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Polyvinylpyrrolidone-based semi-interpenetrating polymer networks as highly selective and chemically stable membranes for all vanadium redox flow batteries



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HIGHLIGHTS

- Polyvinylpyrrolidone-based semiinterpenetrating polymer networks were designed.
- The PVP-based SIPNs were employed in vanadium redox flow batteries (VRFBs).
- The CEs of VRFBs reached almost 100% at a current density from 40 to 100 mA cm $^{-2}$.
- The EEs of VRFBs were more than 3% higher than those of VRFBs with Nafion 212.
- The good chemical stability was proved by an immersion test and a cycling test.

A R T I C L E I N F O

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G R A P H I C A L A B S T R A C T



ABSTRACT

Vanadium redox flow batteries (VRFBs) with their high flexibility in configuration and operation, as well as long cycle life are competent for the requirement of future energy storage systems. Nevertheless, due to the application of perfluorinated membranes, VRFBs are plagued by not only the severe migration issue of vanadium ions, but also their high cost. Herein, we fabricate semi-interpenetrating polymer networks (SIPNs), consisting of cross-linked polyvinylpyrrolidone (PVP) and polysulfone (PSF), as alternative membranes for VRFBs. It is demonstrated that the PVP-based SIPNs exhibit extremely low vanadium permeabilities, which contribute to the well-established hydrophilic/hydrophobic microstructures and the Donnan exclusion effect. As a result, the coulombic efficiencies of VRFBs with PVP-based SIPNs reach almost 100% at 40 mA cm⁻² to 100 mA cm⁻²; the energy efficiencies are more than 3% higher than those of VRFBs with Nafion 212. More importantly, the PVP-based SIPNs exhibit a superior chemical stability, as demonstrated both by an *ex situ* immersion test and continuously cycling test. Hence, all the characterizations and performance tests reported here suggest that PVP-based SIPNs are a promising alternative membrane for redox flow batteries to achieve superior cell performance and excellent cycling stability at the fraction of the cost of perfluorinated membranes.

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1. Introduction

Due to the gradual depletion of fossil fuels, the development of renewable energies, such as solar and wind energy, has been vitalized with some promising progress that has been achieved in the last decades [1-4]. Their inherent intermittence characteristics. however, make renewable energies unreliable power sources for mature electrical power infrastructures. The electrochemical storage technologies, which can efficiently convert the electricity generated from the renewable energies into chemicals and reversibly release the electricity according to demand, are therefore particularly indispensable to level the fluctuation of power generation and enable the intermittent renewable energies to be integrated into the electrical grid [5,6]. Redox flow batteries (RFBs) have gained increasing attention as one of competent electrochemical storage technologies over the past few decades and some significant improvements have been made in not only the development of novel redox couples but also in the optimization of operation conditions [7–9].

Among these RFBs, vanadium redox flow batteries (VRFBs) invented by Skyllas-Kazacos in the 1980s, which employ the same vanadium element in four different chemical states, have been widely investigated due to their significant merits [2,10-12]. Specifically, the inherent issue of crossover contamination can be minimized with the application of the same vanadium element and the electrolyte can be readily regenerated during the course of routine maintenance procedures [13]. Moreover, the electrochemical kinetics of redox couples (V(II)/V(III) in the negative half-cell and V(IV)/V(V) in the positive half-cell) are sufficiently high and reversible, which can guarantee high efficiency and excellent electrochemical reversibility for practical applications [14,15]. Furthermore, the vanadium redox couples possess a suitable potential, which can potentially reduce the gassing side reactions and withstand deep charge and discharge process [2,16].

Despite their significant merits, the commercialization of VRFBs has been hampered by the relatively high cost, which is partially induced by the expensive perfluorinated membranes. Based on the cost analysis made by department of energy of USA, the separator cost covered the major component of total system costs (44% for 0.25 MWh and 27% for 4 MWh) [7,17]. The fabrication of novel membranes with the high chemical stability, low vanadium permeability, desired ionic conductivity and low cost is one of the critical research objectives for the VRFB research community [12,18]. In most reported works, the sulfonated polymer, either by direct copolymerization of sulfonated monomers or postsulfonation of existing polymers, have been widely researched for VRFBs [19–23]. Meanwhile, anion exchange membranes (AEMs) have been gradually applied in VRFBs due to the Donnan exclusion effect that can largely reduce the transmembrane diffusion of vanadium ions [24,25]. However, the chemical stability of functional groups, including the pyridinium groups and quaternary ammonium groups, is the critical issue for AEMs in the harsh acid environment [26-29]. We also noticed that nanofiltration (NF) membranes have also been vitalized in the VRFBs recently [30–32]. The nanopores in NF membranes are utilized to transport the ions with small hydrated ionic sizes while blocking the vanadium ions with relatively larger ionic sizes. Despite the significantly lower cost of NF membranes, the pore sizes need to be carefully tailored and this is highly dependent on the fabrication procedure and/or the ratio between the inorganic additive and the organic polymer [32,33].

In this work, we fabricated a new category of membrane, namely semi-interpenetrating polymer networks (SIPNs), and applied them in VRFBs. In fact, SIPNs have been widely developed as proton exchange membranes [34] and anion exchange membranes [35,36] for the fuel cell membrane application since SIPNs possess a series of unique properties as well as the versatile of polymer candidates. However, there is no report on the application of SIPNs in VRFBs except the recent work reported by Wu et al. [37]. Herein, we selected polysulfone (PSF) and polyvinvlpvrrolidone (PVP) as the hydrophobic polymer and hydrophilic polymer respectively to form SIPNs, as illustrated in Fig. 1. After the dissolution of the two polymers in a solvent to form a miscible solution, the polymer backbones become entangled with each other and form a well-established hydrophilic/hydrophobic microstructure after the evaporation of the solvent and the photoinduced cross-linked process. Different from NF membranes, the nanopores formed in the hydrophobic backbones are filled with the cross-linked hydrophilic polymer, which will hinder the crossover of vanadium ions, thereby largely reducing the permeability of vanadium ions. Meanwhile, hydrogen bonding networks between the interpenetrated hydrophilic and hydrophobic component will be established, guaranteeing the chemical stability of SIPNs in the harsh environment. More importantly, the pyrrolidone segments in PVP can be protonized by the sulfuric acid. This protonation process endows the hydrophilic domains being positively charged, which largely reduce the vanadium ion permeability due to the Donnan exclusion effect between the protonated pyrrolidone segments and vanadium ions. In this situation, VRFBs assembled with PVP-based SIPNs exhibit superior cell performance and excellent cycling stability. These results testify that PVP-based SIPNs are the promising candidates for the industrial application in redox flow batteries.

2. Experimental

2.1. Materials

Polyvinylpyrrolidone (PVP, MW = 360,000), dimethylformamide (DMF) and 4, 4'-Diazido-2, 2'-stilbenedisulfonic acid disodium salt tetrahydrate (DAS, \geq 99.0%) were purchased from Sigma-Aldrich. Sulfuric acid (95 wt%) and magnesium sulfate heptahydrate (\geq 99.5%) were purchased from VWR. Polysulfone (Udel-P3500) was donated by Solvay Advanced Polymers, LLC. Vanadyl sulfate (VOSO₄·xH₂O (\geq 99%)) was purchased from Shenyang Haizhongtian Fine Chemical Factory. All the chemicals were used as received without any further purification.

2.2. Preparation of SIPNs

The SIPNs were prepared by a photo-induced cross-linked process, as reported elsewhere [38]. Generally, a predetermined weight of PSF and PVP was completely dissolved in DMF to form a homogenous solution (5 wt%). The polymer solution was subsequently cast upon a clean glass plate using a micrometer adjustable film applicator. The plate was then introduced inside a forced convection oven. To completely evaporate the solvents, the oven temperature was dwelled at 120 °C for 12 h and subsequently cooled down room temperature. The membranes with a rough thickness of 50 μ m were then peeled off from the glass plate. After the membranes were submerged into aqueous DAS solution (5 wt %) for 2 h, the membranes were removed from the solution, washed with methanol solution, dried in a vacuum oven at 40 °C for 1 h. Finally, the membranes were irradiated for 30 min with an ultraviolet lamp. The as-prepared membranes were denoted as SIPNs-x, in which x was presented the PVP content in the membrane.

2.3. Material structure characterizations

A field emission scanning electron microscope (FESEM, JEOL 7100) was used to determine the morphology of the membrane



Fig. 1. Illustration of the application of PVP-based semi-interpenetrating polymer networks in vanadium redox flow batteries.

surface and cross-section. Before FESEM observation, the membrane samples were fractured with liquid nitrogen, coated with gold and measured at an acceleration voltage of 5 kV. Fourier transform infrared spectroscopy (FTIR) measurements were performed on Vertex 70 Hyperion 1000 (Bruker) with the assistance of attenuated total reflectance (ATR) accessories. The absorption spectra were recorded from 4000 cm⁻¹ to 400 cm⁻¹ with a resolution of 4 cm⁻¹.

The microstructures of SIPNs were observed by high resolution transmission electron microscopy (HRTEM). The membrane samples were firstly dissolved in DMF to form a diluted solution (0.2 wt %) and cast on copper grids (400 mesh). After drying the solvent by an infrared lamp, the membrane samples were stained with periodic acid by placing the copper grids upon the evaporating aqueous solution containing the periodic acid. TEM images were taken on a

HRTEM (JEOL 2010F TEM) using an accelerating voltage of 200 kV.

2.4. Water uptake, acid uptake and swelling ratio measurements

The SIPNs were immersed in 3 M H_2SO_4 for 10 days to ensure that the doping process was complete. Subsequently, the wet weight (m_{wet}), surface area (A_{wet}) and thickness (T_{wet}) of the membranes were then measured at room temperature after the excess acid solutions on the SIPNs sample surface were quickly wiped off with tissue papers. The SIPNs samples were then dried at 110 °C for 2 h in an oven and quickly weighed in a closed vessel (m_{dry1}). The SIPNs were then treated in DI water at 90 °C for 2 h to remove the residual H₂SO₄ and dried at 110 °C for 2 h in an oven and quickly weighed in a closed vessel (m_{dry2}). During the weight measurement, membrane samples were periodically weighed until a constant value was obtained. The surface area (A_{dry}) and thickness (T_{dry}) of the dried SIPNs were thereafter measured. Accordingly, water uptake (WU), acid uptake (AU) and swelling ratio (SR) were determined by:

$$WU = \frac{m_{wet} - m_{dry1}}{m_{dry2}} \times 100\%$$
(1)

$$AU = \frac{m_{dry1} - m_{dry2}}{m_{dry2}} \times 100\%$$
 (2)

$$SR_1 = \frac{A_{wet}T_{wet} - A_{dry}T_{dry}}{A_{dry}T_{dry}} \times 100\%$$
(3)

2.5. Ionic conductivity and vanadium permeability measurement

The ionic conductivity of the membranes was determined with a potentiostat (EG&G Princeton, model M2273) through a two electrode conductivity clamp using an AC impedance method. The membranes were sandwiched by a pair of Au-coated stainless steel electrodes. The electrodes were then sandwiched between two PTFE plates and placed in a home-made container filled with DI water. A frequency range from 100 kHz to 1 Hz with a wave amplitude of 10 mV was applied to the conductivity clamp to obtain the AC impedance spectra. The membrane resistance (R_{Ω}) can be obtained by calculating the intercept of the high frequency region. All the membrane resistances were measured three times. The ionic conductivity σ can be obtained from:

$$\sigma = \frac{L}{R_{\varrho} \times A} \tag{4}$$

where *L* represents the thickness of the membrane (cm) and *A* represents the surface area of the membrane (cm²).

The permeability of VO²⁺ through the SIPNs was determined by an in-house dialysis cell according to our previous report [39]. The membrane was tightly sandwiched between two chambers with the same volume (40 ml). Chamber A was filled with 1.0 M VOSO₄ + 3 M H₂SO₄ while Chamber B was filled with 1.0 M $MgSO_4 + 3 M H_2SO_4$. The $MgSO_4$ was added to balance the ionic strengths and minimize the osmotic pressure effects between the two sides of membranes. Magnetic stirrers were used in both cells to avoid concentration polarization. Solution samples from Chamber B (1 mL) were collected at regular time intervals and analyzed for vanadium ion concentration by inductively coupled plasma mass spectrometry (ICP-MS). 1 mL of pristine solution (1.0 M MgSO₄ + 3 M H₂SO₄) was immediately added to Chamber B after sampling to maintain a constant solution volume. The vanadium permeability of the membrane was calculated by following equation:

$$V\frac{dc_t}{dt} = A\frac{P}{L}(c_0 - c_t)$$
(5)

where *V* is the volume of solution (40 cm³), *A* the exposed membrane area (cm²), *P* the permeability of vanadium ions (cm² s⁻¹), *L* the membrane thickness (cm), c_0 and c_t the initial vanadium concentration (mol cm⁻³) and the vanadium concentration in Chamber B at time *t* (s), respectively.

After obtain the ionic conductivities and permeabilities for PVPbased SIPNs, we introduced the selectivity to quantify the relationship [40]:

$$\alpha_{V4} = \frac{\kappa RT}{F^2 P_{V4} c_{V4}} \tag{6}$$

where α_{V4} is the dimensionless selectivity for VO²⁺, κ is the conductivity (S m⁻¹), *R* is the universal gas constant (J mol⁻¹ K⁻¹), *T* is the absolute temperature (K), *F* is the Faraday constant (C mol⁻¹), *P*_{V4} is the permeability of VO²⁺ (m² s⁻¹), and *c*_{V4} is the concentration of VO²⁺ in the solution adjacent to the membrane (mol m⁻³).

2.6. Mechanical property measurement

The mechanical properties were measured with a micro-force testing machine (Alliance RT/5, MTS) with a crosshead speed of 5 mm min⁻¹ at room temperature. The SIPNs with and without doped by 3 M H₂SO₄ for 10 days were applied to measure the mechanical property. All samples were cut into a size of 40 mm in length \times 5 mm in width, which were supported by a pair of fixture assemblies. The average values of modulus and the stress at break were determined from load-deformation curves of three tensile measurements. All the measurements were performed at room temperature with 60% relative humidity.

2.7. Chemical stability test

The ex situ chemical stability test was performed according to the previous procedure reported by M. Skyllas-Kazacos and M. A. Hickner [41,42]. The membranes were cut into a size of 30 mm × 20 mm and separately submerged in 20 mL of 0.1 M V(V) + 5 M H₂SO₄. The 0.1 M V(V) + 5 M H₂SO₄ was prepared by diluting the 1 M V(V) + 3 M H₂SO₄ with concentrated sulfuric acid (95 wt%). The 1 M V(V) + 3 M H₂SO₄ was prepared by electrochemically oxidized the solution of 1 M VOSO₄ + 3 M H₂SO₄ with a current density of 20 mA cm⁻² in a flow cell. Solution samples with the generated V(IV) ions were collected at regular time intervals and analyzed for the concentration of V(IV) by an ultraviolet visible spectrophotometer (Perkin Elmer, Model Lambda 20). The absorbance of each mixture was determined at a wavelength number of 764 nm. Meanwhile, the membrane weight was also determined at regular time.

2.8. VRFB single cell performance characterization

The setup of flow cells consisted of two aluminium end-plates, two graphite-plate electrodes, two gold-coated copper current collectors, two polytetrafluorethylene (PTFE) flow channels (1 mm) and two PTFE gaskets. The commercial graphite felts (Sigracell[®] SGL carbon, GFA6 EA) with an uncompressed thickness of 6 mm and a porosity of 93% were employed as the positive and negative electrode. The graphite felts having an uncompressed volume of 30 mm \times 20 mm \times 3 mm (length \times width \times thickness) were annealed at 400 °C for 6 h in air to improve the electrochemical activity and hydrophilic property. The electrode compression ratio was 50%, resulting in a final thickness and porosity of the electrode of 1.5 mm and 86% after assembling.

The single cell was connected to two reservoirs containing 50 mL of 1 M V(V) + 3 M H₂SO₄ and 50 mL of 1 M V(III) + 3 M H₂SO₄ in the positive side and negative side, respectively. Electrolytes were supplied by a peristaltic pump (WT600-2J, Longerpump, China) with a flow rate of 46 mL min⁻¹ (60 rpm). The positive electrolyte was simply prepared by dissolving vanadyl sulfate powder in the sulfuric acid solution, while the negative electrolyte was freshly prepared by electrochemically reduced the solution of 1 M VOSO₄ + 3 M H₂SO₄ into 1 M V(III) + 3 M H₂SO₄ with a current density of 20 mA cm⁻² in an electrolyzer equipped with platinized

titanium mesh electrodes. The two reservoirs were both purged with nitrogen gas (high-purity) and then sealed prior to the tests to minimize oxidation of the active species. The electrochemical performance of VRFBs was performed using a potentiostat/galvanostat (Arbin Instrument, USA) to provide a constant-current. All measurements were performed at room temperature (25 °C). The cut-off voltage was 0.9 V for the discharge process and of 1.7 V for the charge process. The capacity (Ah) and energy (Wh) during the discharge and charge process were recorded by Arbin and the coulombic efficiency (CE) and energy efficiency (EE) can be obtained from:

$$CE = \frac{\text{Discharge capacity}}{\text{Charge capacity}} \times 100\%$$
(7)

$$EE = \frac{\text{Discharge energy}}{\text{Charge energy}} \times 100\%$$
(8)

The voltage efficiency (VE) can be obtained by:

$$VE = \frac{EE}{CE} \times 100\%$$
(9)

3. Results and discussion

3.1. Morphology and microstructure

The SIPNs fabricated by solution-cast method were dense and flexible membranes. After the photo-induced cross-linked process, the transparent membranes became to slight yellow. The microscopic morphologies of the SIPNs were determined by FESEM (Fig. 2a). From the surface and cross-section review, it is clearly observed that a uniform, dense and smooth membrane without the existence of any pores is formed. To uncover the microstructure, transmission electron microscopy (TEM) analyses were performed. As shown in Fig. 2b, the dark regions correspond to the hydrophilic polymer due to their affinity with IO_4^- anions and the bright domains correspond to the hydrophobic polymer (PSF). The hydrophilic polymers will be positively charged to form ionic clusters as a result of a protonation process, as will be discussed below. The ionic clusters with an average size of $1.8 (\pm 0.2)$ nm are uniformly distributed throughout the entire measured area, indicating that the cross-linked PVP and PSF are entangled to form a wellestablished hydrophilic/hydrophobic microstructure.

3.2. Ionic conductivity and vanadium permeability

Firstly, we measured the acid uptake, water uptake and swelling ratio of PVP-based SIPNs at room temperature (Fig. 3a). It is understandable that the water uptake and acid uptake are enhanced with an increase in the PVP content in SIPNs, since PVP is a highly hydrophilic content. For example, when the PVP content reaches 60% in SIPNs, the water uptake and acid uptake of SIPNs-60 (29.8% vs. 33.1%) is about 1.5-fold, 1.1-fold higher than that of SIPNs-40 (11.8% vs. 15.9%), respectively. Correspondingly, the swelling ratio of SIPNs almost linearly increases with the PVP content in SIPNs.

To assess the ionic conductivity of the PVP-based SIPNs, the SIPNs were immersed in 3 M H₂SO₄ before measuring the ionic conductivity. As exhibited in Fig. 3b, an increase in the PVP content in SIPNs significantly enhances the ionic conductivity of SIPNs since the acid can be only doped or reacted with PVP molecules. After being treated in 3 M H₂SO₄, SIPNs-70 possesses an ionic conductivity of 30.4 mS cm⁻¹ at room temperature. Meanwhile, the ionic conductivity increases with elevated temperatures. At 50 °C, the ionic conductivity of SIPNs-70 reaches 55.8 mS cm⁻¹. Although the ionic conductivities of PVP-based SIPNs achieved here are lower than those of Nafion 212 at the same temperature, the ionic conductivity of PVP-based SIPNs is higher than that of anion exchange membranes applied in VRFBs [25,28,43]. Although the detailed ion transport mechanism in PVP-based SIPNs is still unclear, we propose that sulfate ions should be predominantly transported in the SIPNs while the protons will also partially contribute to the internal circuit current, as compared in Fig. 3c-d. This is due to the fact that SIPNs are saturated with the liquid electrolyte (H₂SO₄). Meanwhile. the ionic mobility of protons is much larger than that of sulfate ions $(36.23 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1} \text{ vs.} 8.29 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1})$ [44]. Therefore, the protons resulting from the ionization of the doped sulfuric acid will be also transported in SIPNs.

In the course of the immersion process, the doped acid enables to react with pyrrolidone segments in the PVP-based SIPNs as follows:



That is, a positively charged protonation occurs in the pyrrolidone segments during the immersion process, as presented in Fig. 3d. The protonation process was proved by FTIR and zeta potential. As shown in Fig. 4a, after the acid doping process, two new peaks located at ~1045 cm⁻¹ and ~570 cm⁻¹ respectively emerge in



Fig. 2. (a) Surface morphology and cross-section morphology of SIPNs-60; (b) HRTEM image of SIPNs-60. Some typical hydrophilic channels stained with periodic acid are marked with red arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. (a) Acid uptake (red columns), water uptake (blue columns) and swelling ratio (magenta lines) of SIPNs with different PVP contents; (b) lonic conductivity of SIPNs. The deviations for the conductivity data were within 6%. Schematic illustrations of the ion transport in the proton exchange membranes (Nafion) (c) and the protonated SIPNs (d). The ions are presented for illustration only and the size of ions does not mean the real hydrated ionic size in the VRFBs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. (a) ATR-FTIR spectra of PSF, PVP, SIPNs-60 and acid treated SIPNs-60; (b) Zeta potential of Nafion and PVP dissolved in 0.001 M H₂SO₄ and DI water.

the FTIR spectrum of SIPNs-60, clarifying that the pyrrolidone segments were protonated by the doped acid due to these peaks being attributed to the stretching vibration and out-plane bending vibration of C–N⁺, respectively. The protonation process can also be analyzed by measuring the zeta potential, which indicates the state of surface charge. As shown in Fig. 4b, the PVP in a diluted H₂SO₄ solution exhibits a positive zeta potential of 45.8 mV while it shows a negative zeta potential of -13.3 mV in deionized water, which demonstrates that the pyrrolidone segments are positively charged with the existence of sulfuric acid.

The existence of the protonation process not only enables PVPbased SIPNs to transport ions, but also has a profound influence on the vanadium permeability. Hence, the vanadium permeability through PVP-based SIPNs was measured. As shown in Fig 5a, it is obvious that the concentrations of VO^{2+} ions permeating the PVPbased SIPNs are remarkably lower than that of VO^{2+} ions permeating Nafion 212. The permeability of VO^{2+} ions can be calculated

from the slope of concentration versus diffusion time (Fig. 5b). Nafion 212 exhibits a permeability of 5.24×10^{-7} cm² min⁻¹, which is comparable to or even lower than the results reported in the literature [29,40,45,46]. It is found that all the PVP-based SIPNs have dramatically lower permeabilities compared with Nafion 212. The permeabilities through PVP-based SIPNs increase with an increase in PVP content. The SIPNs-70 possesses a maximum permeability of 0.21 \times 10⁻⁷ cm² min⁻¹, which is still much lower than that of Nafion 212. The dimensionless selectivity defined as the ionic conductivity over vanadium permeability was also calculated based on the equation reported elsewhere [40]. As presented in Fig. 5c, the selectivity of SIPNs-40 (74769.0) is forty-seven times higher than that of Nafion 212 (1544.8). Even the SIPNs-70, which exhibits the highest permeability among PVP-based SIPNs. possesses a selectivity of 23580.8, which is still fourteen times higher than that of Nafion 212. The extremely high selectivity should be attributed to the following reasons. On one hand, the size



Fig. 5. (a) Concentration change of VO²⁺ ions in the MgSO₄ chamber across PVP-based SIPNs and Nafion 212; A comparison of VO²⁺ ions permeability (b) and selectivity (c) of PVP-based SIPNs and Nafion 212; (d) Open circuit voltage decay of fully charged VRFBs with SIPNs-60 and Nafion 212.

of well-established ionic clusters in SIPNs is smaller than that of Nafion 212 [47]. Such small ionic clusters will dramatically hinder the migration of vanadium ions. On the other hand, the ionic clusters are positively charged as a result of the protonation process, which will further reduce the crossover of vanadium ions due to the Donnan exclusion effect between the protonated pyrrolidone groups and vanadium ions, as illustrated in Fig. 3d. Hence, PVP-based SIPNs exhibit an impressive suppression effect on the vanadium ion permeability.

To confirm the superior selectivity of PVP-based SIPNs, a selfdischarge test of fully charged VRFBs assembled with SIPNs-60 and Nafion 212 was also performed (Fig. 5d). As a result of the gradual migration of vanadium ions across the membranes, the open circuit voltage (OCV) slightly descends at first and then rapidly drops to 0.9 V. For the VRFB with SIPNs-60, the maintaining time of OCV above 0.9 V is 170 h, which is 3.36 times as long as that of the VRFB with Nafion 212 (50.6 h). The severe decay of OCV for Nafion 212 compared with SIPNs-60 further demonstrates that the migration of vanadium ions across PVP-based SIPNs is greatly reduced, which is in good accordance with the individual diffusion cell test.

3.3. Mechanical properties

The mechanical properties of PVP-based SIPNs were subsequently measured. As tabulated in Table 1, the tensile strengths and Young's moduli of PVP-based SIPNs reduce with an increase in PVP content, while the elongations at break gradually increase. This behavior demonstrates that SIPNs with high PVP content become more plastic, indicating that PVP takes the role of a plasticizer in SIPNs. The plasticizing effect induces an increased flexibility in the SIPNs. It is worth noting that the tensile strengths and Young's moduli of pristine PVP-based SIPNs are higher than those of Nafion 212, except for SIPNs-70. After treated in 3 M H₂SO₄, the tensile strengths and Young's moduli of PVP-based SIPNs reduce by ca. 25%, which result from the reduction of molecular cohesion in the course of acid treatment. For example, the tensile strength of SIPNs-50 reduces from 35.3 MPa to 26.9 MPa after being treated by sulfuric acid for 10 days. Meanwhile, the elongation at break increases from 79% to 131%. In comparison, with the same treatment, the tensile strength of Nafion 212 reduces from 26.7 MPa to 22.1 MPa, while the elongation at break of Nafion 212 increases from 343% to 363%. The mechanical properties of pristine Nafion 212 measured here are consistent with the values reported elsewhere [48,49]. It is clearly demonstrated that present membranes have excellent mechanical properties, which make the present membranes competent for the compact design of VRFBs.

3.4. Chemical stability

The chemical stability of PVP-based SIPNs was evaluated by measuring the VO^{2+} concentration and weight loss when the

Table 1	l
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Mechanical prop	perties of PVP-based	l SIPNs and	Nafion	212
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Samples	s Pristine			After treated in 3 M H_2SO_4		
	Tensile strength max. (MPa)	Young's Modulus (GPa)	Elongation at break (%)	Tensile strength max. (MPa)	Young's Modulus (GPa)	Elongation at break (%)
Nafion 212	26.7 ± 2.3	0.21 ± 0.018	343.0 ± 20.2	22.1 ± 1.8	0.16 ± 0.013	363.0 ± 23.8
SIPNs-40	46.9 ± 3.2	2.22 ± 0.13	43.5 ± 5.4	33.8 ± 2.4	0.91 ± 0.054	83.4 ± 6.4
SIPNs-50	35.3 ± 2.2	1.81 ± 0.10	79.3 ± 6.7	26.9 ± 2.1	0.75 ± 0.058	131.2 ± 10.9
SIPNs-60	28.1 ± 1.8	1.37 ± 0.11	97.2 ± 10.2	20.5 ± 1.8	0.49 ± 0.031	156.2 ± 12.4
SIPNs-70	20.6 ± 1.4	1.02 ± 0.06	142.5 ± 12.1	14.6 ± 1.1	0.25 ± 0.015	174.9 ± 14.6



Fig. 6. (a) VO²⁺ concentration of solutions containing SIPNs-50, SIPNs-60 and Nafion 212 at different time intervals. (b) The weight loss percentage of SIPNs-50, SIPNs-60 and Nafion 212 at different time intervals.

membrane samples were immersed in 0.1 M VO_2^+ with 5 M H_2SO_4 , as performed elsewhere [50,51]. As shown in Fig. 6a, the concentrations of VO²⁺ derived from the oxidation of polymer in SIPNs-50 and SIPNs-60 slightly increase with the increased immersion duration. Although the generated rates of VO²⁺ in PVP-based SIPNs are higher than that of Nafion 212, yet the total generated rates of VO^{2+} are relatively lower as compared with the results reported in the literature [19,50]. Although the detailed degradation mechanism of the present membranes is still unclear due to there is no new characteric FTIR spectra emerging in the FTIR spectra of PVPbased SIPNs after different immersion durations (Fig. S1), the slight degradation might result from the loss of protonated pyrrolidone groups. This can be proved by the weight loss of the PVPbased SIPNs (Fig. 6b). Similar to the trend of the VO²⁺ generated rate, the weight losses in SIPNs-50 and SIPNs-60 are higher than that of Nafion 212, particularly in the initial 10 days, during which the weight losses might be ascribed to a leaching of low-molecularweight components in the SIPNs. Although the weight loss of SIPNs-50 and SIPNs-60 is higher than that of Nafion 212, the weight losses for SIPNs-50 and SIPNs-60 are only 4 wt % and 5 wt %, respectively. More importantly, there are no pinholes in the crosssection and surface morphologies of the PVP-based SIPNs after the immersion test (Fig. S2).

3.5. Cell performance

The cell performance was then evaluated in a home-made VRFB setup, which was operated at a flow-through mode. The VRFBs assembled with PVP-based SIPNs and Nafion 212 with the same thickness were examined galvanostatically at the current density of 40, 60, 80 and 100 mA cm⁻², respectively. All measurements were performed at room temperature (25 °C). As exhibited in Fig. 7a, at a current density of 40 mA cm⁻², the charge-discharge profile of the battery assembled with SIPNs-60 is almost identical to that of the battery assembled with Nafion 212 in the initial stage, while the charge and discharge capacities of the battery assembled with SIPNs-60 are higher than those with Nafion 212. The cell assembled with SIPNs-60 membrane exhibits a CE of 97.6% and an EE of 90.0%, which are higher than the corresponding values of 94.0% and 85.4% for the cell assembled with Nafion 212. The high CE of PVP-based SIPNs is ascribed to the dramatically low vanadium permeability due to the existence of electrostatic repulsion between the protonized pyrrolidone segments of PVP and vanadium ions.

Also, the single-cell VRFB with SIPNs-60 exhibits a good chargedischarge rate capability as shown in Fig. 7b, in which the capacity only decays from 1.22 A h to 1.04 A h when the current density increases from 40 mA cm⁻² to 100 mA cm⁻². Meanwhile, the voltage plateau gradually declines due to the increased charge/ discharge overpotential caused by a fast charge/discharge rate. The cell performance of single-cell VRFBs with SIPNs with the PVP content ranging from 40 wt% to 70 wt% is then compared in Fig. 7c and Fig. S3. The cell efficiencies calculated from the chargedischarge curves at different current densities are presented in Fig. 7d–f. An improvement in capacity is observed with an increase in the PVP content ranging from 40 wt% to 60 wt%, and beyond this content, a decrease in capacity is found. It is demonstrated that there is a trade-off between the ionic conductivity and vanadium permeability for PVP-based SIPNs. With a low PVP content, the VRFB employing SIPNs-40 membrane exhibits the highest CE, while the lowest VE, which is caused by a large charge/discharge overpotential as a result of low ionic conductivity (high internal resistance). While with the increased PVP content, the VRFB with the SIPNs-70 membrane exhibits the lowest CE and a relatively high VE, which is caused by a large vanadium migration as a result of high permeability. It is noteworthy that the EEs of VRFB assembled with SIPNs-50 and SIPNs-60 are ca. 5% higher compared to that of the VRFB assembled with Nafion 212 at low current density (40 mA cm^{-2}) . Strikingly, even at high current density, the EEs for VRFBs assembled with SIPNs-50 and SIPNs-60 are still ca. 3% higher than those of the VRFB with Nafion 212. This result might be ascribed to the good compatibility between the SIPNs and the thermal-treated graphite felt due to the well-established fine microstructure. These results demonstrate that SIPNs-50 and SIPNs-60 are promising membranes for VRFBs, owing to their superior balance of ionic conductivity and vanadium permeability, which enables the performance of VRFBs assembled with these membranes outperform the benchmark, i.e., Nafion 212.

3.6. Cycling performance

The chemical stability of PVP-based SIPNs is then evaluated during a continuously cycling test, in which the single-cell VRFB with SIPNs-60 was cycled at a current density of 80 mA cm^{-2} . As illustrated in Fig. 8a, the discharge capacity of the VRFB with SIPNs-60 decreases from 1.11 A h to 0.83 A h over 500 cycles with a capacity decay rate of 0.056% cycle⁻¹, which demonstrates that SIPNs-60 exhibits a good capacity retention. In comparison to the VRFB with Nafion 212, the discharge capacity decreases from 1.00 A h to 0.46 A h within 150 cycles. More importantly, the CE of VRFB with SIPNs-60 maintain almost 100% during the 500 cycles, as presented in Fig. 8b. The superior cell performance is ascribed to the excellent chemical stability and high ion selectivity, which endow PVP-based SIPNs bear the harsh environment and alleviate the vanadium migration. This can be verified by measuring the FTIR spectra of SIPNs-60 before and after the cycling test. As presented in Fig. S4, no new characteristic peaks emerges on the control area and active



Fig. 7. Charge-discharge curves of (a) the VRFBs with Nafion 212 and SIPNs-60 at 40 mA cm⁻², (b) the VRFBs with SIPNs-60 at different current densities and (c) the VRFBs with PVP-based SIPNs at 40 mA cm⁻². Coulombic efficiency (d), voltage efficiency (e) and energy efficiency (f) of single-cell VRFB with PVP-based SIPNs and Nafion 212 at different current densities.



Fig. 8. Comparison of discharge capacity (a) and coulombic efficiency (b) of VRFBs with SIPNs-60 and Nafion 212, respectively. The current density for charge and discharge is 80 mA cm⁻².

Table 2

area of SIPNs-60 after the cycling test, clarifying that SIPNs-60 possesses an excellent chemical stability. As for the alleviation of vanadium migration, this can be proved by measuring the molar quantity of total vanadium ions in the positive electrolyte and cathode electrolyte in the course of 60 cycling tests. As shown in Fig. S5, when the VRFB assembled with SIPNs-60, the molar quantity of vanadium ions slightly decreases on the positive side and increases on the negative side, which indicates that there is a positive-to-negative transportation of vanadium ions. In comparison to the VRFB with Nafion 212, the variation amplitude of the molar quantity of total vanadium ions is much larger than that of the VRFB with SIPNs-60 in the 60 cycling tests. It is noteworthy that the volumes of negative and positive were almost unchanged during the cycling tests for the VRFB with SIPNs-60 while the volume of negative electrolyte for the VRFB with Nafion 212 was reduced by 4 mL, as a result of the negative-to-positive transfer of water during the cycling test. These results strongly support the

Cost analysis of PVP-based SIPNs and Nafion 212.

Membrane	Current cost	Future cost (optimistic)	References
Nafion 212	225 \$ m ⁻²	90 \$ m ⁻²	[52,53]
SIPNs-50	24 \$ m ⁻²	8 \$ m ⁻²	Estimation ^a
SIPN-60	21 \$ m ⁻²	7 \$ m ⁻²	Estimation ^a

^a The prices of PVP, PSF and DAS were recorded from Sigma-Aldrich website. The price for the composite membrane was calculated based on the equation: Cost = (PSF price \times PSF content + PVP price* (PVP content-1%) + DAS price \times 1%)/ (density \times thickness). The prices for PSF, PVP and DAS are 591 \$ m^{-2}, 156 \$ m^{-2} and 962 \$ m^{-2}, respectively. The density for the composite membranes is 1.24 g cm^{-3} by a roughly estimation. The thickness is 50 μ m. The coefficient for the levelized cost (future cost) is 3.

fact that the migration of vanadium ions and water in SIPNs-60 is largely hampered. The gradual capacity decay for the VRFB with SIPNs-60 should be caused by the carbon corrosion and the gas side reaction as a result of the applied high charge voltage (1.7 V). This can be proved by the XPS analysis of graphite felt (GF). As illustrated in Fig. S6, after the durability test, the oxygen content of GF increased to 26.8 wt%, in comparison to 20.6 wt% for the initially thermal-treated GF.

Finally, in terms of the cost, we made a simple cost analysis and comparison, as tabulated in Table 2. From this result, it is obviously concluded that PVP-based SIPNs are cheaper than the per-fluorinated membranes (Nafion 212) currently. If PVP-based SIPNs can be produced in a large scale, the cost for these composite membranes will be further reduced.

4. Conclusions

In summary, we have fabricated PVP-based SIPNs and applied them in VRFBs. Although the ionic conductivities of PVP-based SIPNs were relatively lower than those of Nafion 212, these membranes were demonstrated with high ionic selectivities, which were attributed to the extremely low vanadium permeabilities. The reduction in the migration of vanadium ions through PVP-based SIPNs was attributed, in part, to the small well-established ionic clusters, and in part, to the fact that there existed the Donnan exclusion effect between the vanadium ions and protonated pyrrolidone groups as a result of a protonation process among pyrrolidone groups and the doped acid. Hence, the CEs of VRFB with SIPNs-50 and SIPNs-60 reached almost 100% at the current densities ranging from 40 mA cm^{-2} to 100 mA cm^{-2} and the EEs of VRFB with SIPNs-50 and SIPNs-60 were more than 3% higher than those of the VRFB with Nafion 212. More importantly, the PVPbased SIPNs exhibited a superior chemical stability, which was not only demonstrated in ex situ immersion test, but also verified in the continuous cycling test. The VRFB assembled with SIPNs-60 cycled at 80 mA cm⁻² over 500 cycles with a capacity decay rate of 0.056% cycle⁻¹, which proved that SIPNs-60 exhibited with a good capacity retention. Herein, this work strongly demonstrates that PVP-based SIPNs are promising for redox flow batteries to achieve superior cell performance and excellent cycling stability at low cost.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2016.07.081.

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