Influences of Permeation of Vanadium Ions through PVDF-g-PSSA Membranes on Performances of Vanadium Redox Flow Batteries

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The preparation and physical characterization of a poly(vinylidene fluoride)-graft-poly(styrene sulfonic acid) (PVDF-g-PSSA) membrane prepared by a solution-grafting method were described. These membranes exhibited high conductivity with a value 3.22×10^{-2} S/cm at 30 °C. ICP studies revealed that the PVDF-g-PSSA membrane showed dramatically lower vanadium ion permeability compared to Nafion 117. Trivalent vanadium ions had the highest permeability through all these membranes in contrast to pentavalent vanadium ions with the lowest. The VRB with the low-cost PVDF-g-PSSA membrane exhibited a higher performance than that with Nafion 117 under the same operating conditions, and its energy efficiency reached 75.8% at 30 mA/cm². The performance of VRB with the PVDF-g-PSSA membrane can be maintained after more than 200 cycles at a current density of 60 mA/cm².

1. Introduction

The vanadium redox flow battery (VRB) proposed by Skyllas-Kazacos and co-workers[1−3] in 1985 has received considerable attention due to its long cycle life, flexible design, fast response time, deep-discharge capability, and low cost in energy storage. The configuration of the VRB is shown in Figure 1. It consists of two electrolyte tanks with the electrolytes of V(II)/V(III) and V(IV)/V(V) in sulfuric acid solution, two pumps, and a battery stack section where the battery reaction takes place. The electrolytes are pumped into the stack where they are separated by an ion exchange membrane. The ion exchange membrane is usually used to provide proton conduction and effective separation of the anode and cathode electrolytes. The ideal membrane should possess low vanadium ion crossover, high ionic conductivity, good chemical stability, and low cost. Previous studies showed that most early types of commercial ion exchange membranes (e.g., Selemion CMV, DMV, Asahi Glass Co., Japan) are unsuitable due to their degradation by a pentavalent vanadium ion (VO_2^+) in VRB.[4] Although they have excellent chemical stability and high proton conductivity (0.07−0.23 S·cm⁻¹),[5] Nafion (Dupont) membranes suffer from the crossover of vanadium ions through the membrane, which results in decreases in energy efficiency.[6] Furthermore, they are too expensive for current commercial use.

It was reported that the poly(vinylidene fluoride)-graft-poly-(styrene sulfonic acid) (PVDF-g-PSSA) membrane has high conductivity and good structural properties.[7] In our laboratory, we have studied a solution-grafting technique for the preparation of the PVDF-g-PSSA membrane.[8] Some properties of the PVDF-g-PSSA membranes produced by the same method were investigated in this paper. The membranes were measured for
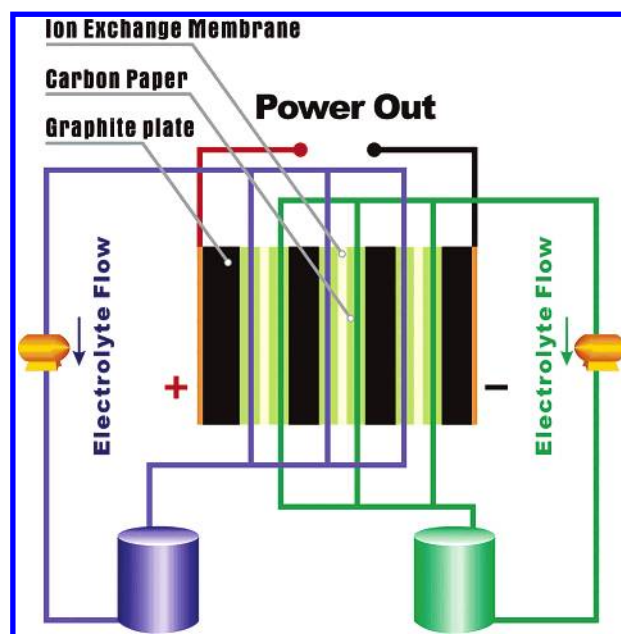

Figure 1. Schematic illustration of a vanadium redox flow battery.

their ion exchange capacity (IEC), proton conductivity, water uptake, and vanadium ion permeability in comparison with the Nafion 117 membrane. It is the first time the PVDF-g-PSSA membrane was employed as a separator in VRB, and the cell performance is also evaluated.

2. Experimental Section

2.1. Membrane Preparation. A piece of PVDF film was soaked in a solution of 0.07 mol/L KOH in alcohol at 80 °C for about 45 min. Then, the membrane was washed with deionized water until reaching a constant pH and quickly immersed in a mixed solution of styrene and tetrahydrofuran

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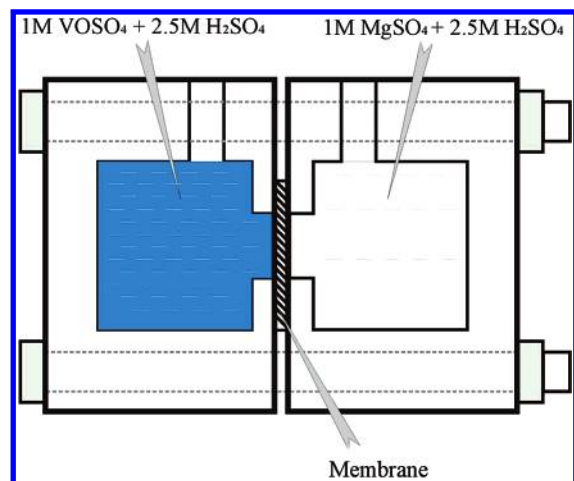*J. Phys. Chem. B, Vol. 109, No. 43, 2005* **20311**

Figure 2. Schematic illustration of the cell for the measurement of vanadium permeability.

with a volume ratio of 4:1. Benzoyl peroxide (BPO), with a concentration of 0.4 g/100 mL, was added as the radical initiator. The grafting reaction was performed at 80 °C under nitrogen atmosphere. Afterward, the membrane was extracted with chloroform to remove the unreacted monomer and any homopolymer. Before sulfonation, the membrane was swelled in 1,2-dichloroethane at 60 °C for 2 h. The sulfonation was conducted by immersing the membrane in concentrated sulfuric acid (98%) for 4 h at 70 °C. Finally, the membrane was washed with deionized water to remove the remaining sulfuric acid.[8]

2.2. Membrane Characterization. The degree of grafting (d.o.g.) was determined gravimetrically according to eq 1

$$d.o.g. = \frac{M_1 - M_0}{M_0} \times 100\% \qquad (1)$$

where M_0 is the mass of the initial PVDF membrane, and M_1 is the mass of the polystyrene-grafted membrane. The IEC of the membranes was evaluated by the methods described previously.[9] The water uptake of the membranes was defined as the ratio of the mass of the absorbed water to that of the dry membrane. It can be calculated from eq 2

$$\text{water uptake} = \frac{W_1 - W_0}{W_0} \qquad (2)$$

where W_1 is the weight of the wet membrane, and W_0 is the weight of the dry membrane.

Proton conductivity of the membranes was determined by measuring the impedance spectroscopy on a cell with the given membrane sample sandwiched between two stainless steel (SS) electrodes. The measurements were carried out on a Solartron 1255 B frequency response analyzer coupled with a Solartron 1287 electrochemical interface in the frequency range of 1 Hz to 1 MHz at 30 °C. The conductivity was calculated according to the electrode area of the cell (0.785 cm^2) and the thickness of the membrane, which was measured with a micrometer.

Figure 2 illustrates the equipment used for the measurement of the permeability of three types of vanadium ions. The V(IV) solution was prepared by dissolving VOSO$_4$·5H$_2$O (A.R., supplied by Shanghia XinYue Co. Ltd) in 2.5 mol/L H$_2$SO$_4$. V(III) and V(V) solutions were prepared by the electrochemical reduction and oxidation of the V(IV) solution, respectively.[10] The left reservoir was filled with 1 mol/L V(III), V(IV), or V(V) ion solution in 2.5 mol/L H$_2$SO$_4$, and the right reservoir was filled with 1 mol/L MgSO$_4$ solution in 2.5 mol/L H$_2$SO$_4$. MgSO$_4$

was used to equalize the ionic strengths of the two solutions and to minimize the osmotic pressure effects.[11] These were continuously stirred using magnetic stir bars during experiments at room temperature. The two solutions were separated by a membrane. Before use, the membrane was immersed in distilled water. The geometrical area of the exposed membrane is 5.0 cm^2 while the volume of the solutions for each reservoir was 20 mL. Samples of solution from the right reservoir were taken at a regular time interval and analyzed for vanadium ion concentration with the method of inductively coupled plasma atomic emission spectrometry (ICP-AES).

The VRBs used in the charge/discharge tests were fabricated by sandwiching the membrane between two pieces of carbon paper (Toray TGPH-120, thickness is 0.35 mm) electrodes and then clamping the sandwich between two graphite polar plates which were graved with flow channels. The area of the electrode for the reaction was 25 cm^2. At the beginning of charge/discharge cycles, 40 mL of 2 mol/L V(IV) in 3.0 mol/L H$_2$SO$_4$ solution was pumped into the cathode side and 40 mL of 2 mol/L V(III) in 3.0 mol/L H$_2$SO$_4$ solution was pumped into the anode side, respectively. To avoid the corrosion of the carbon paper electrode and graphite polar plates, the cell was charged to 1.6 Ah corresponding with a redox couples utilization of 75%. The low voltage limit for discharge was controlled to 0.9 V.

3. Results and Discussion

3.1. Proton Conductivity, Ion Exchange Capacity, and Water Uptake. Some properties of the Nafion 117 membrane and PVDF-g-PSSA membranes are summarized in Table 1. The water uptake and IEC of the PVDF membrane are very small. After they were grafted with polystyrene sulfonated acid, the water uptake and IEC of the membranes increased. In Table 1, the PVDF-g-PSSA-11 and PVDF-g-PSSA-22 membranes correspond to the membranes with degrees of grafting of 11% and 22%, respectively. It can be seen from Table 1 that the PVDF-g-PSSA membrane with the higher degree of grafting shows a higher water uptake, IEC, and conductivity. This is in agreement with the suggestion that the conductivity of ion exchange membranes is largely dependent on two major factors: the number of ion exchange sites per unit volume and the water content of the membrane.[12] The PVDF-g-PSSA-22 membrane possesses higher conductivity in comparison with the PVDF-g-PSSA-11 membrane due to its higher d.o.g. and water uptake. The conductivity of the Nafion 117 membrane at 30 °C was measured as 5.87×10^{-2} S/cm, which is close to the results reported by Lehtinen.[8] The conductivity of the PVDF-g-PSSA-22 membrane reaches 3.22×10^{-2} S/cm, almost half that of Nafion 117. However, the thickness of the Nafion 117 membrane is almost twice that of the PVDF-g-PSSA membrane. It can be speculated that the internal resistance of the VRB with the Nafion 117 and PVDF-g-PSSA membranes are close to each other.

3.2. Permeability of Vanadium Ions. The permeablity of three types of vanadium ions (V(III), V(IV), and V(V)) through the membrane was measured under the same conditions. In this work, we did not measure the permeability of the V(II) ion across the membranes since the V(II) ion is easily oxidized in the air. Figure 3 shows the relationships of the concentration of vanadium ions in the right reservoir with time. It can be seen that the concentration of vanadium ions in the right reservoir for the Nafion 117 membrane increased faster than that for the PVDF-g-PSSA-22 membrane.
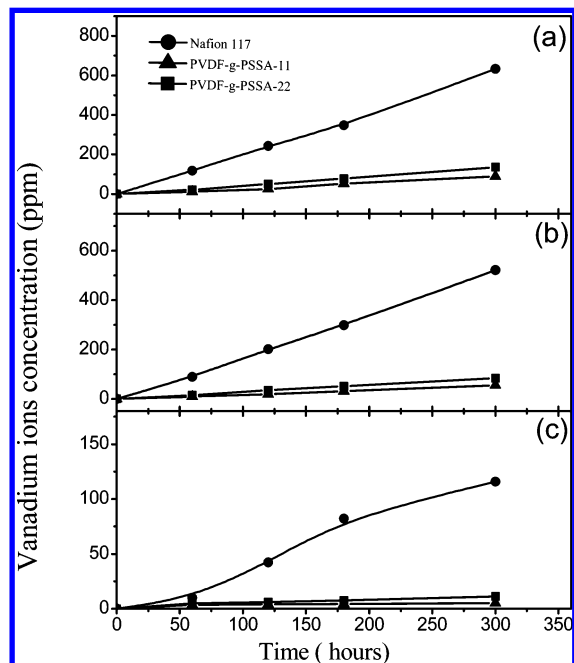
It was supposed that the change in vanadium ion concentration in the left side can always be negligible during the

TABLE 1: Comparison of the General Properties between the Nafion 117 Membrane and PVDF-g-PSSA Membranes

membrane	d.o.g. (%)	thickness (μm)	water uptake (g/g dry membrane)	IEC (mmol/g dry membrane)	conductivity ($\times 10^{-2}$ S/cm)
Nafion117		215	0.260	0.97	5.87
PVDF-g-PSSA-11	11	151	0.162	0.82	0.72
PVDF-g-PSSA-22	22	115	0.264	1.2	3.22

TABLE 2: Comparison of the Permeability of Vanadium Ions through the Membrane between Nafion 117 and PVDF-g-PSSA-22

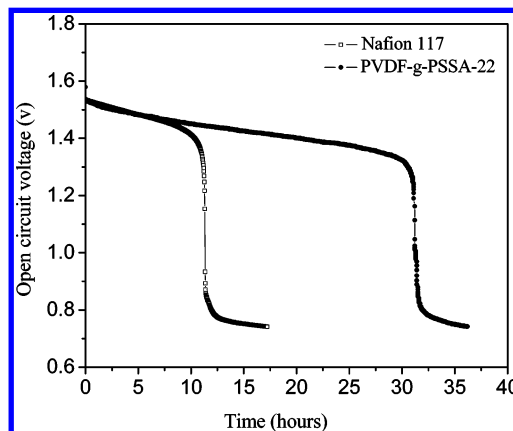| membrane	permeability of V(III) (10^{-7} cm^2/min)	permeability of V(IV) (10^{-7} cm^2/min)	permeability of V(V) (10^{-7} cm^2/min)
Nafion117	35.6	30.0	7.02
PVDF-g-PSSA-11	3.63	2.20	0.17
PVDF-g-PSSA-22	4.14	2.53	0.31

Figure 3. Vanadium ion concentrations in the right reservoir of the cell with Nafion-117 and PVDF-g-PSSA membranes; in the left reservoir, the concentrations of vanadium ions were 1 mol/L.

Figure 4. Open circuit voltage of VRB with a PVDF-g-PSSA-22 membrane and Nafion 117 membrane. Solutions of 40 mL of 2 mol/L V(IV) in 3.0 mol/L H$_2$SO$_4$ and 40 mL of 2 mol/L V(III) in 3.0 mol/L H$_2$SO$_4$ were kept in cycle in the cathode side and anode side, respectively. Before measurement, VRBs were charged to 1.6 Ah corresponding to a redox couples utilization of 75%.

calculation of permeability due to the fact that the concentration of the vanadium ion in the right reservoir is low. Inside the membrane, a pseudo-steady-state condition was used. Accordingly, the flux of the vanadium ion is constant, and its concentration in the right reservoir as a function of time is given by eq 3 as follows

$$V_B \frac{dc_B(t)}{dt} = A \frac{P}{L} (c_A - c_B(t)) \tag{3}$$

where c_A is the vanadium ion concentration in the left reservoir, and $c_B(t)$ refers to the vanadium ion concentration in the right reservoir as a function of time. A and L are the area and thickness of the membrane, P is permeability of the vanadium ions, and V_B is the volume of right reservoir, respectively. An assumption is also made here that P is independent of concentration.

The vanadium ion permeability P inside the membrane was calculated and listed in Table 2. Among the three vanadium ions, the V(III) ions had the highest permeability through the membranes and the V(V) ions had the lowest. The permeability of the V(III), V(IV), and V(V) ions decrease in the following order: Nafion 117 > PVDF-g-PSSA-22 > PVDF-g-PSSA-11. It also can be found that the two PVDF-g-PSSA membranes

were shown to have dramatically lower vanadium ion permeability compared to that of the Nafion 117 membrane. It could be estimated that the VRB using the PVDF-g-PSSA membrane will have a higher Coulombic efficiency than the one using the Nafion 117 membrane for their low permeation rates of vanadium ions.

3.3. Vanadium Redox Flow Battery Performance. The 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 Figure 4. The electrolytes solutions pumped through the cell unceasingly during the self-discharge test. As illustrated, the OCV value gradually decreased with storage time at first and then rapidly to ca. 0.7 V. From Figure 4, it can also be seen that maintaining the time of OCV above 1.0 V of VRB with the PVDF-g-PSSA-22 membrane is about 30 h, which is nearly three times longer than that of VRB with Nafion 117. This means that the rate of self-discharge of VRB with Nafion 117 is faster than that of VRB with the PVDF-g-PSSA-22 membrane. The self-discharge of VRB is mainly due to the crossover of vanadium ions through the membrane between the cathode and anode, that is, V(II) and V(III) from anode to cathode and V(IV) and V(V) from cathode to anode.

Charge−discharge curves of a single cell at different current densities are shown in Figure 5. By comparing the charge−discharge curves of VRBs with the Nafion 117 and PVDF-g-PSSA-22 membranes, it can be seen that the average discharge voltage of the VRB with the Nafion 117 membrane is lower than that of the VRB with the PVDF-g-PSSA-22 membrane, which indicates that the resistance of Nafion 117 is a little bit
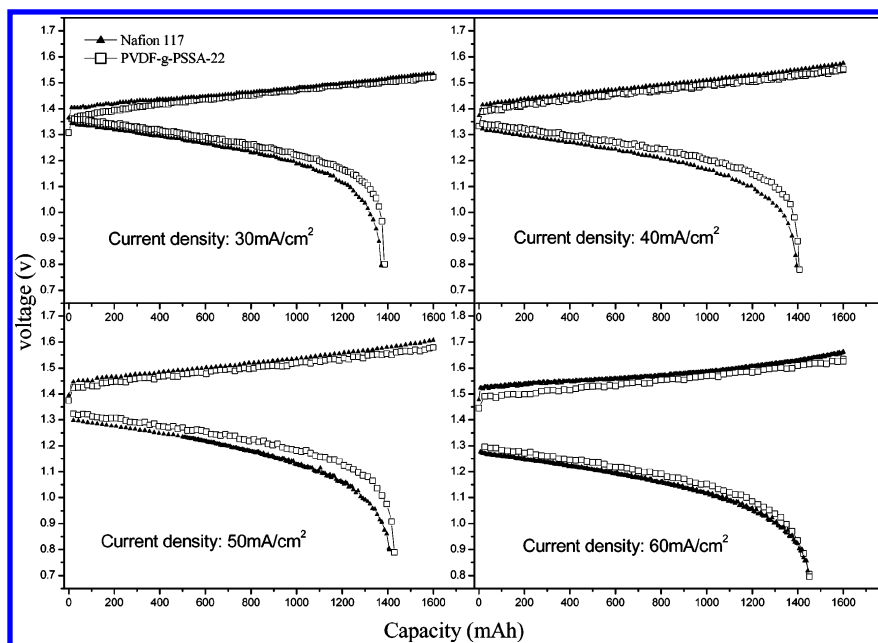
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Figure 5. Charge−discharge curves of VRBs with a PVDF-g-PSSA-22 membrane and Nafion 117 membrane at various current densities with an electrode area of 25 cm^2. Solutions of 40 mL of 2 mol/L V(IV) in 3.0 mol/L H$_2$SO$_4$ and 40 mL of 2 mol/L V(III) in 3.0 mol/L H$_2$SO$_4$ were cycled in the cathode side and anode side, respectively. Charge capacity was controlled to be 1.6 Ah corresponding to a redox couples utilization of 75%.
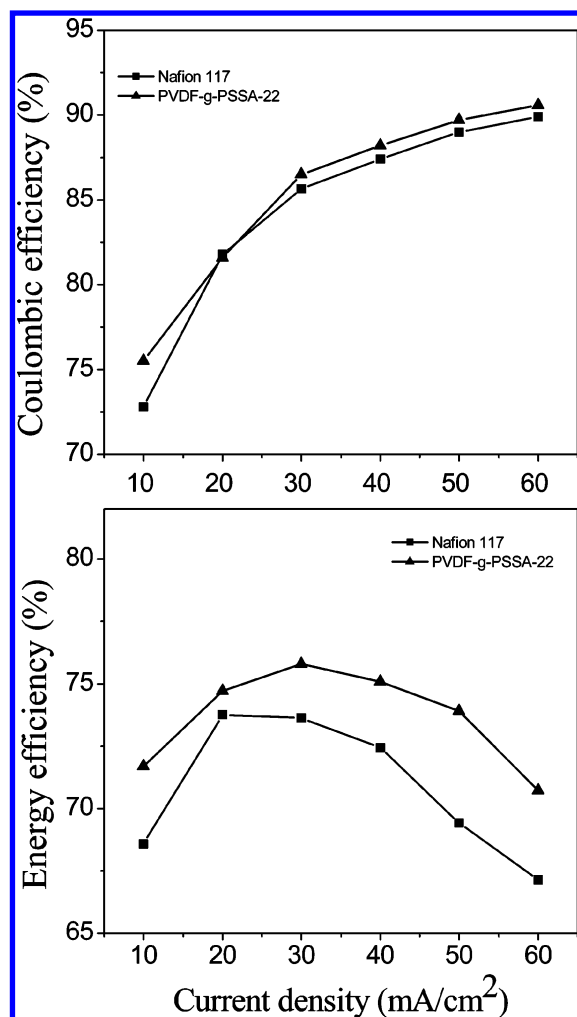

Figure 6. Coulombic efficiency and energy efficiency of VRBs with a PVDF-g-PSSA-22 membrane and Nafion 117 membrane.

Figure 7. Discharge capacity of VRB with a PVDF-g-PSSA-22 membrane during cycling at a current density of 60 mA/cm^2. The charge capacity was kept to be 1.6 Ah corresponding to a redox couples utilization of 75%.

current densities; therefore, the amount of vanadium ions that cross over the membranes will be reduced.

The relationships of the Coulombic efficiency and the energy efficiency with charge/discharge current density are illustrated in Figure 6. As shown, the Coulombic efficiency increases from ca. 70% to ca. 90% when the current density increases from 10 to 60 mA/cm^2. In addition, increased Coulombic efficiency and energy efficiencies were obtained with the PVDF-g-PSSA-22 membrane over the entire range of current densities compared to the Nafion 117 system. There appears to be a maximum energy efficiency of the VRB, which is 75.8% for the PVDF-g-PSSA-22 membrane at 30 mA/cm^2 and 74.7% for the Nafion 117 membrane at 20 mA/cm^2. The differences of the Coulombic and energy efficiencies between the VRB with the Nafion 117 and PVDF-g-PSSA-22 membranes are also partly attributed to the difference of vanadium ions permeability through membranes.

The cycle performance of the VRB employing a PVDF-g-PSSA-22 membrane at a current density of 60 mA/cm^2 is

larger than that of PVDF-g-PSSA-22. As expected, the discharge capacity increases with the charge/discharge current density. This is attributed to the shorter charge/discharge time at high
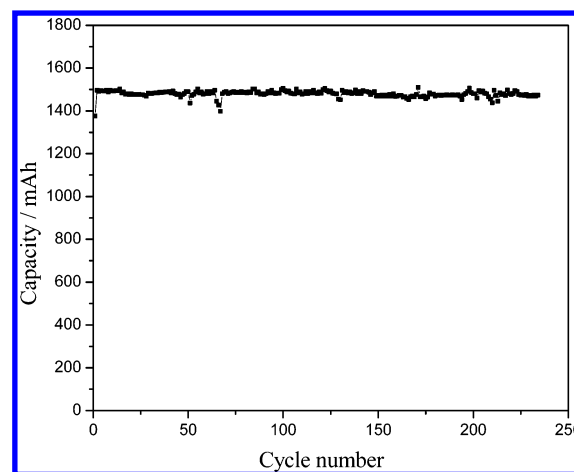
presented in Figure 7. As shown, there is no decay of capacity after the cell was cycled for more than 200 cycles. It means that the PVDF-g-PSSA membranes possess high stability in vanadium solutions and thus are able to maintain cell capacity and performance.

4. Conclusions

A PVDF-g-PSSA membrane prepared by a solution-grafting method showed high proton conductivity and low vanadium ion permeability. The VRB with a PVDF-g-PSSA membrane showed a lower self-discharge rate and higher Coulombic and energy efficiencies. The results from cycling experiments revealed that the PVDF-g-PSSA membrane has good chemical stability in vanadium solutions. Furthermore, the solution-grafting method of preparing a PVDF-g-PSSA membrane is very simple, which could lead to a significant cost reduction for the production of a commercial redox flow battery.

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