system (CT3008 W, Neware Inc. China). The in-house designed flow battery is similar to our previous work [16]. The single cell consisted of two acrylic flow channels (6 mm thickness), four silicone gaskets (1.5 mm thickness) and the negative and positive electrodes separated by a membrane. Both negative and positive electrodes were made of two pieces of carbon felt (6 mm thickness pre-compressed, Sigratherm® GFA-05, SGL Carbon, Germany), which were compressed to the membrane by clamping the graphite substrates (20 mm × 25 mm × 9 mm) on both sides. Electrolytes of 20 ml were fed into the compartments using the acrylic flow channels and were circulated to and from the reservoirs at 3 ml s^{-1} (mean linear flow velocity) using a 2-channel peristaltic pump (WT-600-2J, Longerpump, China). Measurements were conducted with 20 ml 1 M V (IV) + 4 M H_2SO_4 solution as the positive electrolyte and 20 ml 1 M V (III) + 4 M H_2SO_4 solution as the negative electrolyte. The cell was initially charged to 1.7 V and discharged to 1.0 V at 40 mA cm^{-2} and then cycled at this current density for 20 cycles before finally being charged-discharged at 80, 60, 40 and 20 mA cm^{-2}. The coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) for the charging-discharging process were calculated from:

$$CE = \frac{t_d}{t_c} \times 100\% \tag{2}$$

$$VE = \frac{V_d}{V_c} \times 100\% \tag{3}$$

$$EE = CE \times VE \tag{4}$$

where t_d is the discharge time, t_c is the charge time, V_d is the average discharge voltage, V_c is the average charge voltage.

2.2.4. Chemical stability

The chemical stability of membranes was investigated according to the method reported elsewhere [28]. A PBI membrane sample and a Nafion 211 membrane were immersed in 50 mL electrolyte solution (1 M V (V) in 5 M total sulfate) at room temperature for three months. The weight and ASR of each sample were recorded before and after being soaked in V (V) solution to observe the weight and conductivity changes. The membrane oxidative stability was determined by weight change (%) and conductivity change (%) which can be calculated by the following:

$$\text{Weightchange}(\%) = \frac{W_0 - W_1}{W_0} \times 100\% \tag{5}$$

$$\text{Conductivity change}(\%) = \frac{\rho_0 - \rho_1}{\rho_0} \times 100\% \tag{6}$$

where W_0 and W_1 are the respective weights of the membranes before and after immersion in V (V) solution, ρ_0 and ρ_1 are the respective conductivities of the membranes before and after immersed in V (V) solution.

3. Results and discussion

3.1. Ion Conductivity and vanadium permeability of PBI

The physical properties of PBI and Nafion samples are summarized in Table 1. The conductivity of N211 and the PBI after equilibration in 1 M $VOSO_4$ + 4 M H_2SO_4 solution were evaluated. The measured conductivity of N211 in VRFBs electrolyte environment is 50.7 mS cm^{-1}, which is comparable to the 50 mS cm^{-1} reported by Tang et al. [29]. The measured conductivity of Nafion in VRFB solution is lower than that of Nafion in pure water. The lower conductivity is ascribed to the high concentration of sulfuric acid [30] and some of the ion transport channels being occupied by vanadium cations [29]. PBI membranes, widely used in high-temperature PEM fuel cells, have much lower proton conductivities at room temperature. However, the measured conductivity of PBI in this work is 15.8 mS cm^{-1}, which reached nearly one third of the ion conductivity of N211. This can be explained by the acidic solution, which improves the conductivity of PBI membranes. Once the PBI membrane is soaked in a sulfuric acid solution, the membrane state is changed, sulfuric-doped free volumes are formed, which can conduct ions under an electric field in a fashion similar to an aqueous solution. Thus, transporting ions through the PBI is enhanced by the sulfuric-doped free volume in the porous matrix. As a result, the sulfuric acid solution environment help improve the conductivity of PBI membranes.

Table 1
Physical properties of PBI and Nafion samples.

Membrane	VO^{2+} permeability (cm^2 min^{-1})	Conductivity (mS cm^{-1})
PBI	Undetectable	15.8
Nafion	1.8×10^{-6}	50.7

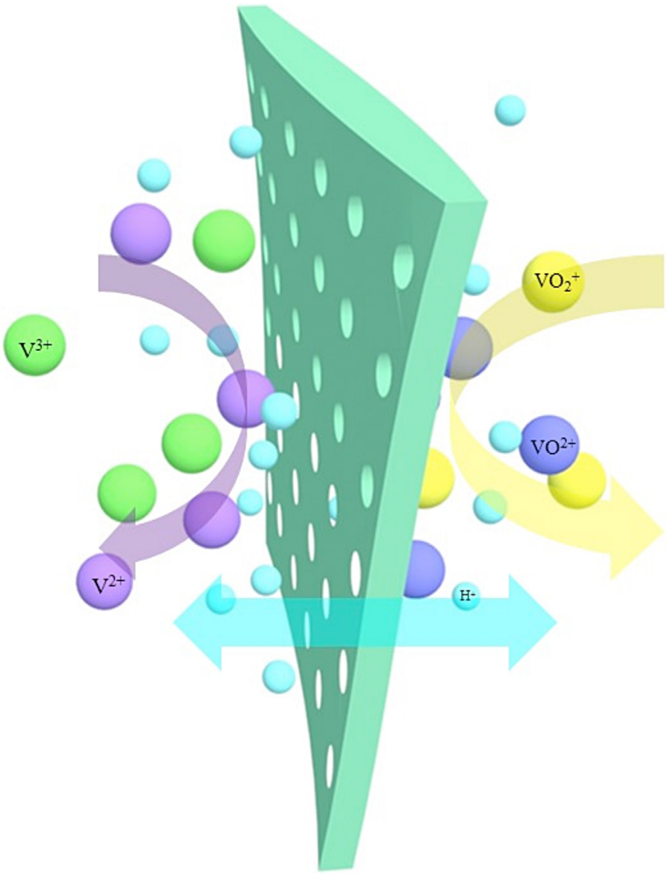

Fig. 3. Schematic of the PBI membrane in VRFB.

For Nafion, the vanadium deficient solution concentration changed from 0 to 8.1×10^{-2} M in 48 hours and the VO^{2+} permeability of Nafion 211 is calculated to be 1.8×10^{-6} cm^2 min^{-1}, similar to previously reported values [16]. For the PBI membrane, there is no detectable VO^{2+} ion in deficient solution by ICP measurement (the detection limit is 10^{-4} M) within 48 hours, indicating that the vanadium ion permeability of the PBI membrane is two orders of magnitude lower than that of Nafion membrane. In addition, for Nafion 211, the permeation of vanadium ions could be observed by the change of the vanadium deficient solution from clear to blue within 1 h and becoming darker over the period of two weeks. However, nearly no color change in the solution for PBI membranes for the entirety of the two week period. There is still no

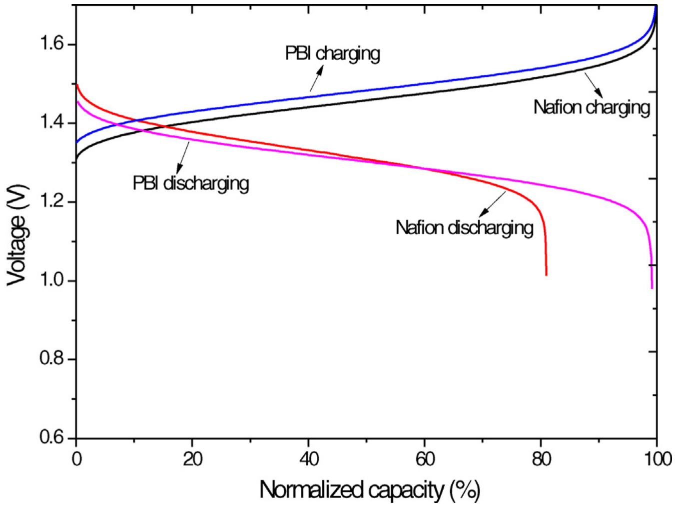

Fig. 4. The charging-discharging curve of VRFB at 20 mA cm^{-2}.

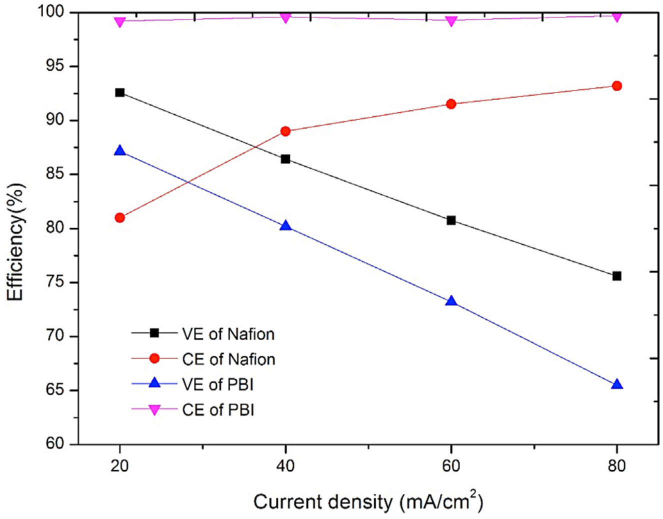

Fig. 5. Coulombic efficiency, voltage efficiency of VRFB at various current densities.

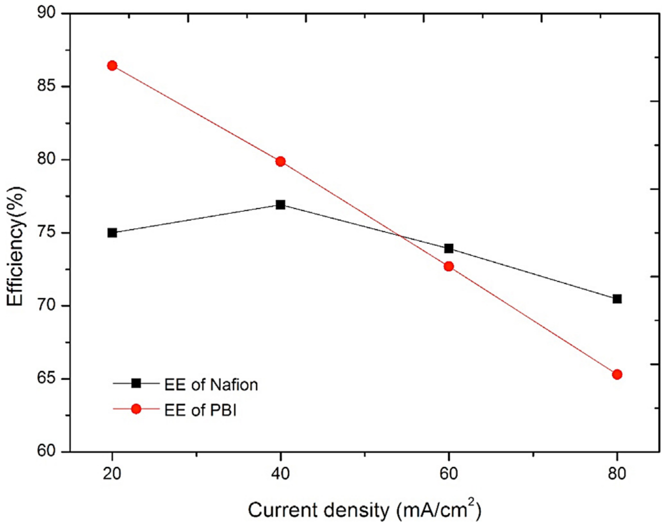

Fig. 6. Energy efficiency of VRFB at various current densities.

detectable VO^{2+} ion in deficient solution by ICP measurement (the detection limit is 10^{-4} M). The high vanadium permeability of Nafion membranes is caused by the sulfonic acid functional groups. In addition, the large diameter of the water channels (typically 4 nm) facilitates the permeation of vanadium ions through Nafion. In contrast, previous studies showed that the pore size of PBI membranes should range from 0.5 nm to 2 nm [19,20], which is much smaller than that of Nafion. The PBI membrane is also nonionic and contains no functional groups. PBI membranes allow the transport of protons and limit the transport of vanadium ions due to size-exclusion effects, as displayed in Fig. 3.

3.2. VRFB performance at different current densities

The charge-discharge curves of VRFB assembled with the PBI membrane and Nafion 211 at 20 mA cm^{-2} are shown in Fig. 4. Nafion 211 has a lower charge voltage than the PBI membrane and a higher discharge voltage due to Nafion 211's lower resistance. Nafion 211 is expected to possess a higher voltage efficiency than PBI, due to this lower resistance. However, it suffers from large vanadium permeation, resulting in a lower coulombic efficiency. The coulombic efficiency of the Nafion 211 at 20 mA cm^{-2} is 82%, which is similar to results found in the literature. Coulombic efficiency observed in PBI-based VRFB is larger than 99%, suggesting that there is little to no vanadium ion crossover during cell operation.

Figs. 5 and 6 illustrate the coulombic efficiency, voltage efficiency and the energy efficiency of the VRFBs at different operating current densities. It is shown that the PBI -based VRFB exhibits 99% coulombic efficiency for all the tested current densities. The coulombic efficiency of the VRFB assembled with Nafion 211 increased with the increase in current density because the time for vanadium ion permeation is decreased. As a consequence of the higher ohmic loss and activation loss at higher current densities, the VE of both VRFBs decreases with current density. Compared to PBI membranes, Nafion membranes possess an advantage in VE with increased current density, suggesting that membrane resistances play an important role on VE at higher current density, as expected. The EE of PBI membrane decreases monotonically with increasing current density from 20 mA cm^{-2} to 80 mA cm^{-2} due to the dramatic decrease of VE. The EE of Nafion 211 increased initially due to the increase CE and then decreased due to the decrease of VE. From the results, PBI has relatively lower VE at high current densities due to the lower ionic conductivity compared to that of Nafion 211. Though the VE of PBI-based VRFB is relatively low, the PBI-based VRFB has acceptable energy efficiency of 79% at 40 mA cm^{-2}. More importantly, it should be noted that the PBI-based VRFB has higher energy efficiencies than Nafion membranes at low current density (less than 40 mA cm^{-2}), making it highly promising for low current density operating applications.

3.3. VRFB cycling performance

The capacity fade, CE and VE change versus cycle number were investigated are shown in Figs. 7 and 8. The results show that the present VRFB has a capacity decay rate of 0.3% per cycle, which is four times lower than that of the Nafion-based VRFB (1.3% per cycle), indicating that PBI has large advantage over Nafion 211 at maintaining capacity. The improvement in cycling performance is attributed to its extremely low vanadium ion permeability.

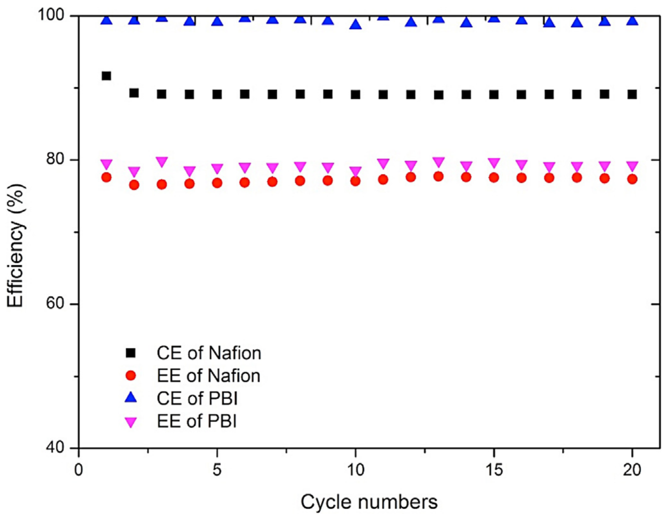

Fig. 7. Energy efficiency and coulombic efficiency of VRFB in the cycling test.

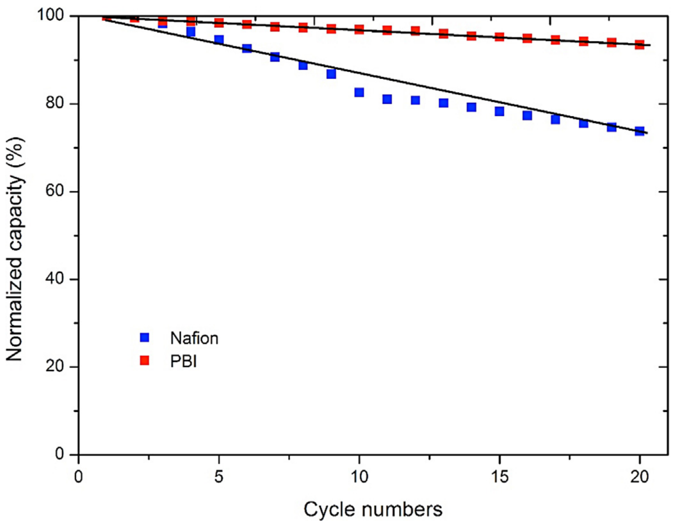

Fig. 8. Normalized capacity changes of VRFB in the cycling test.

Table 2
Chemical stability test results.

Membrane	Weight change	Conductivity change
PBI	2.9%	4.4%
Nafion	2.1%	5.6%

3.4. The chemical stability test

The chemical stability of the PBI membrane is examined by an ex-situ chemical stability method. The shape and color of both the Nafion and PBI membranes kept good after soaking testing in 1 M V^{5+} at room temperature for 120 days. The test results are summarized in Table 2. The weight change of the two membranes are 2.1% and 2.9%, respectively. The change in conductivity of the two membranes are 4.4% and 5.6%, respectively. These results show that PBI membranes are decently durable in the highly corrosive and oxidative environment of the V^{5+} solution in this soaking testing. As previously mentioned, the highly stable polymer backbone ensures the chemical stability of PBI membranes. It should be noted that the durability of PBI membranes need to be further tested with long term cycle tests for application.

4. Conclusions

In this work, the PBI membrane is employed as a porous membrane for VRFB and compared with Nafion membrane by investigating the conductivity, the vanadium ion permeability, chemical stability and the cell performance. Our investigations show that the PBI-based VRFB results in a coulombic efficiency of 99% at current densities ranging from 20 $mA\,cm^{-2}$ to 80 $mA\,cm^{-2}$, as opposed to a coulombic efficiency of 82% to 94% exhibited in a Nafion-based VRFB. In addition, the cycling performance tests demonstrate that the PBI-based VRFB system has a capacity decay rate of 0.3% per cycle, which is four times lower than that of the Nafion-based VRFB (1.3% per cycle). The improvements in the coulombic efficiency and cycling performance are attributed to the low vanadium ion permeability. Furthermore, the PBI membrane is observed to possess moderate conductivity in the VRFB system even at room temperature, with an acceptable voltage efficiency of 79% at 40 $mA\,cm^{-2}$. We suggest that this is due to sulfuric acid solution mitigating the low ionic conductivity of the PBI membrane. Moreover, the PBI-based VRFB has higher energy efficiencies than the Nafion-based VRFB at low current density (less than 40 $mA\,cm^{-2}$), making it highly promising for its application at low current density operation. Durability tests show that the PBI membrane maintains chemically stable, suggesting that it is feasible to incorporate the use of PBI membrane in a VRFB system. Based on the results, the PBI membrane is found to be a promising candidate for VRFB due to its high coulombic efficiency, low cost and good chemical stability. We believe that the ionic conductivity of the PBI membrane can be improved by changing the chemical structure or adjusting its pore structure to further improve its performance at high current density in future works.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2014.11.185.

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