

# Nafion/TiO<sub>2</sub> hybrid membrane fabricated via hydrothermal method for vanadium redox battery

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**Abstract** To improve the performance of Nafion membrane as a separator in vanadium redox battery (VRB) system, a Nafion/TiO<sub>2</sub> hybrid membrane was fabricated by a hydrothermal method. The primary properties of this hybrid membrane were measured and compared with the Nafion membrane. The Nafion/TiO<sub>2</sub> hybrid membrane has a dramatic reduction in crossover of vanadium ions compared with the Nafion membrane. The results of scanning electron microscope, energy dispersive X-ray spectroscopy, and X-ray diffraction of the hybrid membrane revealed that the TiO<sub>2</sub> phase was formed in the bulk of the prepared membrane. Cell tests identified that the VRB with the Nafion/TiO<sub>2</sub> hybrid membrane presented a higher coulombic efficiency (CE) and energy efficiency (EE), and a lower self-discharge rate compared with that of the Nafion system. The CE and EE of the VRB with the hybrid membrane were 88.8% and 71.5% at 60 mA cm<sup>-2</sup>, respectively, while those of the VRB with Nafion membrane were 86.3% and 69.7% at the same current density. Furthermore, cycling tests indicated that the Nafion/TiO<sub>2</sub> hybrid membrane can be applied in VRB system.

**Keywords** Vanadium redox battery · Nafion/TiO<sub>2</sub> hybrid membrane · Hydrothermal method · Vanadium permeability · Electrochemical performance

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## Introduction

Vanadium redox flow battery (VRB) has been well accepted as energy storage system since it was initially proposed by Skyllas-Kazacos in 1985 [1–4]. It employs V(II)/V(III) and V(IV)/V(V) redox couples in the negative and positive half-cell electrolytes which are separated by an ion exchange membrane (IEM) [5]. IEM is one of the key components in VRB system, which is used to prevent cross-mixing of the positive and negative electrolytes, but still to allow the transport of ions, such as proton, to complete the circuit during the passage of current. For the VRB system, an ideal membrane should possess good chemical stability, low permeability of vanadium ions, high proton conductivity, low cost, and so on [6, 7].

Nafion membrane (Du Pont. Co. Ltd, USA) has been generally used in VRB [6, 8] and proton exchange membrane fuel cells (PEMFC) [9, 10] due to its high ionic conductivity and excellent chemical stability. However, due to the poor ionic selectivity of Nafion membrane between proton and vanadium ions, the undesired transport of vanadium ions across it occurs in the charge–discharge process, which is a crucial obstacle to improve the performance of VRB including coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) [11]. Because vanadium ions transfer mainly in the form of hydrate vanadium ions [8], a significant amount of water transfers across the membrane, which can lead to a reduction in cell capacity due to concentration of active species on one side and dilution on the other side [12, 13]. In order to reduce the permeation of the vanadium ions and improve performance of Nafion membrane in VRB system, modifications of Nafion-based membrane are widely studied using different methods, such as layer-by-layer self-assembled technique [14], interfacial polymerization [15], impregnating method [16], and sol–gel method [17–19]. However, most of these methods require complicated operations and sometimes expensive or toxic reagents.

Nafion/TiO<sub>2</sub> hybrid membranes have been applied in PEMFC and direct methanol fuel cells due to its excellent water retention ability and electrochemical performance [20, 21]. Their results inspired us to exploit a Nafion/TiO<sub>2</sub> hybrid membrane as a separator in VRB to reduce the permeation of the vanadium ions and improve performance of the VRB. Hydrothermal method as an effective and simple method was widely used to prepare TiO<sub>2</sub> [22–24]. So far, few preparation of Nafion/TiO<sub>2</sub> hybrid membrane via the hydrothermal method and its application in VRB has been reported.

In this work, the Nafion/TiO<sub>2</sub> hybrid membranes were prepared by the hydrothermal method. The primary properties of the hybrid membrane such as water uptake, area resistance, ion exchange capacity (IEC), and vanadium permeability were determined in comparison with unmodified Nafion membrane. The distribution of Ti element in the surface and cross-section of the modified Nafion membrane was analyzed by scanning electron microscope (SEM)-EDX and X-ray diffraction (XRD) techniques. The performances of VRB single cell including charge–discharge curves, open-circuit voltage and cycle performance with the modified and unmodified Nafion membranes were investigated.

## Experimental

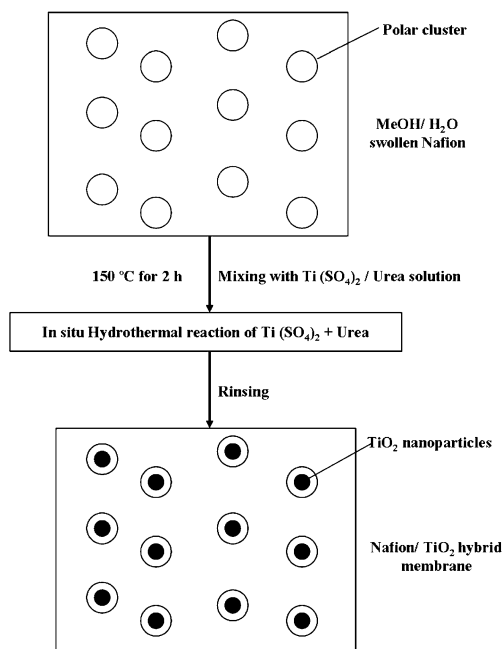
### Materials

Nafion membrane (Nafion 117) was purchased from DuPont Co. Ti(SO<sub>4</sub>)<sub>2</sub> was purchased from Sinopharm Chemical Reagent Co. Ltd, urea was from Guangzhou Chemistry Reagent Factory. VOSO<sub>4</sub>·nH<sub>2</sub>O was prepared in our laboratory. All chemicals were used as received without further purification.

### Preparation of the hybrid membrane

Prior to modification, the Nafion membrane was pretreated according to [25]. The membrane was first cleaned in a 3% (wt) H<sub>2</sub>O<sub>2</sub> solution at 80 °C for 1 h, rinsed in deionized water at 80 °C for 30 min, and then treated in 1.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution at 80 °C for 30 min. Finally, it was rinsed in deionized water at 80 °C for several times to remove the trace of H<sub>2</sub>SO<sub>4</sub>, and then stored in deionized water for use.

All pretreated membranes were dried at 110 °C under vacuum for 24 h and weighted before the hydrothermal reaction. The process of fabrication of Nafion/TiO<sub>2</sub> hybrid membranes was illustrated in Fig. 1. In a typical procedure, a piece of Nafion membrane (6×6 cm) was firstly swollen in the MeOH/H<sub>2</sub>O=3:1 (vol/vol) for 24 h at room temperature. Then the swollen membrane and the 80 mL premixed Ti(SO<sub>4</sub>)<sub>2</sub>/urea



**Fig. 1** Process of formulation of Nafion/TiO<sub>2</sub> hybrids membrane

solution ( $n_{\text{TiSO}_4}/n_{\text{urea}}=1:2$ ) were transferred to a 100 mL Teflon-lined stainless steel autoclave. The reaction system was kept at 150 °C for 2 h and then cooled to room temperature. When the membrane was taken from the mixed solution, it was quickly soaked in deionized water for several times to wash away excess reactants adhering to the membrane surface. The resulting membranes were stored in deionized water for use.

### Primary properties of the hybrid membrane

The IEC of the membranes is calculated by following equation described by Kazacos [26].

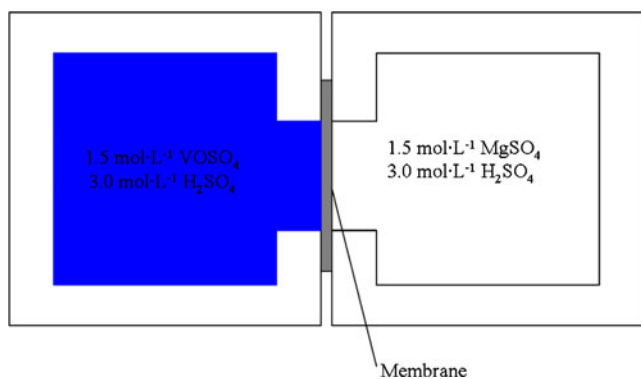
$$\text{IEC} = \frac{M_{0, \text{NaOH}} - M_{\text{E}, \text{NaOH}}}{W_{\text{d}}} \quad (1)$$

where,  $M_{0, \text{NaOH}}$  is the moles of NaOH in the flask at the beginning of titration,  $M_{\text{E}, \text{NaOH}}$  is the moles of residual NaOH after the membrane equilibrated within it for 48 h, and  $W_{\text{d}}$  is the weight of the dry membrane (g).

The water uptake is another important property of ion exchange membranes. Water uptake was calculated according to the following equation [27]:

$$\text{Water uptake}(\%) = \frac{W_{\text{w}} - W_{\text{d}}}{W_{\text{d}}} \times 100\% \quad (2)$$

where,  $W_{\text{w}}$  and  $W_{\text{d}}$  are weight of the membranes in wet and dry state, respectively.



**Fig. 2** Equipment for the measurement of VO<sup>2+</sup> permeability

The weight uptake of TiO<sub>2</sub> was determined relative to that of the weight of Nafion membrane, which was calculated as the following equation:

$$\text{TiO}_2 \text{ content (\%)} = \frac{W_m - W_i}{W_i} \times 100\% \quad (3)$$

where,  $W_m$  is the weight of dry Nafion/TiO<sub>2</sub> hybrid membrane, and  $W_i$  is the weight of Nafion membrane, respectively.

Area resistance (AR) of the membrane was determined according to the method proposed by Hwang [28]. Prior to AR measurement, the membranes were immersed into a solution of 1.5 mol·L<sup>-1</sup> VOSO<sub>4</sub> in 3.0 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> for 24 h. A conductivity cell was separated into two compartments filled with 1.5 mol·L<sup>-1</sup> VOSO<sub>4</sub> in 3.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution. The effective area of membrane ( $S$ ) was 1.0 cm<sup>2</sup>. Two platinum electrodes with an area of 1×1 cm were held at a fixed distance apart and a constant depth of immersion. The electric resistances of the conductivity cell with a membrane ( $r_1$ ) and without the membrane ( $r_2$ ) were measured by electrochemical impedance spectroscopy over a frequency range of 100 kHz to 100 mHz using a PARAST electrochemistry workstation (USA, AMETEK, Inc.) at room temperature. In this work,  $r_1$  and  $r_2$  values were obtained by interpolating the impedance data to the real axis on the high frequency side (49,535~39,194 Hz), respectively. AR was calculated from the following equation:

$$\text{AR} = (r_1 - r_2)S \quad (4)$$

The equipment for the measurement of the permeability of vanadium ions through the membrane was illustrated in

Fig. 2 [17, 27]. The membrane was exposed to a solution of 1.5 mol L<sup>-1</sup> VOSO<sub>4</sub> in 3.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> on left side and a solution of 1.5 mol L<sup>-1</sup> MgSO<sub>4</sub> in 3.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> on the right side. MgSO<sub>4</sub> was used to equalize the ionic strengths of the two solutions and to minimize the osmotic pressure effects. The effective area of the exposed membrane was 1 cm<sup>2</sup> and the volume of the solutions for each reservoir was 30 mL. The two solutions were continuously stirred during measurements at room temperature. Samples in the right reservoir were taken at a regular time interval and analyzed for vanadium ions concentration by a UV-vis spectrometer.

The vanadium ion permeability is calculated by the following equation [18, 29].

$$V_R \frac{dc_R(t)}{dt} = A \frac{P}{L} [c_L - c_R(t)] \quad (5)$$

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 the permeability of the vanadium ions, and  $V_R$  is the volume of right reservoir. It is supposed that the change of vanadium ion concentration in the left reservoir can always be negligible and a pseudo-steady-state condition is used inside the membrane.

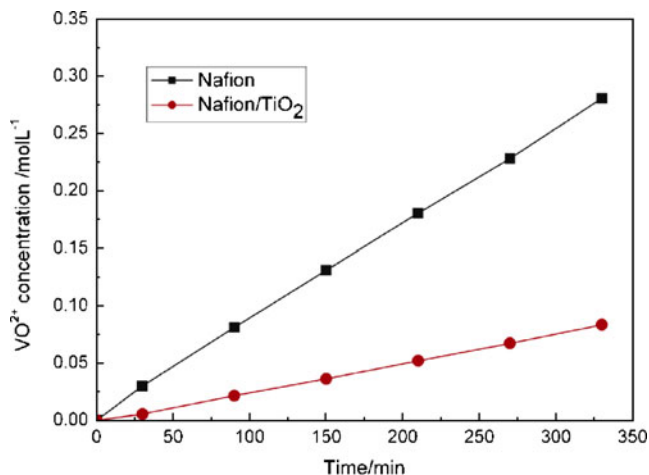
Both the morphologies and energy dispersive X-ray spectroscopy (EDS) of the membranes were observed by a JSM-6360LV scanning electron microscope. XRD of the Nafion/TiO<sub>2</sub> hybrid membrane was obtained by a MXPAHF X-ray diffractometer from 5° to 80° with a Cu Kα of 1.54056 Å.

#### VRB single cell test

In the charge–discharge tests of the VRB single cell, the mixed solutions of 1.5 M V<sup>3+</sup>/V<sup>4+</sup> in 3.0 M H<sub>2</sub>SO<sub>4</sub> were employed as negative and positive electrolytes. Two pieces of 5 cm thickness carbon felt (Shenhe carbon fiber Materials Co., Ltd.) with effective reaction area of 9 cm<sup>2</sup> were served as the electrodes. Two graphite plates (Wuxi Boyo carbon Co., Ltd.) were used as the current collectors. The VRB single cell was charged and discharged at different current density. To avoid the corrosion of the carbon felt electrode and graphite plates, the upper limit of charge voltage was 1.70 V and the lower limit of discharge voltage was 0.7 V. All charge–discharge tests were carried

**Table 1** Comparison of primary properties between Nafion and Nafion/TiO<sub>2</sub> hybrid membrane

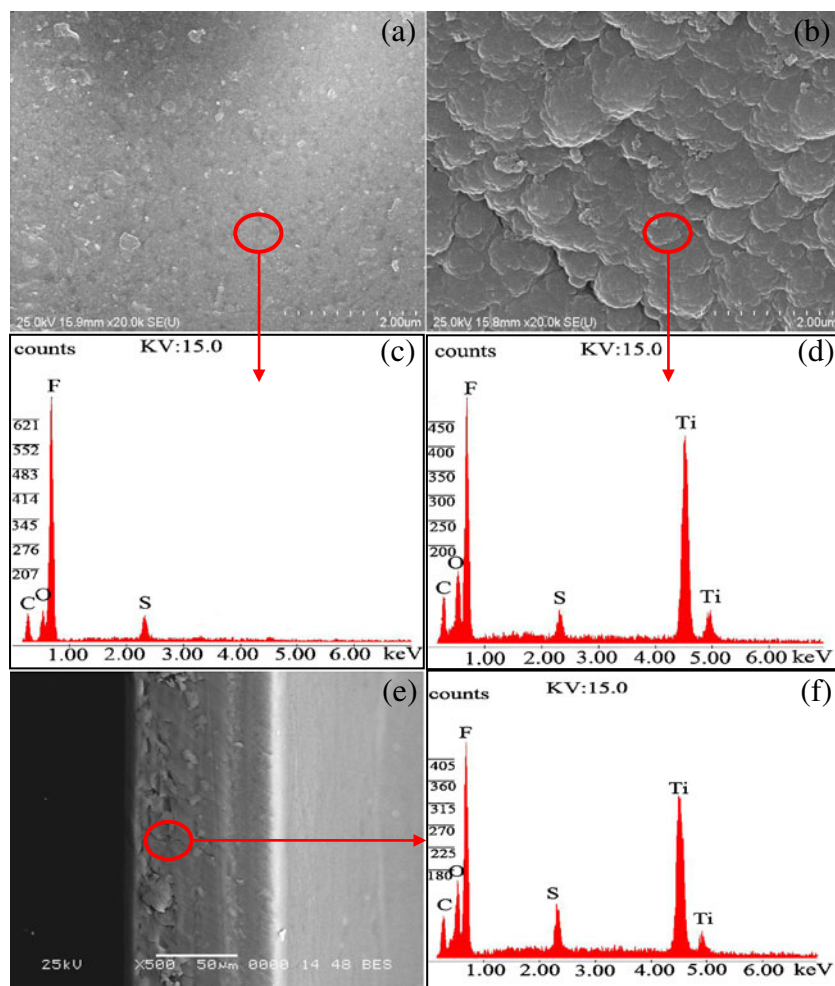
Membrane	Modifier content (wt.%)	Thickness (μm)	IEC (mmol g <sup>-1</sup> )	AR (Ω cm <sup>2</sup> )	Water uptake (%)
Nafion	–	89	0.88	1.04	21.15
Nafion/TiO <sub>2</sub>	8.3	90	0.85	1.05	19.13



**Fig. 3** Change of concentration of VO<sub>2</sub><sup>+</sup> with time in the right reservoir of the cell with Nafion and Nafion/TiO<sub>2</sub> membranes

out using a CT2001C-10 V/2A battery test system (Wuhan Land Co., Ltd.).

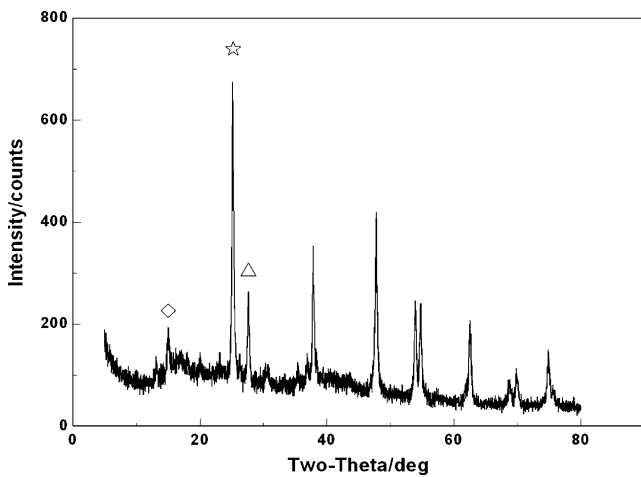
**Fig. 4** SEM images of **a** Nafion membrane surface, **b** Nafion/TiO<sub>2</sub> hybrid membrane surface, **e** the cross-section of Nafion/TiO<sub>2</sub> hybrid membrane; EDS spectra of **c** Nafion membrane surface, **d** Nafion/TiO<sub>2</sub> hybrid membrane surface, **f** the cross-section of Nafion/TiO<sub>2</sub> hybrid membrane



## Results and discussion

### Primary properties of the hybrid membrane

IEC, water uptake, AR, and thickness of the Nafion and Nafion/TiO<sub>2</sub> hybrid membranes were determined and summarized in Table 1. It can be seen that the Nafion/TiO<sub>2</sub> hybrid membrane exhibits nearly the same IEC value (0.85 mmol g<sup>-1</sup>) as that of the Nafion membrane, indicating that the introduction of TiO<sub>2</sub> by hydrothermal synthesis into polar clusters of Nafion membrane does not incorporate the ion exchange groups (-SO<sub>3</sub>H). Compared with the Nafion membrane, the water uptake of the hybrid membrane slightly decreased to 19.13%. It may be due to the fact that the pores of Nafion membrane are partly filled by TiO<sub>2</sub> particles. AR of the Nafion/TiO<sub>2</sub> hybrid membrane is almost similar to that of the original membrane although the thickness of the hybrid one with 8.3% TiO<sub>2</sub> modifier content is slightly increased.



**Fig. 5** XRD patterns of Nafion/TiO<sub>2</sub> hybrid membrane (*star* TiO<sub>2</sub>, *diamond* C-F, *triangle* VO<sub>2</sub>)

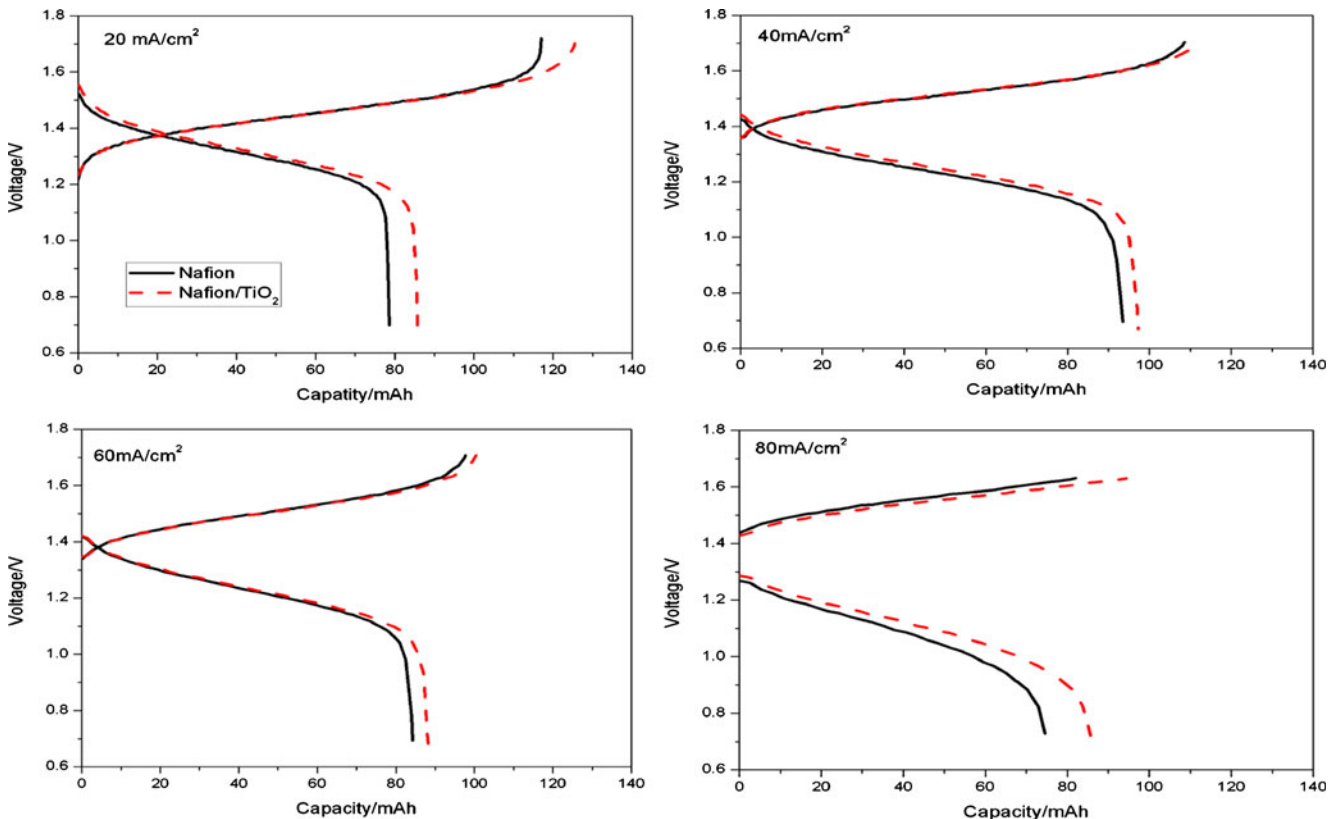
Permeability of vanadium ions

Diffusion of vanadium ions with different oxidation states across the separator is disadvantageous to VRB because it will lead to self-discharge of the battery and lower the coulombic efficiency. The permeability of VO<sup>2+</sup> across the

Nafion and Nafion/TiO<sub>2</sub> hybrid membrane was measured under the same condition. The change of concentration of VO<sup>2+</sup> (vs. time) was presented in Fig. 3. It is obvious that the vanadium ions diffusion through the Nafion membrane is remarkably faster than that through the Nafion/TiO<sub>2</sub> hybrid membrane. By calculating according to Eq. 5, it is found that the vanadium ion permeability (*P*) decreased from 2.26 × 10<sup>-5</sup> to 6.72 × 10<sup>-6</sup> cm<sup>2</sup>·min<sup>-1</sup> after modification. The decrease of permeability could be attributed to the fact that the polar clusters of Nafion membrane have been partly filled by TiO<sub>2</sub> particles, which will be further confirmed by SEM-EDS and XRD analysis.

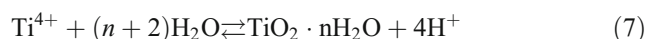
SEM-EDS and XRD analysis

Firstly, compared with the surface of Nafion membrane in Fig. 4a, there is a uniform particle layer located on the surface of Nafion/TiO<sub>2</sub> hybrid membrane in Fig. 4b. Comparing the EDS in Fig. 4c and d, it indicates that Ti element is well formed inside the modified membrane while there is no Ti element in the original Nafion membrane. These results confirm that TiO<sub>2</sub> particles are successfully fabricated in the surface of the fabricated membrane. Secondly, the cross-sectional morphology in Fig. 4e and



**Fig. 6** Charge–discharge curves for VRB with Nafion membrane and Nafion/TiO<sub>2</sub> hybrid membrane at various current densities

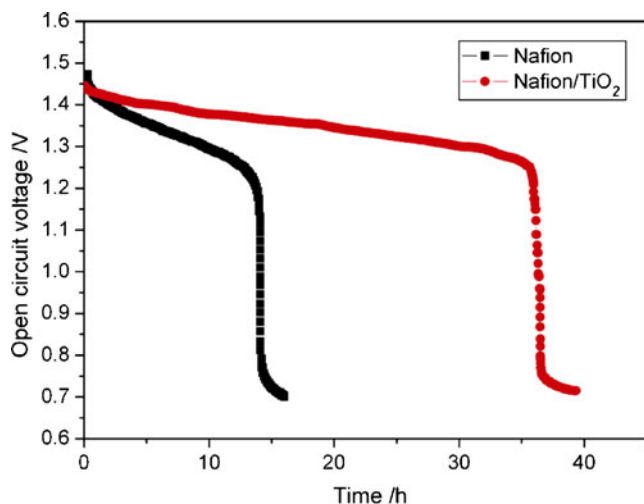
EDS in Fig. 4f show that  $\text{TiO}_2$  particles are located in the bulk of the prepared membrane. This can be explained by the in situ hydrothermal synthesis process within the Nafion membrane. Prior to modification, the polar clusters of the Nafion membrane were swollen by  $\text{MeOH}/\text{H}_2\text{O}$  solution, which is helpful for  $\text{Ti}^{4+}$  and urea molecules to migrate to the polar clusters. When the hydrothermal reaction took place,  $\text{Ti}^{4+}$  and urea reacted to fabricate  $\text{TiO}_2$ . The reaction mechanism is shown in Eq. 6 and 7 [24].



Furthermore, Fig. 5 shows XRD patterns of Nafion/ $\text{TiO}_2$  hybrid membrane. Before the XRD test, the hybrid membrane was used for a 40 cycle charge–discharge test at a current density of  $20 \text{ mA cm}^{-2}$ . There is an obviously characteristic peak of  $\text{TiO}_2$  after charge/discharge cycling. It indicates that Nafion/ $\text{TiO}_2$  hybrid membrane showed a good chemical stability in the VRB.

#### VRB single cell performance

The charge–discharge curves of VRB with Nafion and Nafion/ $\text{TiO}_2$  membranes at different current densities are presented in Fig. 6. It can be seen that with the current density varying from 20 to  $80 \text{ mA cm}^{-2}$ , the discharge capacity of VRB with Nafion/ $\text{TiO}_2$  hybrid membrane is higher than that of VRB with Nafion membrane, which is due to the reduction of permeation of vanadium ions across the hybrid membrane. The mean charge and discharge



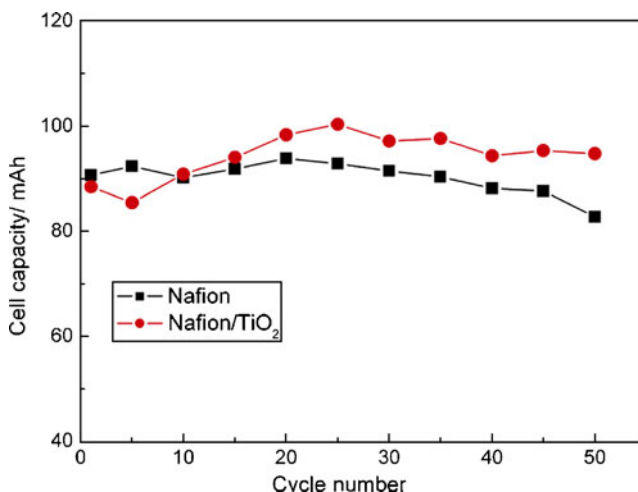
**Fig. 7** Comparison of the Open circuit voltage (OCV) between VRB single cell with Nafion and Nafion/ $\text{TiO}_2$  membranes

**Table 2** Performance of VRB with Nafion and Nafion/ $\text{TiO}_2$  hybrid membrane at  $60 \text{ mA cm}^{-2}$

Membrane	CE (%)	VE (%)	EE (%)
Nafion	86.3	80.6	69.6
Nafion/ $\text{TiO}_2$	88.8	80.5	71.5

voltages of the former are almost the same to that of the latter, which is in agreement with the fact that AR of the hybrid membrane is almost equal to that of the Nafion membrane. Furthermore, the discharge capacity of VRB with the each membrane increases at first, reaches the highest value at  $40 \text{ mA cm}^{-2}$ , and then decreases. This is attributed to the fact that at a low current density, the discharge time is long for a high-charge capacity so that the amount of vanadium ions permeating across the membrane is large, leading to the low discharge capacity [18]; at a high current density, the amount of vanadium ions permeating across the membrane is decreased due to the short discharge time, but the charge capacity at high charge current density is low due to stronger polarization effects [30], also leading to relative low discharge capacity. It is concluded that the lower utilization rate of electrolyte lead to the decrease of capacity at higher current densities.

Open-circuit voltage (OCV) can be used to evaluate 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 charge. The OCV curves of VRB with Nafion and Nafion/ $\text{TiO}_2$  membranes are shown in Fig. 7. It can be seen that the OCV value with the two membranes decreases gradually with the time at first and then drops sharply. As for the VRB with Nafion/ $\text{TiO}_2$  membrane, the time for OCV value remaining beyond



**Fig. 8** Cell capacity of VRB with Nafion or Nafion/ $\text{TiO}_2$  membrane vs. cycle number at a current density of  $60 \text{ mA cm}^{-2}$

1.2 V is nearly 37 h, while for Nafion membrane the value is only about 14 h. This means that the rate of self-discharge of VRB with Nafion membrane is faster than that of VRB with Nafion/TiO<sub>2</sub> hybrid membrane. The self-discharge of VRB is mainly attributed to the crossover of vanadium ions through the membrane.

The results of average CE, average VE, and average EE of the VRB with Nafion and Nafion/TiO<sub>2</sub> hybrid membrane at a current density of 60 mA cm<sup>-2</sup> are listed in Table 2. As shown in Table 2, the VRB employing Nafion/TiO<sub>2</sub> hybrid membrane presents a CE of 88.8%, which is higher than the value of 86.3% for VRB employing Nafion membrane. This is in good agreement with the fact that the high crossover of vanadium ions through the membrane results in a large loss of electrochemical energy [15]. Compared with EE value of 69.6% for Nafion membrane, the overall EE of VRB employing Nafion/TiO<sub>2</sub> hybrid membrane was 71.5%.

The average capacities of VRB with Nafion or Nafion/TiO<sub>2</sub> hybrid membrane during charge–discharge cycling at a current density of 60 mA cm<sup>-2</sup> were given in Fig. 8. The average capacities of VRB with Nafion/TiO<sub>2</sub> hybrid membrane are higher than those of VRB with Nafion membrane. This is owing to the reduction of vanadium ions permeation across the hybrid membrane during the charge–discharge cycling. With cycle number increasing, cell performance of Nafion/TiO<sub>2</sub> hybrid membrane is more stable than that of Nafion membrane in the VRB system.

## Conclusions

Nafion/TiO<sub>2</sub> hybrid membrane for VRB was fabricated by the hydrothermal method. The primary properties of this hybrid membrane, such as the IEC, thickness, AR and water uptake, were nearly unchanged after modification. The permeation of vanadium ions across the membrane was significantly decreased by using the Nafion/TiO<sub>2</sub> hybrid membrane. SEM-EDX and XRD analysis confirmed that TiO<sub>2</sub> particles were well formed in the prepared membrane. At the entire range of current densities (20–80 mA cm<sup>-2</sup>), the discharge capacities of VRB with the Nafion/TiO<sub>2</sub> hybrid membrane were higher than those of VRB with the original Nafion membrane. The VRB single cell with the hybrid membrane showed a higher CE and EE and a lower self-discharge rate than that of Nafion system. Cycling test of VRB with prepared Nafion/TiO<sub>2</sub> hybrid membrane proved that it has good chemical stability in strong oxidization acid conditions.

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