

Short communication

# Nafion/SiO<sub>2</sub> hybrid membrane for vanadium redox flow battery

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## Abstract

Sol–gel derived Nafion/SiO<sub>2</sub> hybrid membrane is prepared and employed as the separator for vanadium redox flow battery (VRB) to evaluate the vanadium ions permeability and cell performance. Nafion/SiO<sub>2</sub> hybrid membrane shows nearly the same ion exchange capacity (IEC) and proton conductivity as pristine Nafion 117 membrane. ICP-AES analysis reveals that Nafion/SiO<sub>2</sub> hybrid membrane exhibits dramatically lower vanadium ions permeability compared with Nafion membrane. The VRB with Nafion/SiO<sub>2</sub> hybrid membrane presents a higher coulombic and energy efficiencies over the entire range of current densities (10–80 mA cm<sup>-2</sup>), especially at relative lower current densities (<30 mA cm<sup>-2</sup>), and a lower self-discharge rate compared with the Nafion system. The performance of VRB with Nafion/SiO<sub>2</sub> hybrid membrane can be maintained after more than 100 cycles at a charge–discharge current density of 60 mA cm<sup>-2</sup>. The experimental results suggest that the Nafion/SiO<sub>2</sub> hybrid membrane approach is a promising strategy to overcome the vanadium ions crossover in VRB.

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**Keywords:** Vanadium redox flow battery; Nafion/SiO<sub>2</sub> hybrid membrane; Vanadium permeability

## 1. Introduction

Vanadium redox flow battery (VRB) proposed by Skyllas–Kazacos group [1–4] in 1985 has received considerable attention due to its long cycle life, flexible design, fast response time, deep-discharge capability, and low pollution emitting in energy storage [5–16]. As shown in Fig. 1, the VRB consists of two electrolyte tanks with the electrolytes of V(IV)/V(V) and V(II)/V(III) in sulfuric acid solution, two pumps, and a battery stack section where the redox electrode reaction takes place. The electrolytes are pumped into the stack separated by an ion exchange membrane. Ion exchange membrane is one of the key materials for VRB and usually used to provide proton conduction to maintain the electrical balance and effective separation of the anode and cathode electrolytes. The ideal membrane for VRB should possess low vanadium ion crossover, high ionic conductivity, and good chemical stability. 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 V(V) in VRB [17].

Perfluorosulfonic polymers such as Nafion are the most commonly used proton exchange membrane material owing to their high proton conductivity, good chemical and thermal stability [18]. However, Nafion membrane suffers from the crossover of methanol and vanadium ions when used in direct methanol fuel cell (DMFC) [19,20] and VRB [12,21], respectively, which results in decreases in energy efficiency. There has been extensive research activity in the modification of Nafion based membrane to reduce the methanol permeability, for example, recasting with inorganic nanoparticles, [22] surface modification with metal thin film, [23] surface modification with layer-by-layer self-assembly polyelectrolyte, [19] hot-pressing with other proton conducting membrane, [24] and *in situ* sol–gel reaction to incorporate inorganic oxide nanoparticles within the pores of Nafion [25]. All of above modification methods may also be used to decrease the crossover of vanadium ions through Nafion membrane and, in general, improves the performance of VRB.

Since the pioneer work by Mauritz et al. [26–29], sol–gel derived Nafion/SiO<sub>2</sub> hybrid membranes have been successfully used in DMFC due to the simple dealing procedure (see Fig. 2) and lower methanol permeability. Nafion/SiO<sub>2</sub> hybrid membranes can reduce the crossover of methanol because of the polar clusters (pores) of the origin Nafion, which is the dominating reason for methanol permeating, had been filled with SiO<sub>2</sub>

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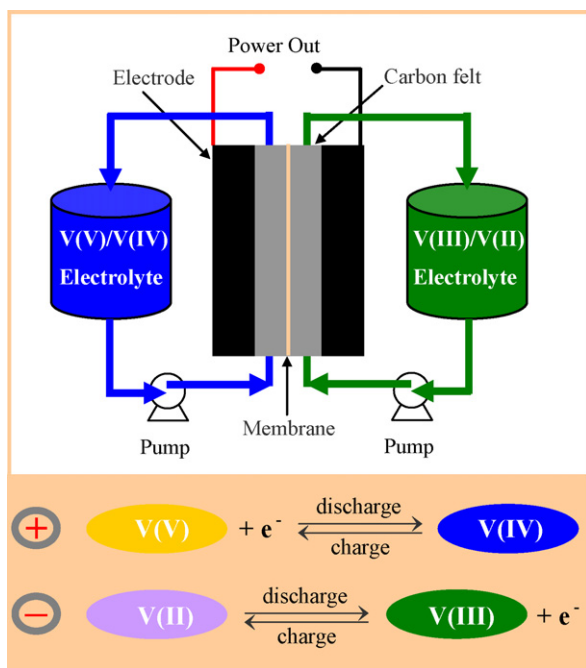


Fig. 1. Schematic illustration of vanadium redox flow battery (VRB).

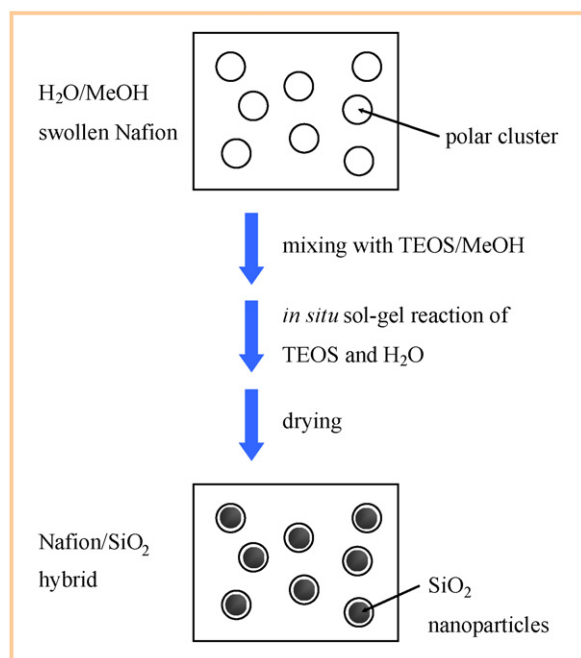


Fig. 2. Schematic depiction of the preparation of Nafion/SiO<sub>2</sub> hybrid membrane.

nanoparticles during the *in situ* sol–gel reaction with TEOS, as shown in Fig. 2 [25,29].

The specific nanostructure of Nafion/SiO<sub>2</sub> hybrid membranes inspired us that this kind of membrane maybe also can lower vanadium ion permeability compared with Nafion membrane. In this work, Nafion/SiO<sub>2</sub> hybrid membrane was measured their ion exchange capacity (IEC), proton conductivity, water uptake, and vanadium ion permeability in comparison with the pristine Nafion 117 membrane. Then, Nafion/SiO<sub>2</sub> hybrid membrane was employed as the separator in VRB, and the cell performance was also evaluated and discussed. Experiment results show that the Nafion/SiO<sub>2</sub> hybrid membrane approach is a promising strategy to inhibit vanadium ions crossover in VRB.

## 2. Experimental

### 2.1. Preparation of Nafion/SiO<sub>2</sub> hybrid membrane

All membranes used in this work were Nafion 117 and denoted as Nafion. Prior to modification, the Nafion membrane was treated according to the standard procedure that is 60 min in a 3 wt.% H<sub>2</sub>O<sub>2</sub> solution at 80 °C, 30 min in deionized water at 80 °C, and 30 min in 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution at 80 °C. After each treatment, the membrane was rinsed in deionized water to remove traces of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>. The membrane was stored in deionized water before use.

Samples were dried at 110 °C under vacuum to determine the initial, dry H<sup>+</sup> form weight before the sol–gel reaction. Nafion/SiO<sub>2</sub> hybrid membrane was prepared according to the *in situ* sol–gel method reported by Mauritz et al. [26–29] Fig. 2 illustrates the preparation of Nafion/SiO<sub>2</sub> hybrid membrane [25,29]. In a typical synthesis, a 6 cm × 6 cm dry Nafion membrane was first swollen overnight in stirred solutions of MeOH:H<sub>2</sub>O = 5:1 (vol/vol) at room temperature. Then the pre-mixed tetraethylorthosilicate (TEOS)/MeOH solutions were introduced into the flask with the Nafion membrane so that the H<sub>2</sub>O:TEOS ratio was 4:1 (mol/mol) while maintaining stirring. After 3 min for the sol–gel reaction, the membrane was removed from the flask, and then quickly soaked in MeOH for 1–2 s to wash away excess reactants adhering to the surface. Finally, the membrane was surface-blotted and dried at 100 °C under vacuum for 24 h. The resulted Nafion/SiO<sub>2</sub> hybrid membrane had a silica content of 9.2 wt.% (see Table 1). The sample was stored in deionized water before use.

### 2.2. Membrane characterization

The water uptake of the membranes was defined as mass ratio of the absorbed water to that of the dry membrane. It can

Table 1  
Comparison of general properties between Nafion and Nafion/SiO<sub>2</sub> hybrid membrane

Membrane	Silica content (wt.%)	Thickness (μm)	Water uptake (wt.%)	IEC (mmol g <sup>-1</sup> )	Conductivity (mS cm <sup>-1</sup> )
Nafion	–	215	26.0	0.97	58.7
Nafion/SiO <sub>2</sub>	9.2	204	21.5	0.96	56.2

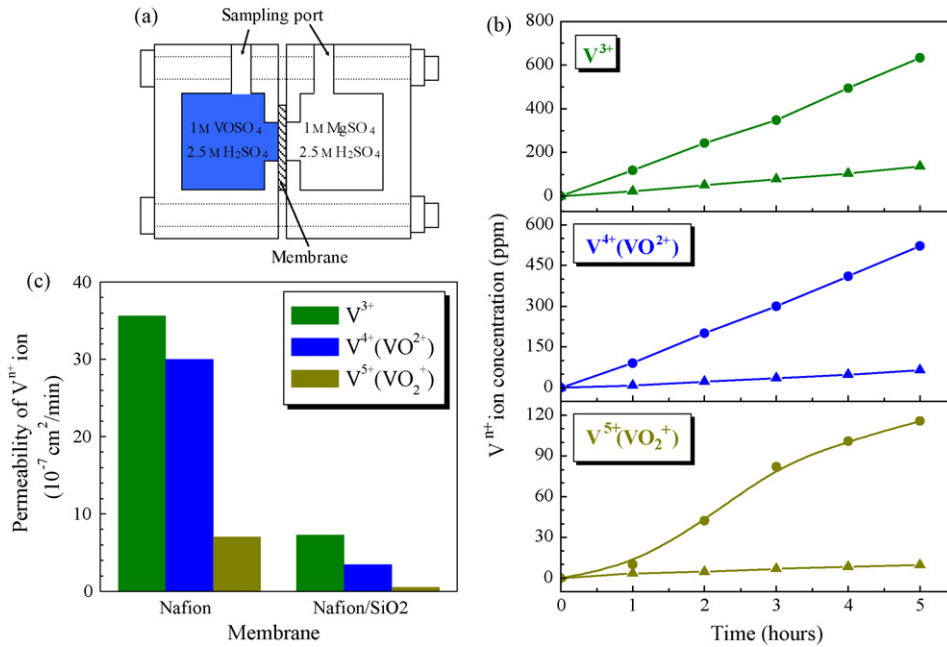


Fig. 3. (a) Schematic illustration of the cell for the measurement of vanadium permeability. (b) Vanadium ion concentration in the right reservoir of the cell with Nafion (●) and Nafion/SiO<sub>2</sub> (▲) membranes. (c) Comparison of the permeability of vanadium ions through the membrane between Nafion and Nafion/SiO<sub>2</sub> hybrid membrane.

be calculated using the equation:

$$\text{water up take} = \frac{(W_w - W_d)}{W_d} \times 100\%$$

where  $W_w$  is the weight of the wet membrane, and  $W_d$  is the weight of the dry membrane. The IEC of the membranes was measured by the method described previously [30].

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 and 100% relative humidity. The conductivity was calculated according to the electrode area of the cell and the thickness of the membrane, which was measured with a micrometer.

Fig. 3(a) illustrates the equipment used for the measurement of the permeability of three types of vanadium ions [12]. The V(IV) solution was prepared by dissolving VOSO<sub>4</sub>·5H<sub>2</sub>O (Shanghai XinYue Co., Ltd.) in 2.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. V(III) and V(V) solutions were prepared by the electrochemical reduction and oxidation of the V(IV) solution, respectively [31]. The left reservoir was filled with 1 mol L<sup>-1</sup> V(III), V(IV), or V(V) ion solution in 2.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, and the right reservoir was filled with 1 mol L<sup>-1</sup> MgSO<sub>4</sub> solution in 2.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. MgSO<sub>4</sub> was used to equalize the ionic strengths of the two solutions and to minimize the osmotic pressure effect [14]. The two solutions 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

was 5.0 cm<sup>2</sup> and the volume of the solution 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 by inductively coupled plasma atomic emission spectrometry (ICP-AES).

### 2.3. Cell tests

The VRB used in the charge–discharge tests was fabricated by sandwiching the membrane (6 cm × 6 cm) between two pieces of carbon felt (Shanghai Xinxing Carbon Materials Co., Ltd., thickness is 5 mm) electrodes and then clamping the sandwich between two graphite polar plates which were grinded with serpentine flow fields. The area of the electrode for the reaction was 25 cm<sup>2</sup>. At the beginning of charge–discharge cycles, 40 mL of 2 mol L<sup>-1</sup> V(IV) in 2.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution was pumped into the cathode side and 40 mL of 2 mol L<sup>-1</sup> V(III) in 2.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution was pumped into the anode side, respectively. To avoid the corrosion of the carbon felt electrode and graphite polar plates, the cell was charged to 1600 mA h with a corresponding redox couples utilization of 75%. The low voltage limit for discharge was controlled to 0.8 V.

## 3. Results and discussion

### 3.1. Physical properties

Mauritz et al. have reported that during the preparation process of sol–gel derived Nafion/SiO<sub>2</sub> hybrid, the TEOS molecules will preferentially migrate to the polar clusters inside the Nafion membrane and the subsequently hydrolysis of sorbed TEOS are confined to these clusters to form SiO<sub>2</sub> nanoparticles filled

Nafion/SiO<sub>2</sub> hybrid membrane, as shown in Fig. 2 [29]. Some properties of the Nafion membrane and Nafion/SiO<sub>2</sub> hybrid membrane are summarized in Table 1. It can be seen that Nafion/SiO<sub>2</sub> hybrid membrane has nearly the same IEC and proton conductivity as pristine Nafion membrane. The slight decrease in water uptake for Nafion/SiO<sub>2</sub> hybrid membrane can be attributed to the filling of polar clusters by SiO<sub>2</sub> nanoparticles, as shown in Fig. 2.

### 3.2. Permeability of vanadium ions

The permeability of three types of vanadium ions, i.e. V(III), V(IV) and V(V), through the membrane was measured under the same condition by using the equipment shown in Fig. 3(a). In this work, we did not measure the permeability of the V(II) ion across the membranes since the V<sup>2+</sup> ion is easily oxidized in the air. Fig. 3(b) 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 Nafion membrane increased faster than that for Nafion/SiO<sub>2</sub> hybrid membrane.

It is supposed that the change in vanadium ion concentration in the left side can always be negligible during the 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 is 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 the equation [12,32]:

$$V_R \frac{dc_R(t)}{dt} = A \frac{P}{L} [c_L - c_R(t)]$$

where  $c_L$  is the vanadium ion concentration in the left reservoir, and  $c_R(t)$  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, respectively.  $P$  is permeability of the vanadium ions, and  $V_R$  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 is calculated and compared in Fig. 3(c). Among the three vanadium ions, the V(III) ion has the highest permeability through the membranes and the V(V) ion has the lowest, which may be attributed to the different diffusion coefficients and the charges of these vanadium ions when they are diffusing in a cation exchange membrane. It is exciting to note that Nafion/SiO<sub>2</sub> hybrid membrane has dramatically lower vanadium ion permeability compared to that of the Nafion membrane, especially for high valence state vanadium ion. It can be estimated that the VRB using the Nafion/SiO<sub>2</sub> hybrid membrane will have a higher coulombic efficiency (CE) than the one using pristine Nafion membrane for its lower permeation rate of vanadium ions.

### 3.3. VRB performance

Fig. 4 displays the charge–discharge plots of a VRB single cell at different current densities. By comparing the charge–

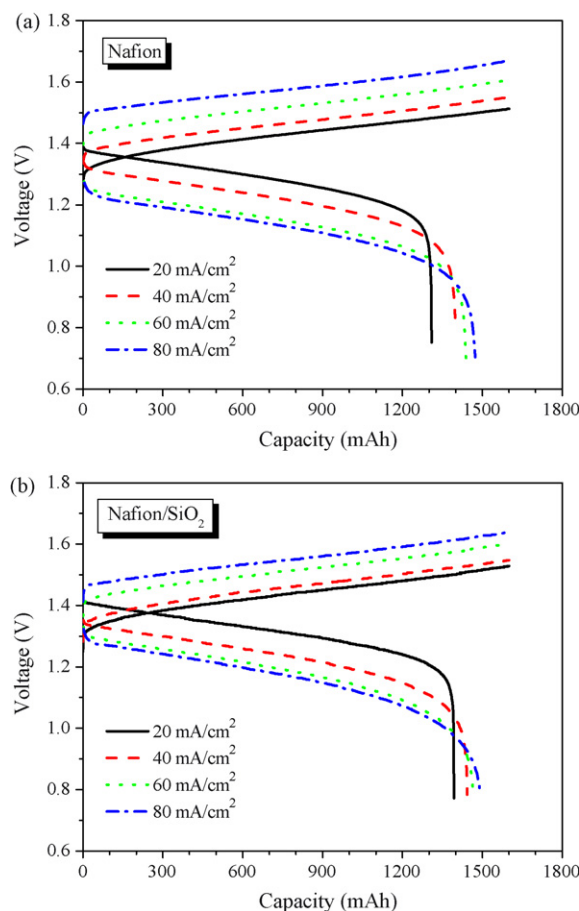


Fig. 4. Charge–discharge curves for VRB with Nafion membrane (a) and Nafion/SiO<sub>2</sub> hybrid membrane (b) at various current densities. Charge capacity was controlled to be 1600 mA h corresponding to a redox couples utilization of 75%.

discharge curves of VRB with Nafion and Nafion/SiO<sub>2</sub> hybrid membranes, it can be seen that the discharge capacity of the VRB with Nafion/SiO<sub>2</sub> hybrid membrane is higher than that of the VRB with Nafion membrane at all charge–discharge current densities, which indicates that Nafion/SiO<sub>2</sub> hybrid membrane has excellent performance to restrain the crossover of vanadium ions. As expected, the discharge capacity increases with the charge–discharge current density increasing. This is attributed to the shorter charge–discharge time at high current densities; therefore, the amount of vanadium ions that cross over the membranes will be reduced.

The relationships of the coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) with charge–discharge current density are illustrated in Fig. 5. As shown, the CE of VRB increases with the increasing of current density, while the VE shows the completely opposite trend. For all current densities and especially at lower current densities (<30 mA cm<sup>-2</sup>), the VRB with Nafion/SiO<sub>2</sub> hybrid membrane shows higher CE and EE than that of Nafion system. It shows a maximum EE of the VRB, which is 79.9% for Nafion/SiO<sub>2</sub> hybrid membrane and 73.8% for the Nafion membrane both at 20 mA cm<sup>-2</sup>. The differences of the CE and EE between the VRB with Nafion and with Nafion/SiO<sub>2</sub> hybrid membranes are

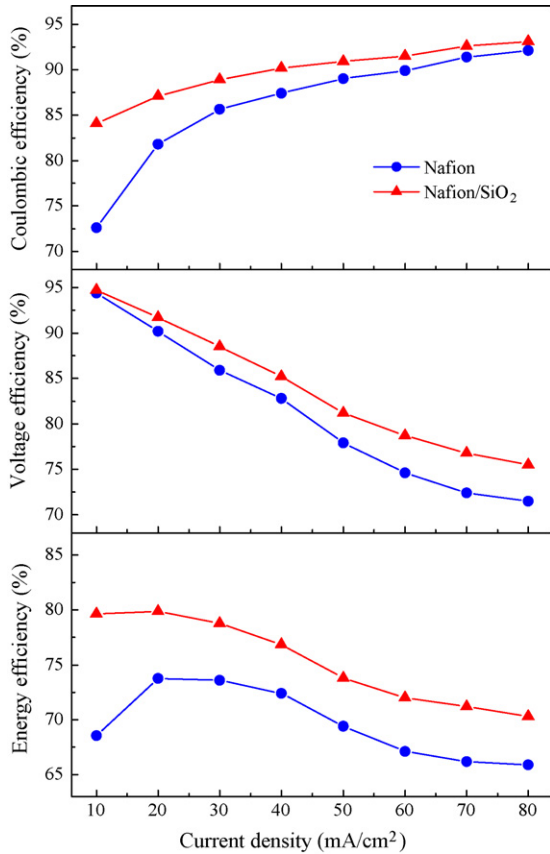


Fig. 5. Effect of current density on coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) of the VRB with Nafion and Nafion/SiO<sub>2</sub> membrane, respectively.

also partly attributed to the difference of vanadium ions permeability through membranes. In the case of VRB with Nafion membrane, vanadium ions will crossover through the polar clusters (pore) of Nafion membrane during the charge–discharge cycles and react with those vanadium ions which have different valence state, resulting in a lower CE and EE. On the contrary, for the VRB with Nafion/SiO<sub>2</sub> hybrid membrane, the transporting of vanadium ions through the membrane has been greatly reduced due to the filling of polar clusters of Nafion by SiO<sub>2</sub>

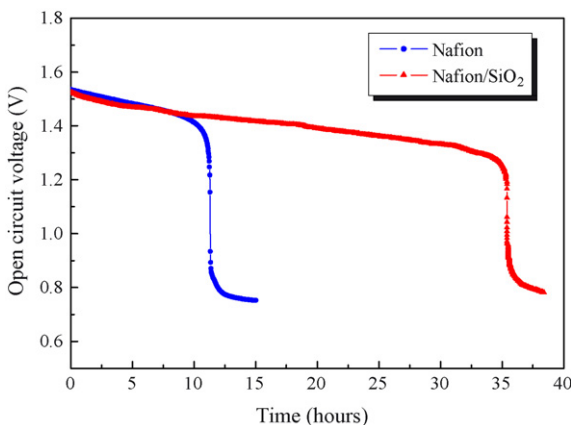


Fig. 6. Open circuit voltage (OCV) of the VRB as a function of time at the state of charge (SOC) of 75%.

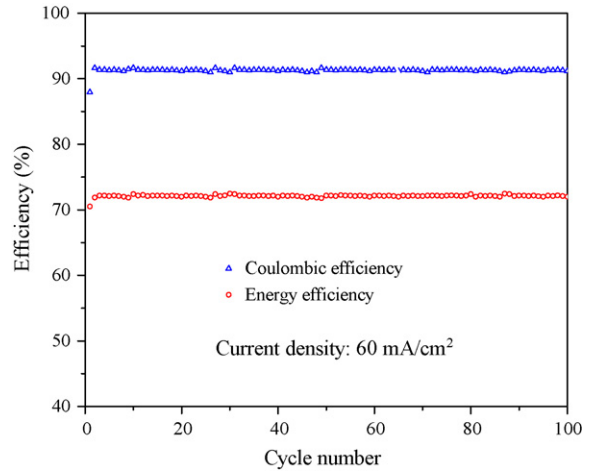


Fig. 7. Cycle performance for VRB with Nafion/SiO<sub>2</sub> membrane. Charge capacity was controlled to be 1600 mA h corresponding to a redox couples utilization of 75%.

nanoparticles [25–29], and hence, a relatively high CE and EE can be achieved.

Open circuit voltage (OCV) of the VRB was monitored at room temperature after it was charged to a 75% state of charge (SOC) and is presented in Fig. 6. The electrolytes solutions were pumped through the cell unceasingly during the self-discharge test. As illustrated, the OCV value gradually decreases with storage time at first and then rapidly drops to ca. 0.75 V. From Fig. 6, it can also be seen that the maintaining time of OCV above 1.0 V of VRB with Nafion/SiO<sub>2</sub> hybrid membrane is about 35 h, which is nearly two times longer than that of VRB with pristine Nafion membrane. This means that the rate of self-discharge of VRB with Nafion is faster than that of VRB with Nafion/SiO<sub>2</sub> hybrid membrane. The self-discharge of VRB is mainly due to the crossover of vanadium ions through the membrane between the cathode reservoir and anode reservoir, i.e., V(II) and V(III) from anode to cathode and V(IV) and V(V) from cathode to anode.

The cycle performance of a VRB single cell employing the Nafion/SiO<sub>2</sub> hybrid membrane at a charge–discharge current density of 60 mA cm<sup>−2</sup> is presented in Fig. 7. As shown, there is nearly no decay of CE and EE up to 100 cycles. It means that Nafion/SiO<sub>2</sub> hybrid membrane possesses high stability in vanadium solutions at strong acid condition and thus is able to maintain the cell performance.

#### 4. Conclusions

Nafion/SiO<sub>2</sub> hybrid membrane was prepared by *in situ* sol–gel method and shows nearly the same IEC and proton conductivity as that of pristine Nafion 117 membrane. Nafion/SiO<sub>2</sub> hybrid membrane displays very lower vanadium ions permeability compared to Nafion membrane, for its polar clusters is filled with SiO<sub>2</sub> nanoparticles. The VRB single cell with Nafion/SiO<sub>2</sub> hybrid membrane shows a higher coulombic and energy efficiencies and a lower self-discharge rate than that of Nafion system does. The results from cycling tests reveal that Nafion/SiO<sub>2</sub> hybrid membrane has good chemical stabil-

ity in vanadium and acid solutions. All experimental results confirm that the Nafion/SiO<sub>2</sub> hybrid membrane approach is a promising strategy to overcome the vanadium ions crossover in VRB. We believe that by optimizing the SiO<sub>2</sub> content in Nafion/SiO<sub>2</sub> hybrid membrane or by using organically modified silicate (ORMSIL) to replace SiO<sub>2</sub>, the performance of the VRB can be further improved. These works are now underway in our lab and will be reported in the near future.

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