



Short communication

Nafion/organically modified silicate hybrids membrane for vanadium redox flow battery

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ABSTRACT

In our previous work, Nafion/SiO₂ hybrid membrane was prepared *via in situ* sol–gel method and used for the vanadium redox flow battery (VRB) system. The VRB with modified Nafion membrane has shown great advantages over that of the VRB with Nafion membrane. In this work, a novel Nafion/organically modified silicate (ORMOSIL) hybrids membrane was prepared *via in situ* sol–gel reactions for mixtures of tetraethoxysilane (TEOS) and diethoxydimethylsilane (DEDMS). The primary properties of Nafion/ORMOSIL hybrids membrane were measured and compared with Nafion and Nafion/SiO₂ hybrid membrane. The permeability of vanadium ions through the Nafion/ORMOSIL hybrids membrane was measured using an UV–vis spectrophotometer. The results indicate that the hybrids membrane has a dramatic reduction in crossover of vanadium ions compared with Nafion membrane. Fourier transform infrared spectra (FT-IR) analysis of the hybrids membrane reveals that the ORMOSIL phase is well formed within hybrids membrane. Cell tests identify that the VRB with Nafion/ORMOSIL hybrids membrane presents a higher coulombic efficiency (CE) and energy efficiency (EE) compared with that of the VRB with Nafion and Nafion/SiO₂ hybrid membrane. The highest EE of the VRB with Nafion/ORMOSIL hybrids membrane is 87.4% at 20 mA cm⁻², while the EE of VRB with Nafion and the EE of VRB with Nafion/SiO₂ hybrid membrane are only 73.8% and 79.9% at the same current density. The CE and EE of VRB with Nafion/ORMOSIL hybrids membrane is nearly no decay after cycling more than 100 times (60 mA cm⁻²), which proves the Nafion/ORMOSIL hybrids membrane possesses high chemical stability during long charge–discharge process under strong acid solutions. The self-discharge rate of the VRB with Nafion/ORMOSIL hybrids membrane is the slowest among the VRB with Nafion, Nafion/SiO₂ and Nafion/ORMOSIL membrane, which further proves the excellent vanadium ions blocking characteristic of the prepared hybrids membrane.

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1. Introduction

Great achievements have been obtained since vanadium redox flow battery (VRB) was pioneered by Skyllas-Kazaco's group in 1985 [1–3]. There are many advantages of VRB systems over other batteries such as zinc bromine battery, sodium sulfur battery and lead acid battery. Especially, VRB system can be easily assembled in a large scale for energy storage, so it is very suitable for peak shaving in plant station, uninterruptible power supply, voltage and frequency control, stabilization of wind turbine output, solar and wind energy

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storage systems and so on [4–11]. Ion exchange membrane is one of the key constituents in VRB system. The membrane serves to separate the negative and positive electrolyte and provide a conduction pathway between the electrolytes. The ideal membrane for VRB should possess low vanadium ion permeability, high proton conductivity and good chemical stability [12,13]. Nafion membrane is the most commonly used proton exchange membrane in VRB system due to its high proton conductivity and good chemical stability in strong acid and oxidation condition [12,14]. However, because of the poor selectivity of Nafion between vanadium ions and proton, the vanadium ions are easily to transport through the membrane and lead to the decrease of coulombic efficiency, voltage efficiency and energy efficiency of VRB system [11,13,15–17]. In order to reduce the permeation of the vanadium ions and improve the performance of VRB, various methods of modification of Nafion membrane have been proposed and a series of satisfied results had been obtained [11,15,17–21].

In our previous work [15], we exploited the Nafion/SiO₂ hybrid membrane as separator for VRB in order to reduce the permeability of vanadium ions and improve the cell performance. Nafion/SiO₂ hybrid membrane was prepared by *in situ* sol-gel method and showed a lot of advantages over pristine Nafion 117 membrane. For example, it has nearly the same ion exchange capacity (IEC) and proton conductivity as that of Nafion 117 and shows much lower vanadium ions permeability compared with the Nafion membrane. The VRB single cell with Nafion/SiO₂ hybrid membrane shows a higher coulombic, energy efficiencies and a lower self-discharge rate than that of Nafion system. Those studies show that the performance of VRB can be remarkably improved by filling Nafion cluster with certain nanoparticles.

In this work, novel Nafion/organically modified silicate (ORMOSIL) hybrids membrane was prepared employing the same method of *in situ* sol-gel reactions using the mixtures of tetraethoxysilane (TEOS) and diethoxydimethylsilane (DEDMS). The properties of the Nafion/ORMOSIL hybrids membrane such as IEC, proton conductivity, vanadium permeability, water uptake, Fourier transform infrared spectra (FT-IR) and cell performance were investigated and discussed. The Nafion/ORMOSIL hybrids membrane is expected to further restrain the permeation of vanadium ions, improve the selectivity of Nafion membrane between vanadium ions and proton, and finally further improve the performance of VRB than that of Nafion/SiO₂ hybrid membrane.

2. Experimental

2.1. Preparation of Nafion/ORMOSIL hybrids membrane

All membranes used in this work were Nafion 117 and denoted as Nafion. Prior to sol-gel reaction, the Nafion membrane was pretreated according to the procedure reported by Damay and Klein [22]. The membranes were first cleaned in a 3-wt.% H₂O₂ solution at 80 °C for 60 min, and then rinsed in deionized water at 80 °C for 30 min. Finally, they were rinsed in 1.0 mol L⁻¹ H₂SO₄ solution at 80 °C for 30 min. After each treatment, the membrane was rinsed in deionized water to remove traces of H₂O₂ and H₂SO₄. The membrane was stored in deionized water before use.

All pretreated membranes were dried at 110 °C under vacuum for 24 h to determine the initial, dry H⁺ form weight before the sol-gel reaction. Nafion/ORMOSIL hybrids membrane was prepared according to the *in situ* sol-gel method reported by Deng et al. [23–25]. The process of preparation of Nafion/ORMOSIL hybrids membrane was illustrated in Fig. 1. Typically, a piece of 7 cm × 7 cm pretreated Nafion membrane was swollen for 24 h in stirred solutions of MeOH:H₂O=5:1 (v/v) at room temperature. MeOH served to swell the membrane to facilitate water permeations and subsequent permeation of TEOS and DEDMS. Then the premixed TEOS/DEDMS/MeOH solutions were introduced into the flask with the Nafion membrane so that the H₂O:TEOS=4:1 and H₂O:DEDMS=2:1 (mol/mol). After 5 min for the sol-gel reaction, the membrane was removed from the flask, and then quickly soaked in MeOH solution for 1–2 s to wash away excessive reactants adhering to the surface. Subsequently, the membrane was surface-blotted and dried at 100 °C under vacuum for 24 h. Finally, the prepared Nafion/ORMOSIL hybrids membranes were stored in deionized water for use.

2.2. Membrane characterization

The ion exchange capacity (IEC) of the membranes is calculated by following equation described by Hwang and Ohya [13].

$$\text{IEC} = \frac{M_{0,\text{NaOH}} - M_{E,\text{NaOH}}}{W} \quad (1)$$

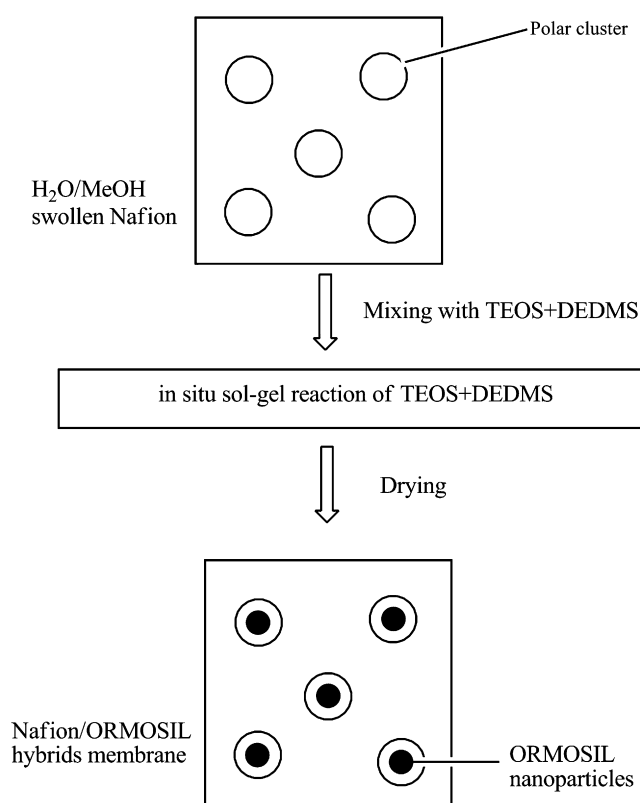


Fig. 1. Process of formulation of Nafion/ORMOSIL hybrids membrane.

where $M_{0,\text{NaOH}}$ is the moles of NaOH in the flask at the start of titration, $M_{E,\text{NaOH}}$ is the moles of residual NaOH after the membrane equilibrated with it for 24 h, and W is the weight of the dry membrane.

Proton conductivity of the membranes was determined according to the previous methods [15]. The measurements were carried out on a Solartron 1255B frequency analyzer in the frequency range of 1 Hz to 1 MHz at room temperature and 100% related humidity.

The water uptake of the membranes was defined as mass ratio of the absorbed water to that of the dry membrane and it was determined according to the method reported by Saccà et al. [26]. The weighed sample was immersed into water at room temperature for 24 h at first. And then, the membrane was taken out and wiped out the absorbed water adhering to the surface quickly and weighed again. The water uptake was determined according to the following equation:

$$\text{water uptake (\%)} = \frac{W_w - W_d}{W_d} \times 100\% \quad (2)$$

where W_w is the weight of the wet membrane, W_d is the weight of the dry membrane.

The weight uptake of ORMOSIL was determined relative to that of the initial unmodified, dry H⁺ form weight of Nafion, which was calculated as the following equation:

$$\text{ORMOSIL content (\%)} = \frac{W_m - W_i}{W_i} \times 100\% \quad (3)$$

where W_m is the weight of dry Nafion/ORMOSIL hybrids membrane, and W_i is the initial dry H⁺ form weight of Nafion membrane, respectively.

The measurement of the permeability of vanadium ions through the membranes was illustrated in Fig. 2 [11,15]. The left reservoir was filled with the solution of 1.0 mol L⁻¹ VOSO₄ in 2.5 mol L⁻¹ H₂SO₄, and the right reservoir was filled with 1.0 mol L⁻¹ MgSO₄

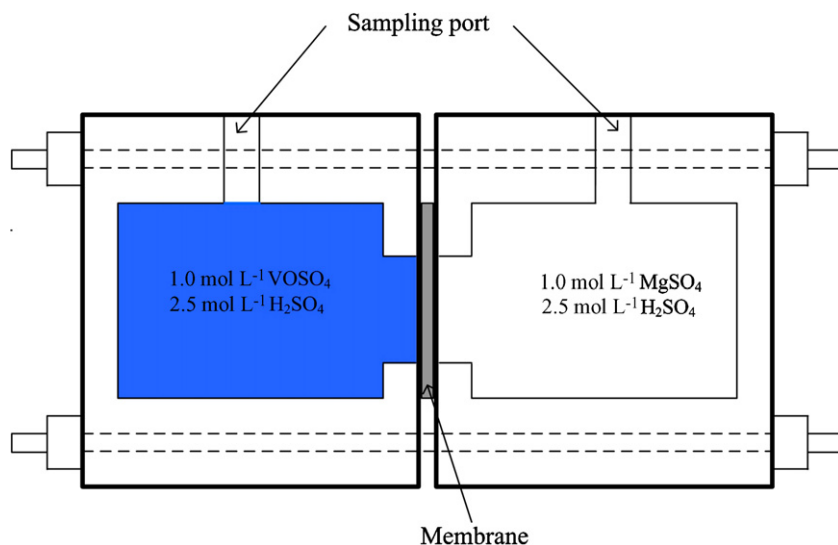


Fig. 2. Equipment for the measurement of permeability of VO^{2+} .

solution in $2.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$. MgSO_4 was used to equalize the ionic strengths of the two solutions and to minimize the osmotic pressure effect [11,27]. The two solutions were stirred using magnetic stir bars during experiments at room temperature. The effective area of the membrane exposed to solutions was 7.0 cm^2 . Samples in the right reservoir were taken at a regular time interval for vanadium ions concentration determination by an UV-1700 UV-vis spectrometer made by Shimadzu Corporation.

The FT-IR spectra were obtained using the Attenuated total reflection (ATR) method in order to confirm the formation of ORMOSIL phase within the hybrids membrane. The analysis was performed on a Thermo-Nicolet Nexus spectrometer in the wave number range of $4000\text{--}600 \text{ cm}^{-1}$ with resolution set at 4 cm^{-1} .

2.3. Cell test

The cell used in experiments was the same as described previously [15]. Two pieces of carbon felt were used as electrodes, serpentine flow fields graphite as polar plates, and silicone rubber as hermetic materials. The area of the electrode for the reaction was 25 cm^2 . Mixtures of 40 mL of $2.0 \text{ mol L}^{-1} \text{V}^{3+}/\text{V}^{4+} + 2.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ solutions were used as negative and positive electrolyte. To avoid the corrosion of the carbon felt electrode and graphite polar plates, the cell was charged to 1600 mAh with a corresponding redox couples utilization of 75% . The low voltage limit for discharge was controlled to 0.8 V . The charge–discharge test was conducted by using a NEWARE battery system (BTS 5V/2.2 A). The coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) of the cell were calculated as following equations [11,17]:

$$\text{CE} = \left(\frac{\text{discharge capacity}}{\text{charge capacity}} \right) \times 100 \quad (3)$$

$$\text{VE} = \frac{\text{(middle point of discharge voltage)}}{\text{middle point of charge voltage}} \times 100 \quad (4)$$

$$\text{EE} = \text{CE} \times \text{VE} \quad (5)$$

Table 1
Comparison of properties between Nafion, Nafion/ SiO_2 and Nafion/ORMOSIL hybrids membrane.

Membrane	Modifier content (wt.%)	Water uptake (wt.%)	Conductivity (mS cm^{-1})	IEC (mmol g^{-1})	Thickness (μm)
Nafion ^a	–	26.0	58.7	0.97	215
Nafion/ SiO_2 ^b	9.2	21.5	56.2	0.96	204
Nafion/ORMOSIL	8.5	23.6	57.5	0.97	217

Superscript letters (a,b) represent data quoted from our previous report [15].

3. Results and discussion

3.1. Primary properties of Nafion/ORMOSIL hybrids membrane

Some properties including the content of ORMOSIL in Nafion/ORMOSIL hybrids membrane, water uptake, IEC, conductivity and thickness of the Nafion/ORMOSIL hybrids membrane were determined and compared with Nafion and Nafion/ SiO_2 membrane as listed in Table 1.

It can be seen from Table 1 that the water uptake and the conductivity of unmodified Nafion membrane are the highest. While the water uptake and the conductivity of Nafion/ORMOSIL and Nafion/ SiO_2 are all slightly decreased because the polar clusters of Nafion membrane are filled or partly filled by ORMOSIL and SiO_2 nanoparticles. At the same time, the IEC and thickness of Nafion/ORMOSIL hybrids membrane are more similar to the Nafion membrane than that of Nafion/ SiO_2 hybrid membrane. The reasons might be due to that the distribution of ORMOSIL phase and organic groups in Nafion/ORMOSIL hybrids membrane are different from SiO_2 phase in Nafion/ SiO_2 hybrid membrane. However, more investigations should be done in the future research.

3.2. Permeability of vanadium ions

To obtain a high coulombic efficiency and low self-discharge rate, the membrane used in VRB system should have low permeability of vanadium ions. In this research, the permeability of the VO^{2+} across the Nafion and Nafion/ORMOSIL membrane was measured under the same condition by using the equipment shown in Fig. 2. The change of concentration of VO^{2+} with time was presented in Fig. 3.

It is obvious that the concentration of VO^{2+} through the Nafion/ORMOSIL membrane is much smaller than that of the VO^{2+} through the Nafion membrane. The permeability of VO^{2+} across the Nafion membrane and the permeability of VO^{2+}

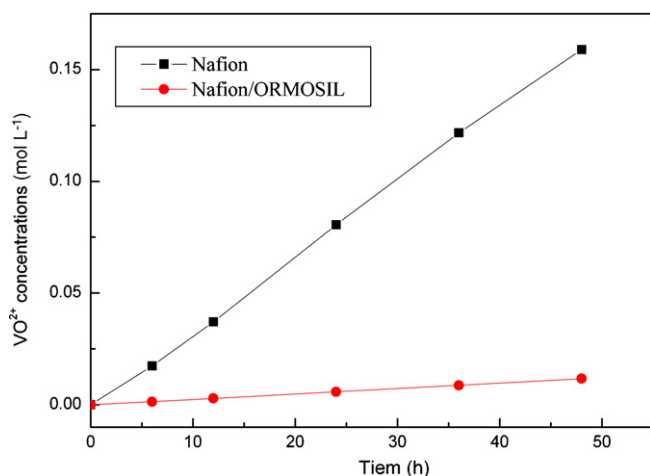


Fig. 3. Change of concentration of VO²⁺ with time in the right reservoir of the cell with Nafion and Nafion/ORMOSIL membranes.

across Nafion/ORMOSIL membrane are $36.9 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ and $1.85 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$, which can be calculated by the methods reported by Luo et al. [11]. This result reveals that the permeation of VO²⁺ across the Nafion/ORMOSIL hybrids membrane decreases significantly, and it can be attributed to that the polar clusters of Nafion membrane have been filled or partly filled by ORMOSIL nanoparticles and reduced the transporting of vanadium ions through the membrane.

3.3. FT-IR study

In order to confirm the formation of Si–O–Si bonds and the presence of Si–CH₃ groups in modified Nafion membrane, FT-IR spectra of Nafion membrane and Nafion/ORMOSIL membrane were determined by using ATR technique and showed in Fig. 4.

For Nafion membrane, the characteristic infrared bands and their assignments are presented in Table 2, which are well in accordance with the results reported by Chen et al. [28].

In the case of the FT-IR spectra of Nafion/ORMOSIL, as shown in Fig. 2(b) and (c), three sharp bands at $\sim 1261 \text{ cm}^{-1}$, $\sim 804 \text{ cm}^{-1}$ and $\sim 848 \text{ cm}^{-1}$ appear, which are assigned to symmetric stretching of C–H bonds ($\sim 1261 \text{ cm}^{-1}$) in Si–CH₃ groups, strong CH₃ rocking ($\sim 848 \text{ cm}^{-1}$) and Si–C stretching ($\sim 804 \text{ cm}^{-1}$) bands [23].

Table 2
Determined FT-IR characteristic bands of Nafion 117.

Characteristic bands	Frequency (cm ⁻¹)
Hydrated H ₃ O ⁺	1735.65 and 1639.22
CF ₂ asymmetric stretching	1203.14
CF ₂ symmetric stretching	1148.43
SO ₃ ⁻ symmetric stretching	1056.88
C–O–C stretching	982.17 and 970.03
C–S stretching	806.11

Also, a weak band at $\sim 2964 \text{ cm}^{-1}$ can be observed, which is corresponding to the asymmetric stretching in the –CH₃ group [23]. Besides the absorption peaks assigned above, IR absorption bands at $\sim 1077 \text{ cm}^{-1}$ and $\sim 1050 \text{ cm}^{-1}$ are found in Fig. 4, which are corresponding to the IR absorption of Si–O–Si groups ($1100\text{--}1000 \text{ cm}^{-1}$) [23,29].

These results imply that Si–O–Si bonds and Si–CH₃ bonds are successfully introduced and well formed within the Nafion/ORMOSIL hybrids membrane. The network structure of the ORMOSIL phase in Nafion/ORMOSIL hybrids membrane can be shown as Fig. 5 reported by Deng et al. [23] and Young et al. [30].

Where the symbols Q=Si(O_{1/2})₄ and D=(CH₃)₂Si(O_{1/2})₂ represent covalently incorporated building blocks within these limited networks. It is obvious that the sequence distribution of D and Q units will affect the nanostructures of ORMOSIL. As expected, with the increase of DEDMS:TEOS, ORMOSIL structures will become more linear, flexible and hydrophobic, and exhibit less shrinkage on drying [23,30]. Therefore, it is significant that the content and ratio of the modifiers are moderate in composite membrane.

3.4. Performance of VRB single cell

The charge–discharge curves of VRB with modified and unmodified Nafion membrane at different current densities are presented in Fig. 6. As it shows, the discharge capacity of VRB with Nafion/ORMOSIL is the highest among the VRB with three kinds of membranes at all charge–discharge current densities. This indicates that the VRB with Nafion/ORMOSIL membrane has the best performance among the three VRB cells. Furthermore, a relatively high discharge voltage of VRB with Nafion/SiO₂ and Nafion/ORMOSIL membrane is obtained at entire charge–discharge current range due to the reduction of permeation of vanadium ions across the hybrids

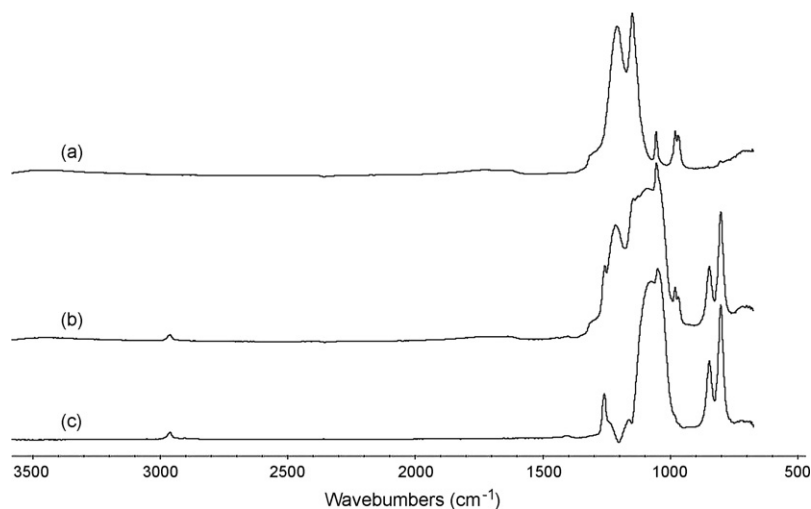


Fig. 4. FT-IR spectra of (a) Nafion membrane, (b) Nafion/ORMOSIL hybrids membrane, and (c) subtraction of (b) and (a).

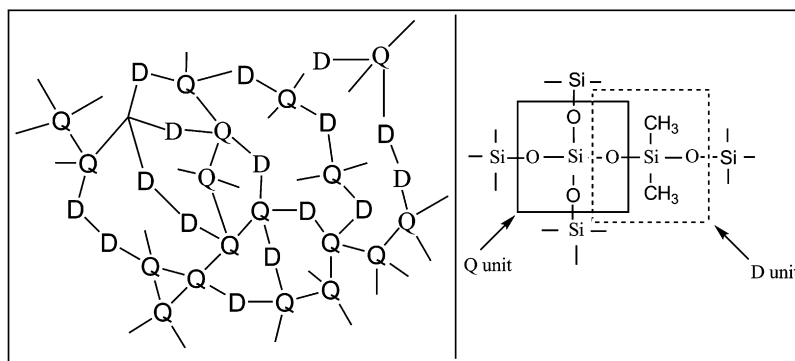


Fig. 5. Hypothesized ORMOSIL phase structure consisting of copolymerized Q and D units within Nafion/ORMOSIL hybrids membrane.

membrane. At the same time, the discharge capacity of VRB with three kinds of membranes all increase with the charge–discharge current densities, which is due to the shorter charge–discharge time at high current densities and the lower amount of vanadium ions can penetrate the membranes.

Our previous study shows that CE, VE and EE of VRB with Nafion/SiO₂ hybrid membrane are higher than that of the VRB with Nafion membrane at current densities of 10–80 mA cm⁻² [15]. On the basis of the former study, the changes of CE, VE and EE with current density of the VRB with Nafion/ORMOSIL membranes were studied and compared with the VRB–Nafion and VRB–Nafion/SiO₂ as shown in Fig. 7.

Fig. 7 reveals that the CE of VRB with three kinds of membranes all increases with the charge–discharge current densities. This can be attributed to the shorter charge–discharge time at high current densities, which can reduce the crossover of vanadium ions and a higher CE is obtained. But the VE of the VRB with three kinds of membrane all decreases with the charge–discharge current densities. And it is due to the increase of ohmic resistance and the overpotentials led by the increase of current densities. EE is the product of CE and VE. The EE of the VRB with three kinds of membranes all increases at the beginning and then decreases with the increase of current density. Furthermore, the CE, VE and EE of the VRB with Nafion/ORMOSIL hybrids membrane are the highest of

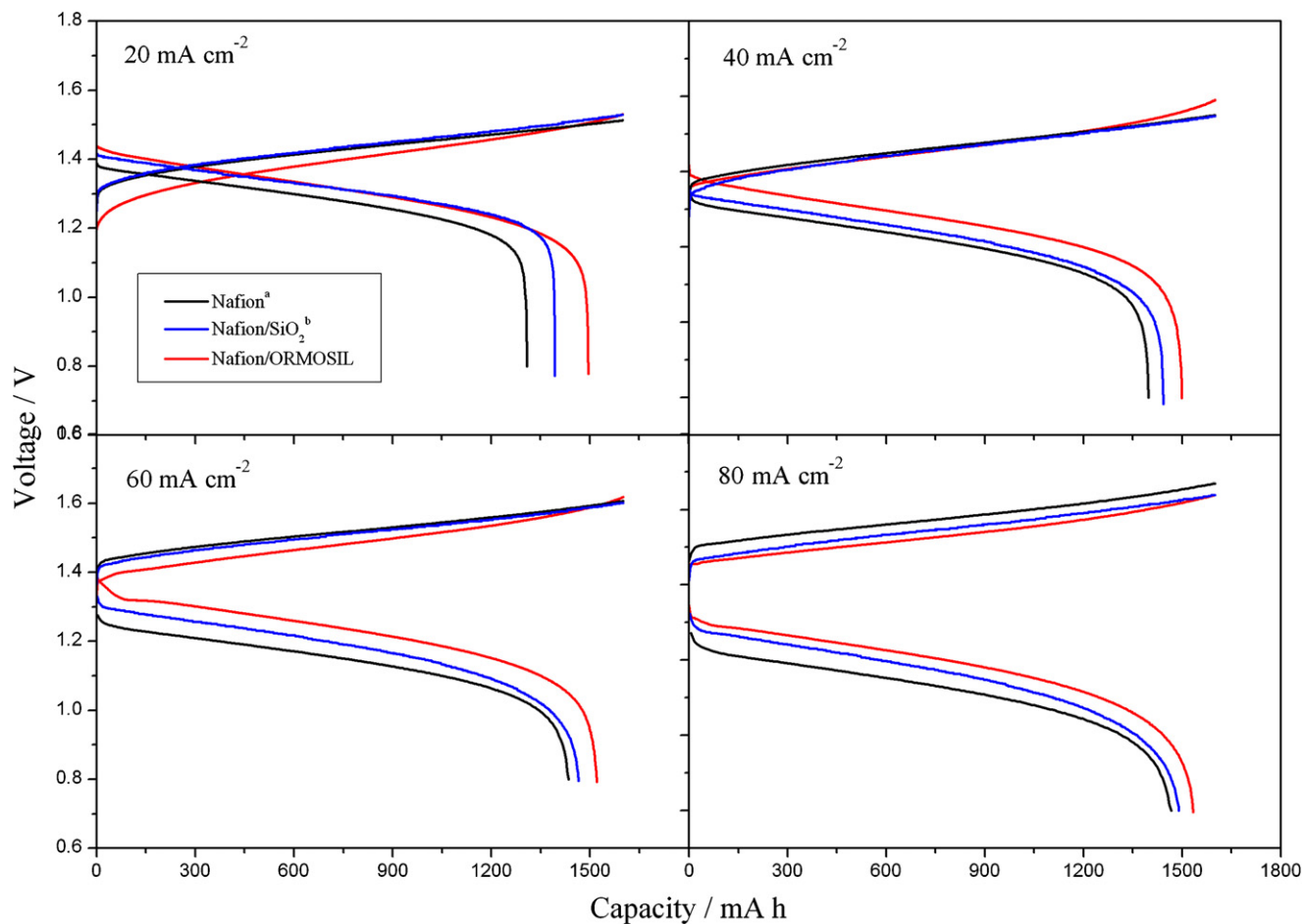


Fig. 6. Charge–discharge curves of VRB with Nafion, Nafion/SiO₂ and Nafion/ORMOSIL hybrids membrane at different current densities. Charge capacity was controlled to be 1600 mA h corresponding to a redox couples utilization of 75%, ^{a,b}Data quoted from previous report [15].

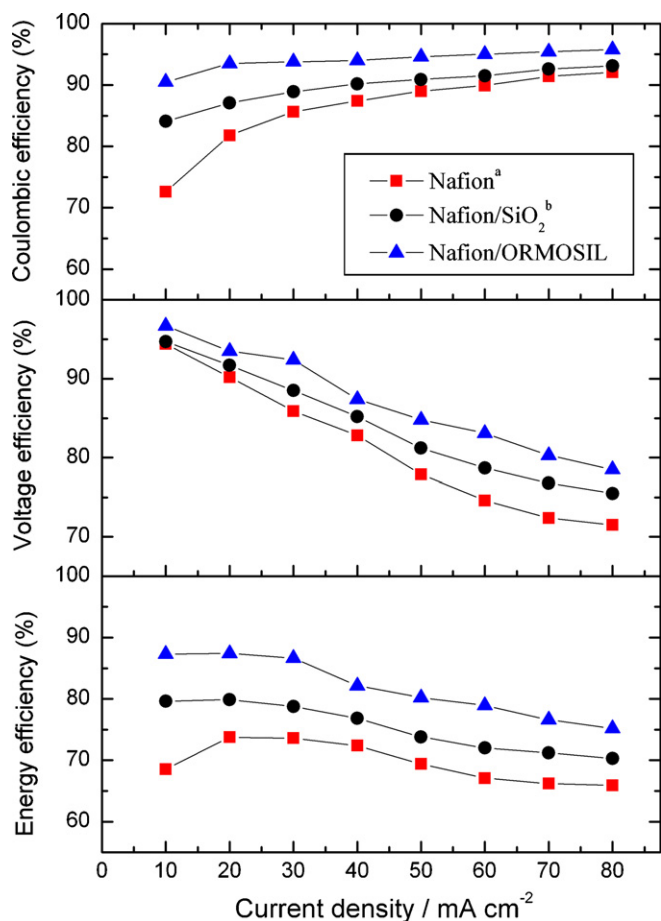


Fig. 7. Change of CE, VE and EE of VRB single cell with Nafion, Nafion/SiO₂ hybrid membrane and Nafion/ORMOSIL hybrids membrane under different current densities, ^{a,b}Data quoted form previous report [15].

the VRB with three kinds of membrane at all current densities. For example, the maximum CE of the VRB with Nafion/ORMOSIL hybrids membrane is 95.8% (80 mA cm⁻²), while the maximum CE of the VRB with Nafion membrane and the VRB with Nafion/SiO₂ membrane are 92.1% and 93.1% at the same current density. The maximum VE of the VRB with Nafion/ORMOSIL hybrids membrane is 96.5% (10 mA cm⁻²), while the maximum VE of the VRB with Nafion membrane and Nafion/SiO₂ membrane are 94.4% and 94.7% at the same current density. The maximum EE of the VRB with Nafion/ORMOSIL hybrids membrane is 87.4% (20 mA cm⁻²), while the maximum EE of the VRB with Nafion membrane and Nafion/SiO₂ membrane are 73.8% and 79.9% at the same current density.

The fact that the CE of VRB with Nafion/ORMOSIL hybrids is higher than that of the VRB with Nafion membrane can be attributed to the ORMOSIL nanoparticles filled or partly filled into the Nafion clusters and restrained the crossover of vanadium ions [15,31–34]. Furthermore, the Nafion/ORMOSIL hybrids membrane has network structure, i.e. Q and D units as shown in Fig. 3. The ORMOSIL phase and the presence of relatively big -CH₃ groups within the hybrids membrane can more efficiently prevent the crossover of vanadium ions than the single Q units in Nafion/SiO₂ hybrid membrane. And thus the CE, VE and EE of the VRB with Nafion/ORMOSIL hybrids membrane are further improved than that of the VRB with Nafion/SiO₂ hybrid membrane.

Open circuit voltage (OCV) can be used to indicate the degree of self-discharge of a cell. In this work, OCV of the VRB was monitored at room temperature after it was charged to a 75% state of

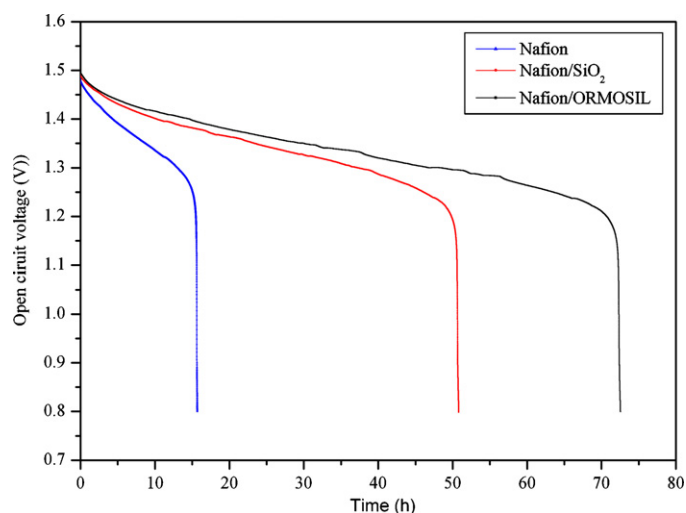


Fig. 8. Comparison of the OCV values between VRB single cell with Nafion, Nafion/SiO₂ and Nafion/ORMOSIL membranes.

charge (SOC). The electrolytes were pumped into the cell unceasingly during the self-discharge test. The OCV of VRB with Nafion, Nafion/SiO₂ and Nafion/ORMOSIL are shown in Fig. 8. As shown, the OCV value of the VRB with three kinds of membranes all decreases gradually with the time at first and then drops sharply. As for the VRB with Nafion/ORMOSIL hybrids membrane, the time for OCV value remaining beyond 0.8V is nearly 73 h. For VRB with Nafion/SiO₂ and Nafion membrane, the value is only about 51 h and 16 h, respectively. The self-discharge of VRB is mainly due to the crossover of vanadium ions through the membrane. This result shows that the self-discharge of VRB has been reduced remarkably by using the modified hybrid membrane and the performance of Nafion/ORMOSIL is superior to that of Nafion and Nafion/SiO₂.

The cycle performance of VRB single cell with Nafion/ORMOSIL hybrids membrane is measured and compared with the VRB with Nafion/SiO₂ hybrid membrane as shown in Fig. 9. As presented, the CE and EE of the VRB cell with Nafion/ORMOSIL are nearly no attenuation over 100 cycles under a charge–discharge current of 60 mA cm⁻², which indicates that the Nafion/ORMOSIL hybrids membrane can be used in VRB system with stable state under

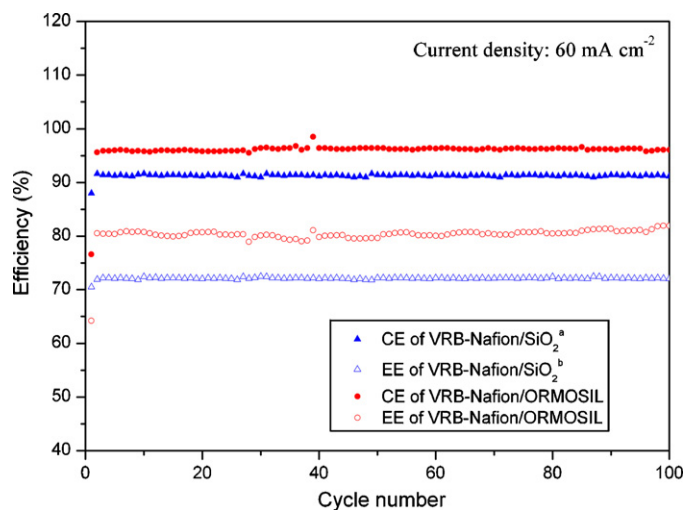


Fig. 9. Cycle performance of VRB with Nafion/ORMOSIL and Nafion/SiO₂ membranes at a current density of 60 mA cm⁻². Charge capacity was controlled to be 1600 mA h corresponding to a redox couples utilization of 75%, ^{a,b}Data quoted form previous report [15].

sulfuric acid solution. In addition, the CE and EE of VRB with Nafion/ORMOSIL membrane are always higher than that of the VRB with Nafion/SiO₂ hybrid membrane, which was in accordance with the aforementioned studies.

4. Conclusions

Novel Nafion/ORMOSIL hybrids membrane for vanadium redox flow battery (VRB) was prepared by *in situ* sol–gel reactions. The primary properties of the prepared membrane and the performance of the VRB with it were investigated. Results showed that the ion exchange capacity (IEC), thickness and the proton conductivity of Nafion/ORMOSIL hybrids membrane were almost the same as unmodified Nafion membrane. The permeation of vanadium ions across the membrane has been reduced significantly by using modified Nafion/ORMOSIL hybrids membrane. The performance of VRB single cell with Nafion/ORMOSIL membrane has been remarkably improved owing to the good vanadium restraining characteristic of novel hybrids membrane. It was found that the coulombic efficiency, voltage efficiency and energy efficiency of VRB with Nafion/ORMOSIL hybrids membrane were much higher than that of the VRB with unmodified Nafion membrane and previously reported Nafion/SiO₂ membrane. The self-discharge of the VRB with Nafion/ORMOSIL hybrids membrane is much slower than that of the VRB with Nafion and Nafion/SiO₂ hybrid membrane. Cycling test of the VRB with prepared hybrids membrane proved that it has good chemical stability in strong oxidization acid conditions. In summary, this novel type of membrane has shown excellent cell performance and is very suitable for use as the ion exchange membrane in VRB.

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