



Short communication

## Nafion/polyvinylidene fluoride blend membranes with improved ion selectivity for vanadium redox flow battery application

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### ABSTRACT

Nafion/PVDF blends are employed to prepare the ion exchange membranes for vanadium redox flow battery (VRB) application for the first time. The addition of the highly crystalline and hydrophobic PVDF effectively confines the swelling behavior of Nafion. In VRB single cell test, the Nafion/PVDF binary membranes exhibit higher columbic efficiency than recast Nafion at various current densities. The blend membrane with 20 wt% of PVDF ( $N_{0.8}P_{0.2}$ ) shows energy efficiency of 85% at  $80 \text{ mA cm}^{-2}$ , which is superior to that of recast Nafion.  $N_{0.8}P_{0.2}$  membrane also possesses twice longer duration in OCV decay test and much lower permeation of  $\text{VO}^{2+}$  compared with recast Nafion. These results indicate that the addition of PVDF is a simple and efficient way to improve the ion selectivity of Nafion, and the polymer blends with optimized mass fraction of PVDF show good potential for VRB application.

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### 1. Introduction

Vanadium redox flow battery (VRB) is an environmentally friendly energy storage device, which was initially fabricated and operated by Skollaskazacos et al. in 1980s [1–3]. It possesses technical advantages such as the independence of output power and energy capacity, the facility of electrolyte solution regeneration and the safety in large-scale energy storage. In a VRB,  $\text{VO}_2^+/\text{VO}^{2+}$  and  $\text{V}^{3+}/\text{V}^{2+}$  serve as positive and negative redox couples respectively, separated by an ion exchange membrane (IEM). The IEM, as a key component of the VRB, acts as a conductor for ions as well as a separator for electrolyte solution. The ideal IEM should not only possess good ion conductivity and chemical stability, but also low permeability for vanadium ions in order to minimize the cross-mixing of these electro-active species.

Perfluorosulfonic polymers, such as Dupont Nafion, are the most common membranes currently used in VRB due to their excellent proton conductivity and chemical stability [4–6]. However, Nafion membranes suffer from their high crossover of vanadium ions, which further leads to the capacity loss and energy efficiency decrease in VRB. In order to overcome this challenge, different modification methods were proposed to increase the ion selectivity of Nafion or reduce its vanadium permeation [7–9]. For example, Nafion/ $\text{SiO}_2$  and Nafion/ $\text{TiO}_2$  hybrid membranes were

synthesized via *in situ* sol–gel method [7,10,11]. Zeng et al. prepared Nafion/polypyrrole composite membranes with electrodeposition techniques [9]. Luo et al. introduced a polyethylenimine layer on Nafion membrane by interfacial polymerization [8]. All these membranes exhibited lower vanadium permeability and higher columbic efficiency than pristine Nafion membranes. However, the amount of modifiers could hardly be accurately controlled in these *in situ* processes and their reproducibility remains susceptible.

Polymer blending is a facile and effective method for polymer modification [12,13]. The compatibility of different polymer constituents would greatly affect the properties (e.g. mechanical stability and ion conductivity) of the polymer blends as a whole [14–16]. Polyvinylidene fluoride (PVDF), a kind of hydrophobic polymer with high crystallinity, high mechanical strength and sufficient chemical stability, is considered to be miscible with Nafion-like ionomers [16–19]. In recent years, the Nafion/PVDF binary blends have been prepared and utilized in proton exchange membrane fuel cells and direct methanol fuel cells [20–23], showing very high selectivity on hydrogen gas and methanol.

Inspired by the good selectivity of Nafion/PVDF blend membranes in PEMFC and DMFC, the introduction of PVDF could be an efficient way to improve the ion selectivity of Nafion in VRB applications. In this work, membranes based on Nafion/PVDF blends with different compositions were prepared, characterized and first applied in VRB. The relationship between membrane properties, polymer miscibility and VRB single cell performances was investigated.

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## 2. Experimental

### 2.1. Membrane preparation

Dry Nafion resin was first obtained by evaporating Nafion dispersion (Dupont, D-520) at 80 °C and subsequently dissolved in N,N-dimethylformamide (DMF) to form 10 wt.% solution. PVDF (Shanghai 3F, FR901) was dissolved in DMF to form 10 wt.% solution. Afterwards, the Nafion solution was poured into the PVDF solution and continuously stirred at 50 °C for 2 h. The mixed solution was cast onto a glass plate and dried at 60 °C for 6 h. The Nafion/PVDF membrane (denoted as N<sub>x</sub>P<sub>y</sub>, where x and y are the mass ratios of Nafion and PVDF, respectively) was peeled off from the substrate and immersed in 1 M H<sub>2</sub>SO<sub>4</sub> overnight. The recast Nafion (denoted as r-Nafion) membrane was cast from a 10 wt.% Nafion/DMF solution. Thicknesses of the as-prepared membrane varied between 95 μm and 100 μm.

### 2.2. Membrane characterization

#### 2.2.1. Water uptake

The dried membrane was immersed in deionized water for 4 days at room temperature. After quickly wiping out the water on the membrane surface by tissue, the weight of the swollen membrane was measured. The water uptake is defined as the weight ratio of the absorbed water to the dry membrane, as shown in Eq. (1):

$$\text{water uptake (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where  $W_s$  and  $W_d$  are the weight of saturated and dry membranes, respectively.

#### 2.2.2. Ion exchange capacity (IEC)

IEC was determined by the conventional titration method. Membrane with fixed weight was immersed in 1 M NaCl solution for 24 h to liberate all fixed H<sup>+</sup> ions of the membrane into the solution. Afterwards, the H<sup>+</sup> concentration in the solution was titrated with 0.01 M NaOH. Finally IEC can be calculated by Eq. (2):

$$\text{IEC} = \frac{\Delta V_{\text{NaOH}} C_{\text{NaOH}}}{W_d} \quad (2)$$

where  $\Delta V_{\text{NaOH}}$  is the consumed volume of NaOH solution,  $C_{\text{NaOH}}$  is the concentration of NaOH solution and  $W_d$  is the dried weight of the membrane.

#### 2.2.3. Mechanical strengths

The stress–strain behavior of the membranes was measured on a tension tester AG-2000A (Shimadzu) at room temperature. Membrane samples were tested by using a programmed elongation rate of 50 mm min<sup>-1</sup>. All samples were kept in deionized water for 4 days before the test to ensure they were saturated with water. For each test, at least three measurements were taken and average value was calculated.

#### 2.2.4. Differential scanning calorimetry

Measurements were performed on a Mettler Toledo DSC 821e instrument at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> flow.

#### 2.2.5. Scanning electronic microscopy (SEM)

SEM (JEOL 6360LV, Japan) was employed to observe the cross-section morphology of the membrane. The cross-section was obtained by breaking the membranes in liquid nitrogen.

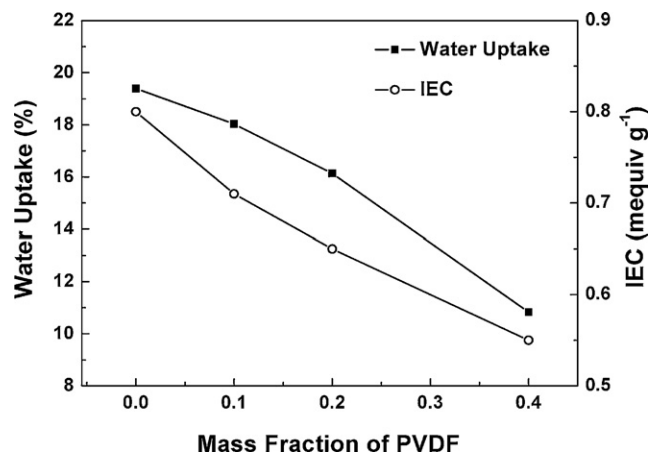


Fig. 1. Water uptake and IEC of membranes with various PVDF contents.

#### 2.2.6. Vanadium permeability

The permeability of VO<sup>2+</sup> through the membrane was determined according to the literature [8]. The left cell was filled with 1.5 M VOSO<sub>4</sub> in 3 M H<sub>2</sub>SO<sub>4</sub> solution, while the right one was filled with 1.5 M MgSO<sub>4</sub> in 3 M H<sub>2</sub>SO<sub>4</sub> solution to equalize the ionic strengths and to minimize the osmotic pressure effects. Magnetic stirrers were used in both cells to avoid the concentration polarization. Samples from the right cell were collected at regular time interval. The concentration of VO<sup>2+</sup> in sample solution was measured by using an UV–vis spectrometer.

### 2.3. VRB single cell performance

The VRB single cell was fabricated by sandwiching a membrane with two carbon felt electrodes, clamped by two graphite polar plates. All these components were fixed between two stainless plates. 1.5 M V<sup>2+</sup>/V<sup>3+</sup> in 3.0 M H<sub>2</sub>SO<sub>4</sub> solution and 1.5 M VO<sup>2+</sup>/VO<sub>2</sub><sup>+</sup> in 3.0 M H<sub>2</sub>SO<sub>4</sub> solution, serving as negative and positive electrolytes respectively, were cyclically pumped into the corresponding half-cell. The active area of the cell was 6 cm<sup>2</sup> and the volume of electrolyte solution was 30 ml in each half-cell. Charge–discharge cycling tests were conducted by LAND CT2001A at various current densities. The maximum voltage of 1.65 V and minimum voltage of 0.8 V for charge and discharge were employed to avoid the corrosion of carbon felts and graphite plates.

## 3. Results and discussion

### 3.1. Water uptake, IEC and mechanical properties

Fig. 1 represents the water uptake and IEC of polymer blends with a different PVDF mass ratio. It can be observed that the water content of polymer blends decreases upon the addition of PVDF. Considering the hydrophobic nature and high crystallinity of PVDF, it is reasonable that the addition of PVDF would extend the crystalline region of the polymer and suppress its water adsorption. Therefore, the blend membrane is less likely to swell in water compared to pure Nafion. Meanwhile, the addition of PVDF causes the decline of IEC.

It is well known that the swelling behavior is closely related to the mechanical stability of membranes. Figs. 2 and 3 demonstrate that polymer blends with higher PVDF content possess higher elastic modulus and tensile strength, which indicates that PVDF can really reinforce Nafion with better mechanical stability. It is considered that the adsorption and diffusion of water molecules in Nafion mainly take place in the hydrophilic region, induced by sulfonic acid groups, while the crystalline region formed from hydrophobic main

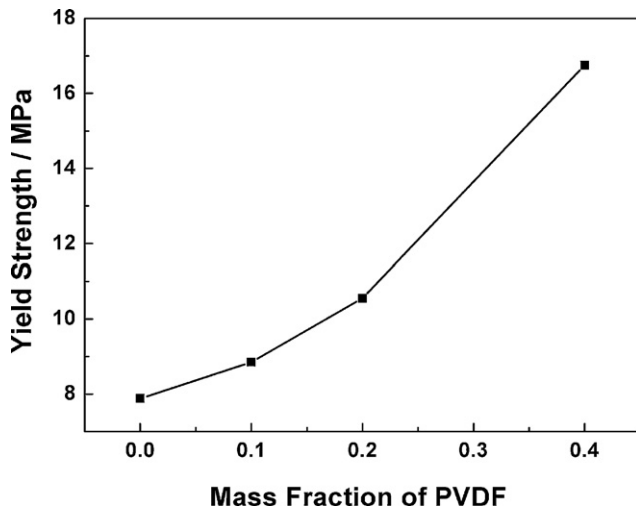


Fig. 2. Tensile strength of membranes with various PVDF contents.

chain provides the membrane mechanical stability. The addition of PVDF might improve the crystallinity of the polymer blends and further improve its mechanical stability. All these results are well in agreement with the swelling behavior of the membranes.

### 3.2. Morphology

The micrographs of membrane cross-sections presented in Fig. 4 reveal the morphology of the polymer blends. Pure Nafion (a) shows smooth and uniform cross-sections. With the addition of PVDF (b and c), grains with size smaller than  $1\ \mu\text{m}$  are detected on the membrane surface. It might be attributed to the aggregation and crystallization of PVDF in the Nafion matrix. With the increasing mass fraction of PVDF, more heterogeneous structure was detected. However, miscibility gaps could hardly be observed in these polymer blends, indicating Nafion and PVDF are highly compatible.

### 3.3. DSC analysis

The DSC thermogram (Fig. 5) also supplies the information of the miscibility. The endotherm peak, corresponding to the melting temperature  $T_m$ , varies with the mass ratio of PVDF. As the PVDF content decreases,  $T_m$  shifts to lower values and the endotherm peak becomes wider. PVDF, regarded as a kind of highly crys-

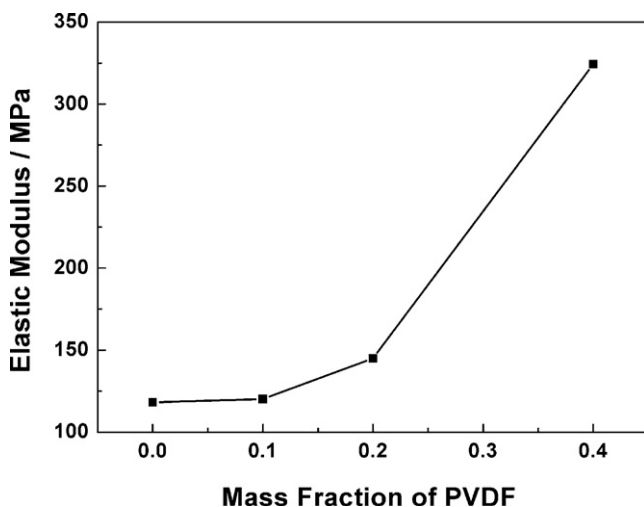


Fig. 3. Elastic modulus of membranes with various PVDF contents.

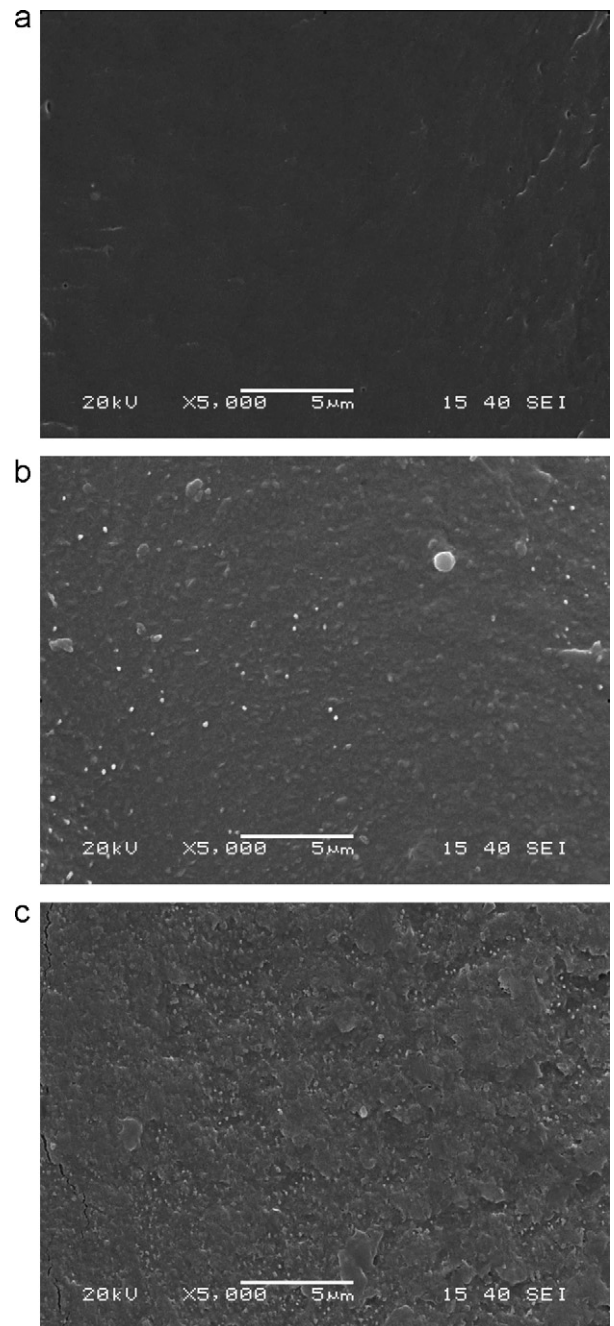


Fig. 4. SEM micrographs of membrane cross-section: (a) r-Nafion; (b)  $N_{0.8}P_{0.2}$ ; (c)  $N_{0.6}P_{0.4}$ .

talline polymer, possess a characteristic  $T_m$ , while Nafion does not. Nafion is considered to induce a so-called “plasticization effect” in the polymer blends [16], which turns the  $T_m$  indeterminate and makes the material more flexible and plastic. This result is in accordance with the mechanical properties, suggesting the intermolecular interaction between Nafion and PVDF [24].

### 3.4. Vanadium permeability

An approximately linear relation between time and the concentration of  $\text{VO}^{2+}$  in the right cell is shown in Fig. 6. The slopes reflect the permeability of  $\text{VO}^{2+}$  through membranes with various blending ratios. It is clear that r-Nafion, with the steepest slope, is easier to be permeated for  $\text{VO}^{2+}$  than the others. As the PVDF content

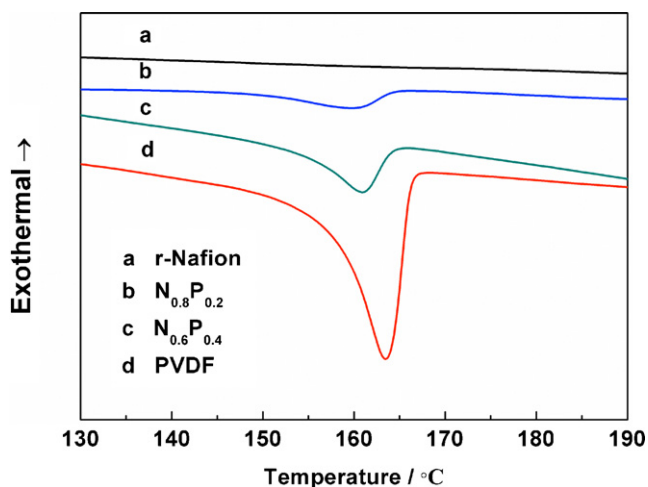


Fig. 5. DSC thermograms of membranes with various PVDF contents.

increases, the membrane exhibits better performance in preventing the  $\text{VO}^{2+}$  permeation. As discussed above, the crystallization of PVDF confines the swelling behavior of the membrane, which is closely related to its ion selectivity. Higher degree of swelling would increase the permeation of different ions and consequently increase the ion conductivity. In a VRB system, excessive swelling raises the permeation of vanadium ions, causing capacity loss of the battery. With the addition of PVDF, swelling is subscribed in a certain extent, by which the membrane maintains reasonably high proton conductivity, yet limits the permeability of vanadium ions.

### 3.5. Single cell performance

VRB single cells were fabricated with a series of membranes with various blending ratios. The membrane thickness varied between 95  $\mu\text{m}$  and 100  $\mu\text{m}$ . Charge–discharge cycling tests were conducted at different current densities.

The results from Fig. 7 clearly indicate that the addition of PVDF to a membrane helps to improve the coulombic efficiency (CE) in VRB performance. All the blend membranes exhibit higher CE than r-Nafion at the current density ranging from 40 to 80  $\text{mA cm}^{-2}$ . The CE increases with increasing content of PVDF. The cell with  $\text{N}_{0.6}\text{P}_{0.4}$  shows the highest CE, about 4% higher than that with r-Nafion. Higher coulombic efficiency indicates less cross-mixing of vanadium ions. In VRB operation, the membrane is exposed to the aqueous

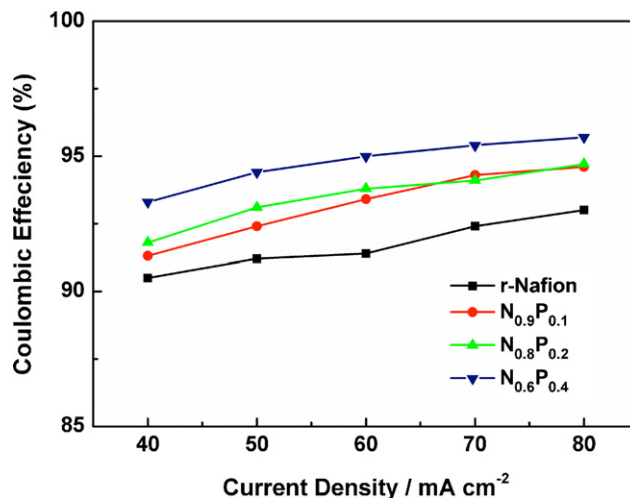


Fig. 7. VRB coulombic efficiency at different current densities.

solution of vanadium ions. Hence, the swelling condition directly affects the permeation and cross-mixing of vanadium ions. It is in accordance with the lower water uptake and  $\text{VO}^{2+}$  permeability of Nafion/PVDF blend membranes.

The voltage efficiency (VE) of the cells with  $\text{N}_{0.9}\text{P}_{0.1}$  and  $\text{N}_{0.8}\text{P}_{0.2}$  are comparable to that of r-Nafion, as seen in Fig. 8, suggesting similar resistance of these membranes. It might be attributed to the good miscibility between PVDF and Nafion, which promises reasonably high proton conductivity. However, the cell with  $\text{N}_{0.6}\text{P}_{0.4}$  exhibits apparently lower VE compared with the others. This result implies that the mass ratio of PVDF should be controlled in an optimized range; otherwise this highly hydrophobic polymer would remarkably decrease the ion conductivity of the blend membrane.

The energy efficiency (EE), a key parameter to evaluate the energy conversion rate of VRB, is presented in Fig. 9. As PVDF content increases, EE becomes higher, until the mass fraction of PVDF reaches 0.2. As EE is the product of CE multiplying VE, the membrane performing higher EE possesses both high ion conductivity and low vanadium permeability. Therefore,  $\text{N}_{0.8}\text{P}_{0.2}$ , which exhibits the highest EE, is a better choice than pure Nafion for VRB from a comprehensive view. The mass fraction 0.2 may be the optimized content of PVDF for the blend membrane, restricting the swelling behavior to an extent, by which the vanadium cross-mixing is effectively diminished and adequate conductivity

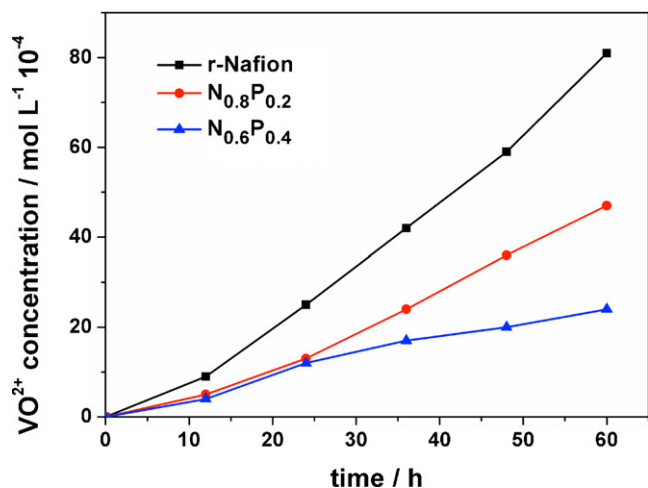


Fig. 6.  $\text{VO}^{2+}$  concentration in the right cell.

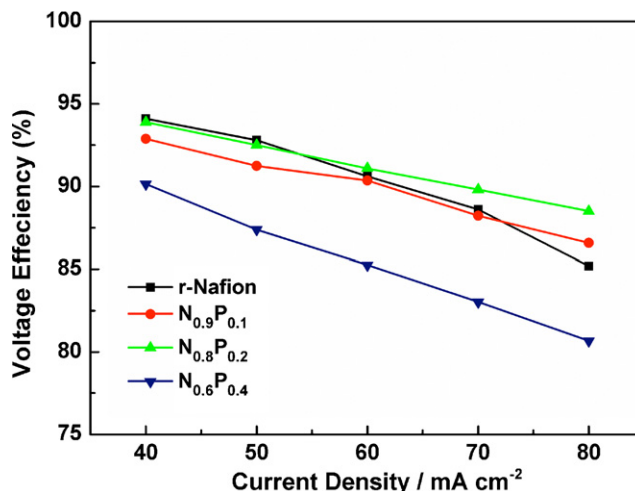


Fig. 8. VRB voltage efficiency at different current densities.

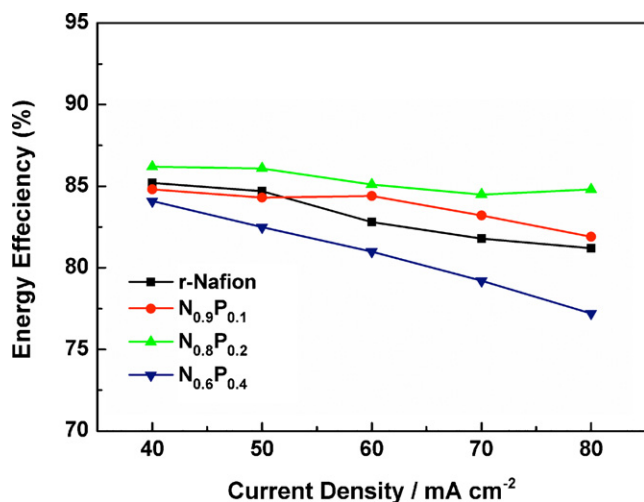


Fig. 9. VRB energy efficiency at different current densities.

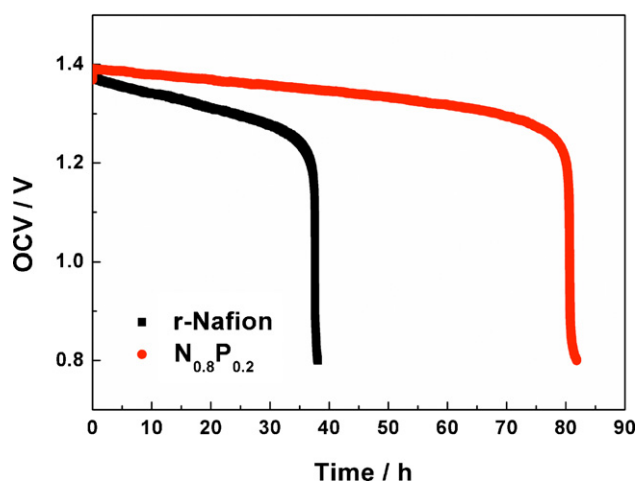


Fig. 10. VRB self-discharge curves.

for protons is preserved. Although the  $N_{0.6}P_{0.4}$  membrane shows lower EE, according to the work by Song et al. [20], chemical modification might be a helpful way to improve its ion conductivity and comprehensive performance.

Self-discharge test was conducted to investigate the transfer of vanadium ions across  $N_{0.8}P_{0.2}$  and r-Nafion under “on-line” conditions. In this test, 30 ml 1.5 M  $V^{2+}/V^{3+}$  in 3.0 M  $H_2SO_4$  solution and 30 ml 1.5 M  $VO_2^+/VO_2^+$  in 3.0 M  $H_2SO_4$  solution were cyclically pumped into negative and positive half cells, respectively. Self-discharge began at the state of charge (SOC) of 50%, i.e. the capacity of 600 mAh. The process stopped when the open circuit voltage (OCV) was lower than 0.8 V. As demonstrated in Fig. 10, the OCV degradation almost follows a linear relationship with the change of time until the OCV descends to 1.3 V. Obviously, the capacity of the cell with  $N_{0.8}P_{0.2}$  decreases much slower than that with r-Nafion. The entire self-discharge procedure of the VRB cell with  $N_{0.8}P_{0.2}$  lasts for more than 80 h, while the OCV of the cell with r-

Nafion comes down to 0.8 V in less than 40 h. This result reveals that  $N_{0.8}P_{0.2}$  significantly lowers the permeation rate of vanadium ions, which is well-matched with the “off-line” test of  $VO_2^+$  permeability.

#### 4. Conclusions

In this work, ion exchange membranes were prepared from Nafion/PVDF resin with various mixing ratios via the facile and well-reproducible blending method. Water uptake and mechanical properties were characterized, showing that the addition of PVDF confines the swelling behavior of the membrane. The SEM micrographs and DSC diagram confirms the compatibility of the polymer blends. The test of vanadium permeability and self-discharge verifies the improved ion selectivity of Nafion after the introduction of PVDF. In VRB single cell test, the blend membranes exhibit comparative performances to recast pure Nafion. The performance of  $N_{0.8}P_{0.2}$  membrane even comprehensively overmatched that of r-Nafion, suggesting the optimized mass fraction of PVDF is about 0.2. Knowing that lower Nafion consumption means lower cost, further effort can be made to improve the performance of membranes with higher PVDF content by chemical modification.

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