



Short communication

A multilayered membrane for vanadium redox flow battery

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ABSTRACT

In order to reduce the vanadium ions permeability of membranes used in vanadium redox flow battery (VRB) while keeping its chemical stability, sulfonated poly(ether ether ketone) (SPEEK)/polypropylene (PP)/perfluorosulfonic acid (PFSA) layered composite membrane (we name it as S/P/P membrane) has been fabricated and characterized. In the S/P/P membrane, polypropylene plays a role of central layer, which is sandwiched by SPEEK and PFSA layer. Results show that S/P/P membrane presents a very low permeability of vanadium ions, accompanied by slightly higher area resistance than that of Nafion 212 membrane (N212). The VRB single cell with S/P/P membrane shows higher coulombic efficiency but lower voltage efficiency in comparison with the one with N212. The performance of VRB with S/P/P membrane can be maintained after more than 50 cycles. Our experimental results suggest that the S/P/P membrane approach is a promising strategy to suppress the migration of vanadium ions in VRB, while retaining an outstanding VRB performance.

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1. Introduction

Recently, vanadium redox flow battery (VRB) has received considerable attention as a large-scale electrochemical energy storage system due to its long cycle life, flexible design, quick response time, and deep-discharge capability [1–3]. VRB employs V (II)/V (III) and V (IV)/V (V) redox couples in its negative and positive electrolytes, respectively, and H₂SO₄ as the supporting electrolyte. An ion exchange membrane is critical for VRB, which aims at separating the anode and cathode electrolytes effectively, namely, no migration or a very low permeability of V ions, while allowing the transport of ions to complete the circuit during passage of current.

Among ion exchange membranes, perfluorosulfonic acid (PFSA) such as Nafion (DuPont) is most commonly used due to their high chemical stability and proton conductivity. However, PFSA membranes usually suffer from high cost and especially high vanadium ions permeability when used in VRB. In order to reduce the migration of V ions, many approaches such as inorganic doping, surface modification, and layering have been put forward to modify the Nafion membranes. Although some modified Nafion membranes were found to have lower vanadium species migration than the pure ones [4–7], they are far too expensive to be afforded, hence limit their commercial application for VRB systems.

It was reported that the sulfonated poly(ether ether ketone) (SPEEK) membrane has low methanol and vanadium ions permeability when used in direct methanol fuel cell [8,9] and VRB [10],

respectively. One of the major obstacles is the degradation of the SPEEK membrane. To prevent this problem, multilayered composite membrane containing a layer of SPEEK membrane and two outer layers of Nafion membrane has been fabricated [11–13]. The Nafion layer of multilayered composite membrane was designed to prevent oxidation degradation of the SPEEK membrane. However, the poor interlayer binding between the SPEEK membrane and the Nafion membrane achieved by hot-pressing or immersing the SPEEK layer into the Nafion-containing solution may lead to delamination of the two different layers because of their different swellability under the aqueous conditions. The delamination will increase the resistance or reduce the mechanical strength of the multilayered composite membrane [14]. To overcome these difficulties, we present here a novel approach involving multilayered membranes. With this approach, a sandwich-type S/P/P membrane is fabricated. The composite membrane was composed of three layers: the PFSA layer, the SPEEK layer and the transition central layer. SPEEK layer has the advantage of low cost as well as the ability of suppressing the permeation of vanadium ions and PFSA layer offers good antioxygenic property. The transition central layer is based on a porous polypropylene (PP) (porosity: 68.8769%, average pore diameter: 1.271 μm) film, on which a PFSA layer and a SPEEK layer on the two sides are bonded. Moreover, this central layer is expected to block the vanadium ions permeation and to improve the mechanical strength effectively resulted from a decrease in the pore size after SPEEK and PFSA resin being embedded in the hole of the PP membrane and thus reduce the channel size for V (IV) ions diffusion. When used in VRB, the SPEEK (low vanadium ions crossover) and PFSA (good anti-oxidation ability) layer are in contact with negative and positive half-cell electrolytes, separately. In

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our multilayered membrane, oxidation degradation of the SPEEK membrane is greatly alleviated, and the migration of vanadium ions is effectively suppressed. Furthermore this sandwich-type membrane can ensure its structure stability without delamination between the SPEEK layer and the PFSA layer. Except for good cell performance, this design offers as well a good mechanical strength.

2. Experimental

2.1. Chemicals

Poly(ether ether ketone) (Victrex, PEEK 450 PF) was used as received. Polypropylene membrane (thickness = 140 μm) for Ni-MH battery was obtained from ChangZhou YingKe Battery Membrane Co., Ltd. PFSA resin was obtained from ShanDong DongYue Group. Dimethylsulfoxide (DMSO) and sulfuric acid (98 wt.%) were used as received without further purification.

2.2. Preparation of composite membrane

SPEEK were prepared following the procedure reported in the literature [10]. SPEEK (1.5 g) was dissolved in DMSO (20 mL) to form solution under mechanical stirring at 30 °C. PFSA resin (6 g) was dissolved in DMSO (60 mL) at 140 °C. Both SPEEK and PFSA solution were sonicated about 20 min via ultrasonic.

The preparation of S/P/P composite membrane follows a two-step process. First, PFSA solution (20 mL) was poured into a purpose-made glass plate and PP membrane was immersed in it. The casting membrane was dried at 90 °C for 16 h to remove solvents. In the second step, 20 mL SPEEK solution was poured onto the PP. After dried at 80 °C for 16 h and cooled to room temperature, the resulting cast membrane was peeled off from the glass plate in deionized water and immersed into 2 M H_2SO_4 solution for 24 h to make the PFSA membrane H^+ forms, the membrane was rinsed with deionized water to remove any H_2SO_4 residues.

2.3. Characterizations of S/P/P membrane

The area resistance of the membranes and the permeability of vanadium ions through the membrane were measured by using the methods described in literature [10]. For the area resistance measurements, the membrane was exposed to a solution of 1.5 M VOSO_4 in 2.0 M H_2SO_4 on both sides in a conductivity cell. The resistances of the cell with (R_1) and without membrane (R_2) were measured. The active area of the membrane was 28 cm^2 and its thickness (L) was measured. The area resistance R (Ωcm^2) and the conductivity σ (mS cm^{-1}) of the membrane can be calculated using the following expressions:

$$R = (R_1 - R_2) \times S \quad (1)$$

$$\sigma = \frac{L}{R} \quad (2)$$

To measure the permeability of V (IV) ions, the membrane was exposed to a solution of 1.5 M VOSO_4 in 2 M H_2SO_4 (left reservoir) and a solution of 1.5 M MgSO_4 in 2 M H_2SO_4 (right reservoir). MgSO_4 in the right reservoir was used to equalize the ionic strengths of the solutions in both sides and to minimize the osmotic pressure effects. Both solutions were circulated simultaneously through the cell compartments which were separated by membranes with an effective surface area of 28 cm^2 . Samples (5 mL) of the solution from the right reservoir were taken at regular time intervals and the concentration of vanadium ions was analyzed by a UV-vis spectrometer. The experiments were carried out at room temperature. Cross-section of the membrane was observed with a

FEI INSPECT F scanning electron microscope (SEM) equipped with an Energy Dispersive X-rays spectrometer (EDX).

2.4. Cell tests

For the VRB single cell used in the charge–discharge tests, carbon felt served as electrodes, and conductive plastic plates served as current collectors. The active area of the electrode was 28 cm^2 . The negative and positive electrolytes consisted of 1.5 M VOSO_4 in 2.0 M H_2SO_4 . The SPEEK and PFSA layer are exposed to negative and positive half-cell electrolytes, respectively, in order to use the advantages of the SPEEK layer (low permeability of vanadium ions) and PFSA layer (good antioxygenic property). To avoid overcharging the positive electrolyte, the negative electrolyte volume was 80 mL but the positive one was 170 mL. At the end of the first charge process 90 mL positive electrolyte were taken out of the reservoir very quickly. To avoid corrosion of the carbon felt and the conductive plastic plates, the upper limit of the charge voltage was 1.65 V, and the lower voltage limit for discharge was maintained at 0.75 V.

3. Results and discussion

3.1. SEM property

SEM/EDX images of the S/P/P membrane on cross-section before and after the charge–discharge tests are shown in Figs. 1 and 2, respectively. In Fig. 1(a), the sandwich-type structure of the S/P/P membrane can be seen clearly. No cracks are found throughout the whole membrane, indicating that the SPEEK and PFSA resins were successfully deposited into holes of the PP membrane and an integral layered membrane structure was formed. The thickness of each layer is about 67, 130, and 45 μm , respectively. Fig. 1(b) shows the distribution of the elements in the cross-section of the S/P/P membrane. The concentration of F is high near the up layer and low in the bottom layer of the membrane, which is in good agreement with the expected structure of the S/P/P membrane. In Fig. 2(a), the SEM micrograph shows no delamination through the whole membrane cross-section after the charge–discharge tests. This indicates that the SPEEK and the PFSA resins have completely filled the holes of the PP layer and are well coupled to the PP layer. The results further confirm that the bonding and linking effect of the PP layer avoids the delamination of the SPEEK layer from the PFSA layer. The thickness of the S/P/P membrane and PFSA layer change very little before and after the charge–discharge tests, while SPEEK layer change about 10 μm . This may due to the non-uniformity of the SPEEK layer and errors of the EDX measurement. Comparing the EDX elemental analysis of Fig. 2 with that of Fig. 1, we found the elements content in the membrane after the charge–discharge tests were similar to those before the charge–discharge tests.

3.2. Membrane characterization

The area resistance of the S/P/P membrane is 1.58 Ωcm^2 , which is higher than that of N212 (0.6 Ωcm^2), but is close to the area resistance of S/T/P membrane (1.3 Ωcm^2) [10]. The conductivity of the S/P/P membrane is 15.2 mS cm^{-1} , which is higher than those of N212 (8.3 mS cm^{-1}) and Nafion 117 (8.58 mS cm^{-1}) [5]. This may due to the high degree of sulfonation of SPEEK. The further studies on this matter will be undergone in our lab.

The time dependence of V (IV) ions concentration in MgSO_4 solution is illustrated in Fig. 3. It is clear that the vanadium ions diffusion through the N212 is considerably faster than those diffusion through the S/P/P membrane. The permeability of VO^{2+} across the S/P/P membrane and the permeability of VO^{2+} across the N212 are $1.95 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ and $8.23 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$, which can

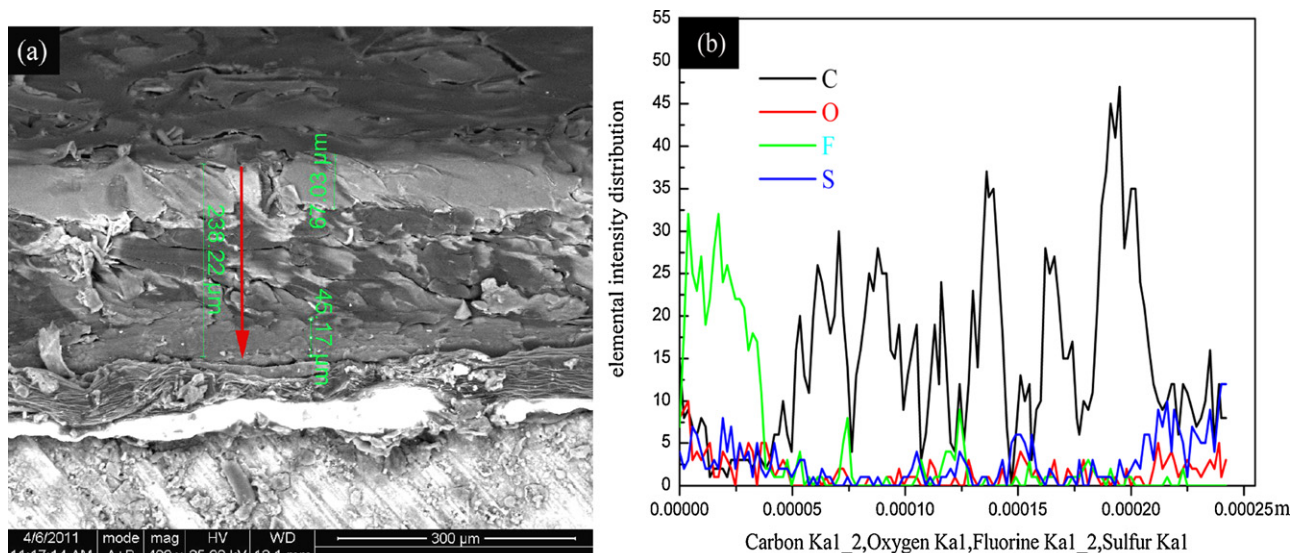


Fig. 1. SEM micrograph and EDX analysis of the cross-section of S/P/P membrane before and after the charge–discharge tests. (a) SEM images. The red vertical line with arrows indicates the direction of EDX analysis. (b) EDX analysis elemental intensity distribution curves.

be calculated by using the pseudo-steady-state condition [7]. This result reveals that the permeation of VO^{2+} across the S/P/P membrane decreases significantly, and it can be attributed to that the different microstructures between SPEEK membrane and Nafion membrane [10]. The microstructures of Nafion membrane are composed of the extremely high hydrophilic sulfonic functional groups and extremely high hydrophobic fluorocarbon backbone, which gives rise to some hydrophobic/hydrophilic nano-separation, especially in the presence of water. These sulfonic groups are well interconnected because of the high flexibility of the fluorocarbon of the Nafion membrane, which can form hydrophilic domains and hence allow vanadium ions to permeate through as well as proton and water. However, in the SPEEK membrane the hydrophobic/hydrophilic separation is small because of its less hydrophobic backbone, and there is less acidic sulfonic acid group. Furthermore, the high rigidity of the backbone of SPEEK results in narrow proton channels and a branched structure with many dead-end pockets.

As a result, the sandwich-type structure of S/P/P membrane can reduce the permeability of vanadium ions resulted from a decrease in the pore size after SPEEK and PFSA resin being embedded in the hole of the PP membrane and thus reduce the channel size for V (IV) ions diffusion.

3.3. VRB single cell performance

The charge–discharge curves of VRB with S/P/P membrane and N212 at a current density of 50 mA cm^{-2} are presented in Fig. 4. The discharge capacity of the VRB with S/P/P membrane is higher than that of the VRB with N212 because the lower permeability for vanadium ions will reduce the self-discharge of the VRB single cell. Besides, the average charge voltage of VRB based on S/P/P membrane is higher than that of the VRB based on N212, which is due to the large IR drop caused by the high area resistance of the S/P/P membrane.

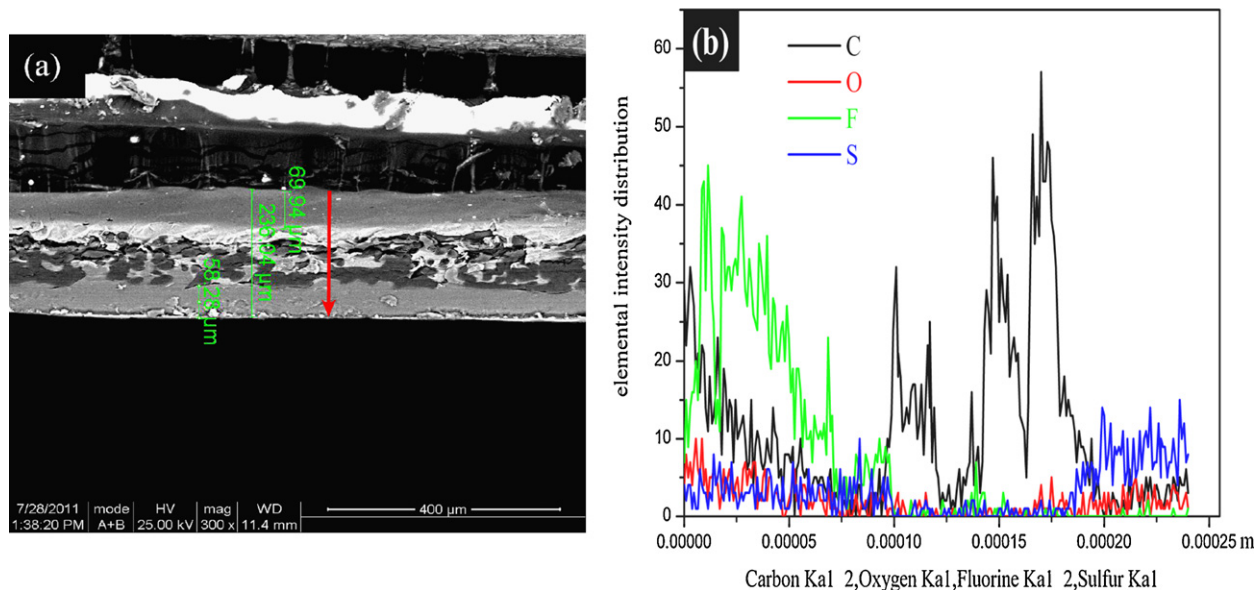


Fig. 2. SEM micrograph and EDX analysis of the cross-section of S/P/P membrane before and after the charge–discharge tests. (a) SEM images. The red vertical line with arrows indicates the direction of EDX analysis. (b) EDX analysis elemental intensity distribution curves.

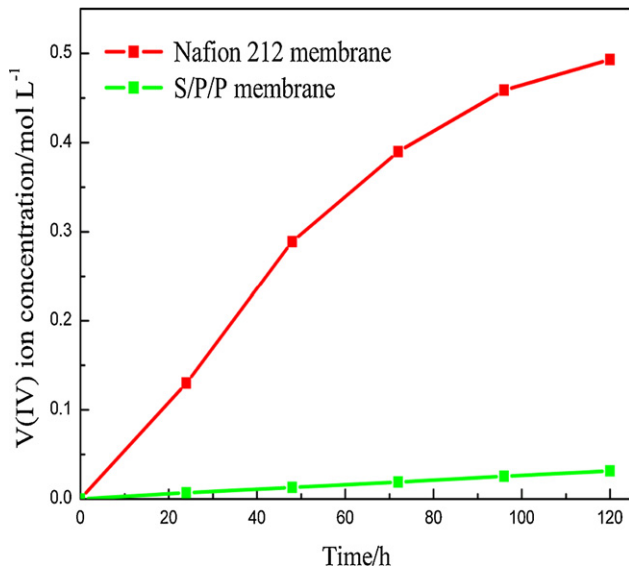


Fig. 3. Vanadium ion concentration in the right reservoir of a VRB single cell with a Nafion 212 membrane and an S/P/P membrane, respectively.

Open circuit voltage (OCV) of the VRB was monitored at room temperature after it was charged to a 75% state of charge and is presented in Fig. 5(a). As shown, the OCV value gradually decreases with storage time at first and then drops sharply. The time of OCV with S/P/P membrane can last for more than 68 h beyond 0.85 V, while only 36 h for the VRB with N212. It is indicated that the self-discharge of VRB caused by the crossover of vanadium ions can be reduced remarkably by using the S/P/P membrane. However, the OCV results for PFSA/PP are of no meaning for VRB due to the irregular change of the volume of negative and positive electrolytes. Due to this poor V ion-resistant performance, the PFSA/PP membrane will not be applicable in VRB systems. That is why the PP sandwiched by SPEEK and PFSA layer is developed in this work. The efficiency with cycle number for the S/P/P membrane is shown in Fig. 5(b). As shown, the VRB with S/P/P membrane shows higher columbic efficiency (CE) and energy efficiency (EE) than those of N212, which results from the lower permeability for vanadium ions.

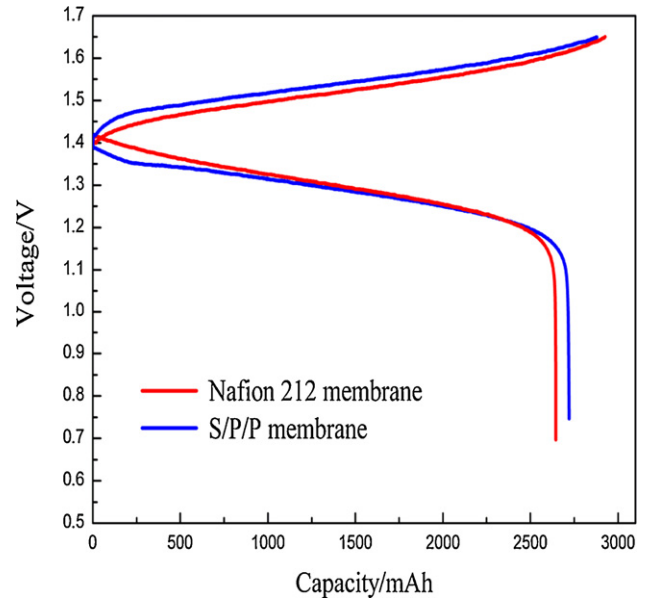


Fig. 4. Charge–discharge curves of a VRB single cell with a Nafion 212 membrane and an S/P/P membrane respectively, at current density of 50 mA cm⁻².

However, voltage efficiency (VE) is lower because the high area resistance of the S/P/P membrane. There is nearly no decline of CE and EE up to 50 cycles. The VE of VRB with S/P/P membrane drops a little quicker than that with N212 in this specific case. However, this is not a general trend. Repeated experiments show that, sometimes N212 drops quicker. This dropping of VE can be explained as the different accumulation time of the dark red precipitation by the heat from different pumps. Fig. 5(b) is one of the most typical curves we have measured (all of the measured VE data have similar behavior and the VE values are always within the same range), only with fluctuations of a small amplitude. After the charge–discharge test, the VRB cell was opened for a check of the S/P/P membrane there are no delamination and degradation phenomenon, which indicates that the membrane has high stability in strong acidic vanadium solutions.

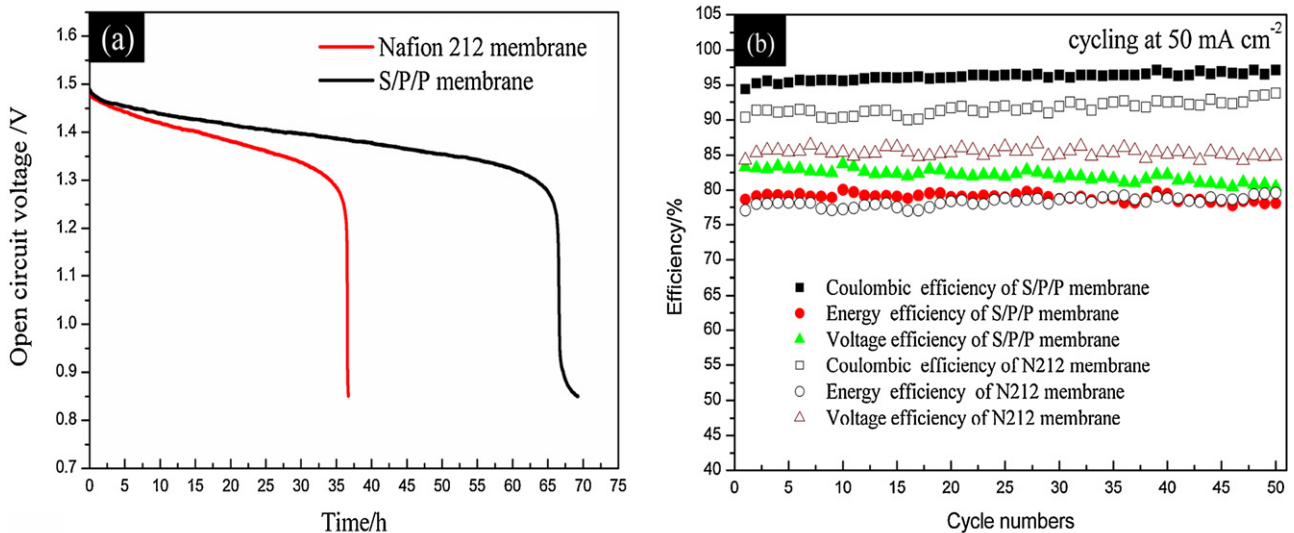


Fig. 5. Performance comparison of VRB with Nafion 212 and S/P/P membranes: (a) OCV values and (b) efficiency.

4. Conclusions

A sandwich-type S/P/P composite membrane consisting a layer of PFSA, the transition central layer and a layer of SPEEK has been prepared by solution casting. The PFSA layer and the SPEEK layer were tightly linked with improved interface stability due to the effect of the porous PP layer. The PFSA layer of the S/P/P membrane serves as a shield preventing the oxidation degradation of the composite membrane by VO^{2+} ions in the positive half-cell electrolyte of the VRB while the SPEEK layer is expected to block the vanadium ions permeation. The S/P/P membrane displays much lower vanadium ions permeability compared to N212 one. The VRB single cell with an S/P/P membrane has higher CE, EE, and a lower self-discharge rate than that with a N212 membrane. In summary, this novel type of membrane has shown excellent cell performance and is expected to have commercial prospects as a separator for VRB systems.

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