



Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery

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ARTICLE INFO

Article history:

Received 18 May 2009

Received in revised form 19 July 2009

Accepted 14 August 2009

Available online 22 August 2009

Keywords:

Vanadium redox flow battery

Water transfer

Vanadium ions transfer

Nafion membrane

ABSTRACT

Diffusion coefficients of the vanadium ions across Nafion 115 (Dupont) in a vanadium redox flow battery (VRFB) are measured and found to be in the order of $V^{2+} > VO_2^+ > VO_2 > V^{3+}$. It is found that both in self-discharge process and charge–discharge cycles, the concentration difference of vanadium ions between the positive electrolyte (+ve) and negative electrolyte (–ve) is the main reason causing the transfer of vanadium ions across the membrane. In self-discharge process, the transfer of water includes the transfer of vanadium ions with the bound water and the corresponding transfer of protons with the dragged water to balance the charges, and the transfer of water driven by osmosis. In this case, about 75% of the net transfer of water is caused by osmosis. In charge–discharge cycles, except those as mentioned in the case of self-discharge, the transfer of protons with the dragged water across the membrane during the electrode reaction for the formation of internal electric circuit plays the key role in the water transfer. But in the long-term cycles of charge–discharge, the net transfer of water towards +ve is caused by the transfer of vanadium ions with the bound water and the transfer of water driven by osmosis.

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1. Introduction

Vanadium redox flow battery (VRFB) is a kind of energy storage device, which was first put forward by Skyllas-Kazacos in 1984 [1]. In this battery, tetravalent vanadium ions (VO_2^+) and pentavalent vanadium ions (VO_2) are employed as the positive electro-active materials, and bivalent vanadium ions (V^{2+}) and trivalent vanadium ions (V^{3+}) are employed as the negative electro-active materials. Due to the advantages of the independence of output power and storage capacity, quick response, room temperature operation and long cycle life, several commercial VRFB systems for the application of UPS, load leveling, hybrid with wind energy and solar energy have been set up.

Cation exchange membranes are widely served as the separator in a VRFB. One of the main obstacles encountered when operating a VRFB is that the inevitable loss of energy capacity caused by the crossover of vanadium ions across the cation exchange membrane [2–5]. Thus, in order to optimize the operating conditions which can reduce the crossover of vanadium ions and prolong the long-term stability of the electrolyte, it is necessary to study the transfer behaviors of vanadium ions and water in an operating VRFB.

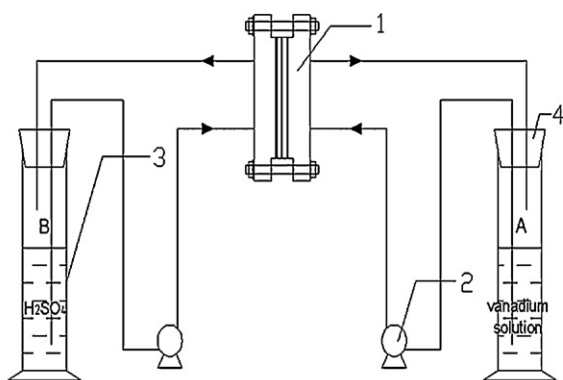
The diffusion coefficients of vanadium ions across the cation exchange membrane (CMS, CMV and CMX) had been determined using a dialysis cell as reported in literature [3]. But the diffusion coefficients of vanadium ions across a Nafion membrane had not been investigated. Moreover, the transfer behavior of water across the cation exchange membrane (Nafion 112, Gore L-01009 and Gore L-570) during self-discharge process at different initial SOC had been studied with a static dialysis cell [4]. It showed that when the electrolytes were at an initial SOC of 100% and 50%, the water transferred towards +ve. During the electrolytes discharged from 50 to 0% SOC, the water transferred towards –ve. But the transfer of vanadium ions in self-discharge process and the transfer of water and vanadium ions in charge–discharge cycles had not been reported yet. In the above-mentioned works, most of the studies were focused on small-scale and static sets, the transfer of water and vanadium ions in an operating VRFB stack had not been studied.

Due to the high proton conductivity and excellent chemical stability [6,7], Nafion membrane is considered as a suitable choice for the application in a VRFB. In this work, the diffusion coefficients of V^{2+} , V^{3+} , VO_2^+ and VO_2 across Nafion 115 were detected. Then, in order to well understand the mass transfer behaviors in an operating VRFB, the transfer of water and vanadium ions in self-discharge process and charge–discharge cycles were investigated by employing a kilowatt-class stack based on Nafion 115. At last, the reasons that caused transfer of water and vanadium ions in both self-discharge process and charge–discharge process were analyzed.

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1 - dialysis cell; 2 - pump; 3 - measuring cylinder; 4 - rubber plug.

Fig. 1. Schematic diagram of the dialysis cell employed for determining the diffusion coefficients of vanadium ions.

2. Experimental

2.1. Determination of diffusion coefficients for vanadium ions

In order to determine the diffusion coefficients of the vanadium ions penetrating through Nafion 115 (DuPont, USA), a dialysis cell with Nafion 115 was employed in the experiments. The effective area of the membrane was 50 cm². As shown in Fig. 1, the solutions containing V²⁺, V³⁺, VO²⁺ and VO₂⁺, respectively, were put in the enrichment side. The deficiency side was always the sulfuric acid.

In order to eliminate the osmosis of the anions, the total concentration of sulfate ion (SO₄²⁻) in both sides of the solutions were all 4.0 mol L⁻¹. The concentrations of vanadium ions were all 1.0 mol L⁻¹. There was 400 mL solution in each side of the cell. In this work, the decrease of vanadium concentration in the enrichment side caused by the diffusion of vanadium ions can be approximately ignored. 1 mL solution was sampled from the deficiency side about every 2 h in order to measure the amount of vanadium ions transferring from the enrichment side. Automatic potentiometric titration instrument (Model ZDJ-4A, Shanghai Precision & Scientific Instrument Corporation, China) was employed to analyze the concentration of vanadium ions with different valence state. The experiments mentioned above were carried out at room temperature unless otherwise specified.

2.2. VRFB stack and system

A kilowatt-class VRFB stack was employed to investigate the transfer of water and vanadium ions during self-discharge process and charge–discharge cycles. The stack was manufactured by filter-pressing 15 VRFB single cells. The effective area of each electrode was 875 cm². For each single cell, it was prepared with two carbon felt electrodes at each side of the membrane as positive electrode and negative electrode, respectively, graphite bipolar plates, PVC frames and gaskets. The VRFB system was assembled by connecting the stack with the positive and negative electrolyte tanks by two pumps and pipes as described elsewhere [6]. The volume of the electrolytes was 23 L containing 1.5 mol L⁻¹ VO²⁺ in positive electrolyte (+ve) and 1.5 mol L⁻¹ V³⁺ in negative electrolyte (-ve), respectively.

The charge–discharge performances of the VRFB stack were conducted by using a charge–discharge controller (Model BT 2000, Arbin Instruments Corp., USA). The upper limit voltage of charge was 23.25 V, corresponding to the SOC value of 65%. The lower limit voltage of discharge was 15 V.

2.3. Investigation on water transfer across Nafion 115 in an operating VRFB

The water transfer across Nafion 115 in both self-discharge process and charge–discharge cycles were investigated. For the former, after charging to 23.25 V, the stack was started to self-discharge. In such case, the electrolytes were forced into the positive and negative parts of the stack respectively by the pumps. The volume of +ve and -ve were recorded every several hours to measure the transfer of water across the membrane. The open circuit voltage (OCV) was recorded automatically by the charge–discharge controller. The water transfer behavior across Nafion 115 at an initial SOC of 0 was also investigated.

Water transfer behavior in charge–discharge cycles was also measured. In such experiments, the stack was charged to the upper limit voltage of 23.25 V and was discharged to the lower limit voltage of 15 V for each cycle. The volume of +ve and -ve were recorded about every 10 cycles.

2.4. Investigation on vanadium transfer across Nafion 115 in an operating VRFB

The self-discharge in a VRFB caused by the transfer of vanadium ions with different valence state across the ion exchange membrane was actually undesirable and unavoidable, which resulted in the energy loss of VRFB.

The transfer of vanadium ions across Nafion 115 in self-discharge process and charge–discharge cycles were measured by determining the concentration of vanadium ions and the corresponding volume of the electrolytes. The concentration of vanadium ions with different valence was determined by using an automatic potentiometric titration instrument (Model ZDJ-4A, Shanghai Precision & Scientific Instrument Corporation, China). The processes of self-discharge and charge–discharge were performed using the same operating methods as described in Section 2.3. The experiments mentioned above were carried out at room temperature unless otherwise specified.

3. Results and discussion

3.1. Diffusion coefficients of vanadium ions across Nafion 115

In this paper, the diffusion coefficients of vanadium ions across Nafion 115 were determined by using the method as described in Section 2.1. The diffusion coefficients of vanadium ions across Nafion 115 were calculated using the formulas as follows [8]:

$$\frac{dn_B(t)}{dt} = D \frac{A}{L} (C_A - C_B(t)) \quad (1)$$

in which D is the diffusion coefficients of vanadium ions (m² s⁻¹); A is the effective area of the membrane (m²); L is the thickness of the membrane (m); C_A is the concentration of vanadium ions in enrichment side (mol L⁻¹); C_B is the concentration of vanadium ions in deficiency side (mol L⁻¹); and t is the test time (s).

Assuming the volume of deficiency side (V_B) is a constant. Besides, the value of C_A can be approximately regarded as constant by employing a large volume (400 mL) of solution. Eq. (1) can be changed to:

$$V_B \frac{dC_B(t)}{dt} = D \frac{A}{L} (C_A - C_B(t)) \quad (2)$$

$$\frac{dC_B(t)}{C_A - C_B(t)} = \frac{DA}{V_B L} dt \quad (3)$$

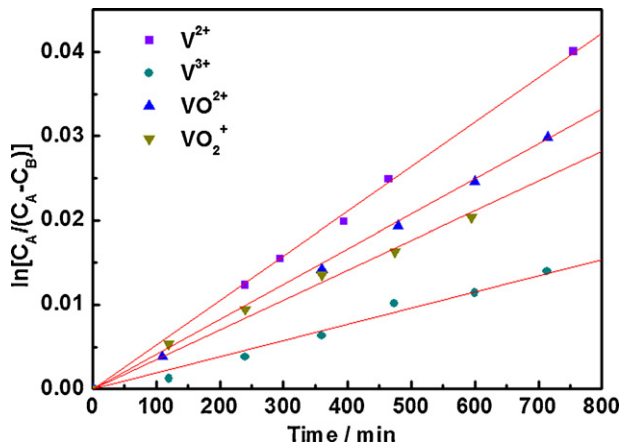
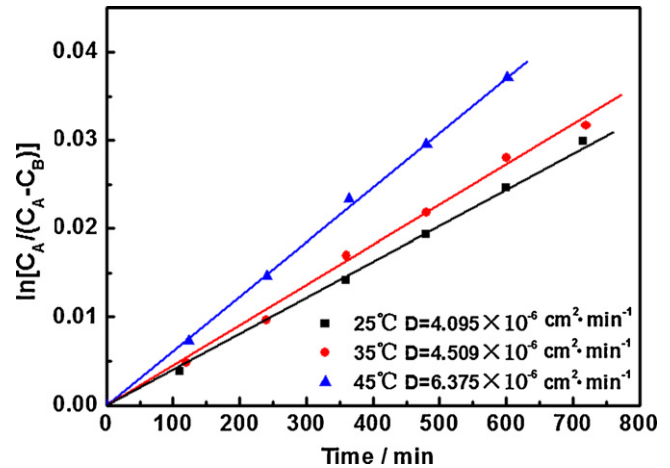
Fig. 2. Plots of $\ln(C_A/(C_A - C_B))$ vs. t .Fig. 3. Diffusion coefficients of VO_2^+ at different temperature.

Table 1

Diffusion coefficients of vanadium ions across Nafion 115.

Vanadium ions	V^{2+}	V^{3+}	VO_2^+	VO_2^+
Diffusion coefficient/ $\times 10^{-6} \text{ cm}^2 \text{ min}^{-1}$	5.261	1.933	4.095	3.538

$$-\int_0^{C_B} \frac{d(C_A - C_B(t))}{C_A - C_B(t)} = \frac{DA}{V_B L} \int_0^t dt \quad (4)$$

$$\ln\left(\frac{C_A}{C_A - C_B}\right) = \frac{DA}{V_B L} t \quad (5)$$

If plotting $\ln(C_A/(C_A - C_B))$ vs. t as shown in Fig. 2, the slope which corresponding to the value of $(DA/V_B L)$ can be obtained. Consequently, the diffusion coefficient D can be calculated from the value of $(DA/V_B L)$. The results obtained by the methods above-mentioned are listed in Table 1. It can be seen that the diffusion coefficient of V^{2+} across Nafion 115 is the largest one. The diffusion coefficients of vanadium ions is in the order of $\text{V}^{2+} > \text{VO}_2^+ > \text{VO}_2^+ > \text{V}^{3+}$.

The diffusion coefficients of V^{3+} , VO_2^+ and VO_2^+ across several kinds of membrane had been determined with a static dialysis cell [9,10]. It was found that the diffusion coefficient of VO_2^+ across Nafion 117 was $3 \times 10^{-6} \text{ cm}^2 \text{ min}^{-1}$ [9] and $3.655 \times 10^{-6} \text{ cm}^2 \text{ min}^{-1}$ [10], which was closed to that obtained in this work ($4.095 \times 10^{-6} \text{ cm}^2 \text{ min}^{-1}$). The diffusion coefficient of VO_2^+ was $7.02 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ [9]. And the value of V^{3+} was $3.56 \times 10^{-6} \text{ cm}^2 \text{ min}^{-1}$ [9], which was larger than the value obtained in this work ($1.933 \times 10^{-6} \text{ cm}^2 \text{ min}^{-1}$).

The diffusion coefficients of VO_2^+ in Nafion 115 membrane at different temperature were measured. The results are shown in Fig. 3. It can be seen that the diffusion coefficient of VO_2^+ increased with the increasing of temperature. The increasing rate is about $3\% / ^\circ\text{C}$.

3.2. Transfer of water and vanadium ions in the self-discharge process at an initial SOC of 0

The crossover of vanadium ions cannot be avoided if the electrolytes flow continuously at both sides of the membrane. Thus, the transfer behaviors of water and vanadium ions are important for understanding both self-discharge and charge–discharge processes of a VRFB. The transfer of water and vanadium ion was investigated at an initial SOC of 0 (in the case of VO_2^+ in +ve and V^{3+} in –ve). The results are shown in Figs. 4–7.

As shown in Fig. 4, it can be seen that both the volume of the electrolytes and the amount of vanadium ions decreased in +ve while increased in –ve. It seems that the transfer direction of water and that of vanadium ions are similar. The changes of the amount and concentration of V^{3+} and VO_2^+ in both +ve and –ve with respect to the self-discharging time are shown in Figs. 5 and 6, respectively. Because V^{3+} and VO_2^+ do not react with each other, the change rate of the vanadium amount in +ve and –ve can reflect the diffusion rate of V^{3+} and VO_2^+ . In Fig. 5, it shows that the amount of V^{3+} increased from 0 to 7 mol in +ve while decreased from 35.2 to 28 mol in –ve. And the amount of VO_2^+ decreased from 34.8 to

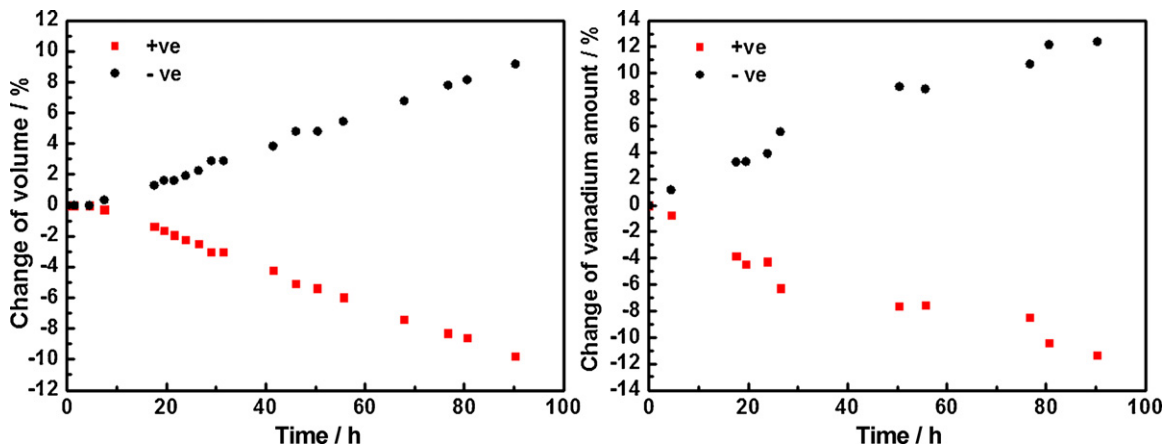


Fig. 4. Change of volume and vanadium amount in both +ve and –ve in the self-discharge process (the electrolytes were at an initial SOC of 0).

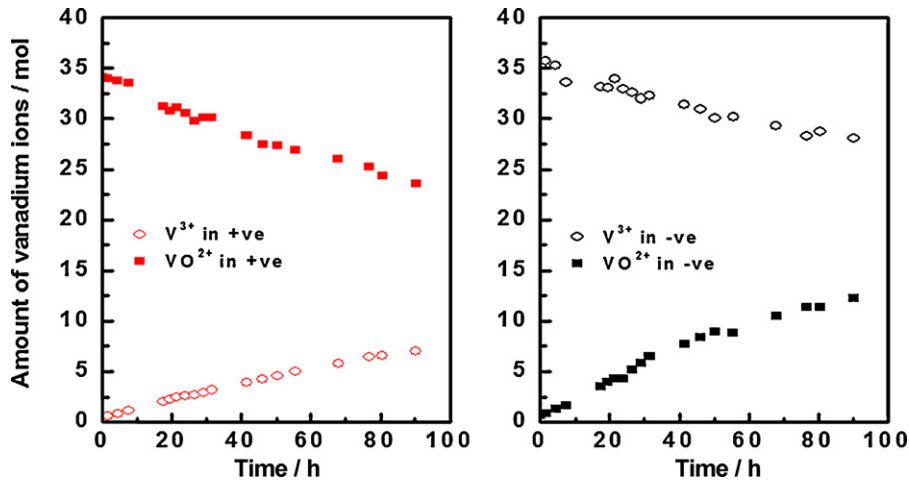


Fig. 5. Change of V^{3+} and VO^{2+} amount in +ve and –ve in the self-discharge process (the electrolytes were at an initial SOC of 0).

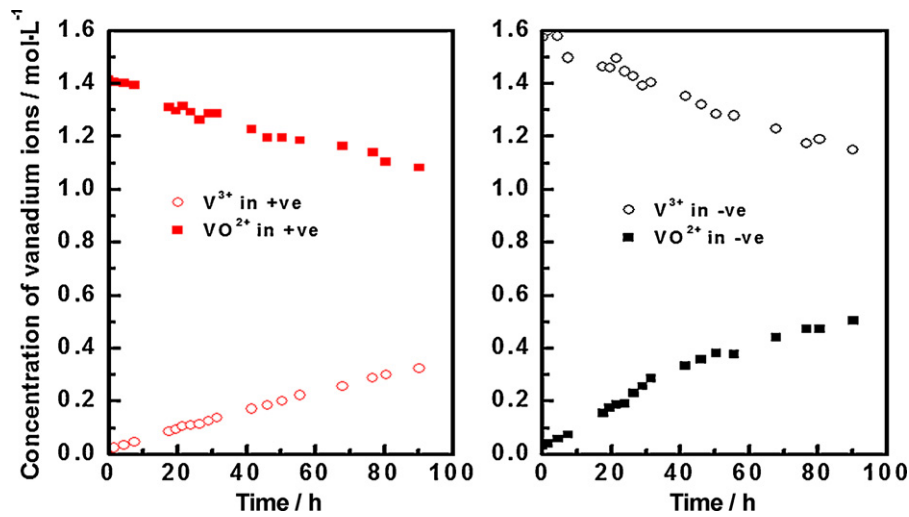


Fig. 6. Change of V^{3+} and VO^{2+} concentration in +ve and –ve in the self-discharge process (the electrolytes were at an initial SOC of 0).

23.2 mol in +ve while increased from 0 to 12 mol in –ve. It means that about 7 mol V^{3+} transferred from –ve to +ve, and about 12 mol VO^{2+} transferred from +ve to –ve. From Fig. 6, it can be seen that the concentration of V^{3+} increased from 0 to 0.32 mol L^{-1} in +ve while

decreased from 1.57 to 1.14 mol L^{-1} in –ve. And the concentration of VO^{2+} increased from 0 to 0.5 mol L^{-1} in –ve while decreased from 1.41 to 1.08 mol L^{-1} in +ve. It indicates that the concentration difference of V^{3+} between +ve and –ve was always a little larger than that of VO^{2+} . The ratio of “ VO^{2+} amount/ V^{3+} amount” that transferring across Nafion 115 is about 1.72, which is closed to the ratio of “diffusion coefficient of VO^{2+} /diffusion coefficient of V^{3+} ” (2.12 as shown in Table 2) if taking the difference of concentration difference into account.

During the transfer of vanadium ions across the membrane, in order to balance the charges, there should be a certain amount of protons with the equivalent positive charges transferring oppositely to the transfer direction of vanadium ions, as described in Eqs. (6) and (7). For example, if 1 mol VO^{2+} transfers from +ve to –ve, there will be 2 mol protons transferring from –ve to +ve to balance the charges (as described in Eq. (6)). For the same reason, if 1 mol V^{3+} transfers from –ve to +ve, there will be 3 mol protons transferring from +ve to –ve (as described in Eq. (7)). Assuming that there are 2.5 molecules of water dragged across Nafion 115 with each proton [11], thus the change of electrolyte weight caused by the transfer of vanadium ions and the protons can be calculated according to the change of the amount of V^{3+} and VO^{2+} (as shown in Fig. 5). The transfer of 1 mol VO^{2+} from +ve to –ve will result in a weight decrease of 65 g in +ve, corresponding to a volume decrease of 50 mL (the density of the vanadium solution is about 1.3 g cm^{-3}

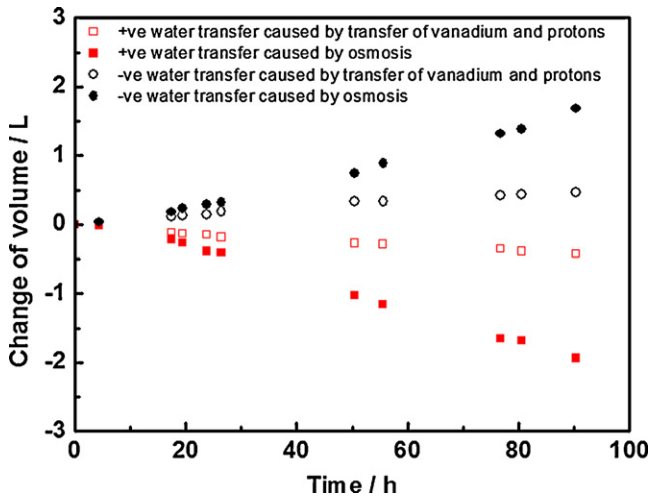


Fig. 7. Water transfer caused by osmosis and transfer of vanadium ions and protons in the self-discharge process (the electrolytes were at an initial SOC of 0).

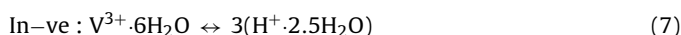
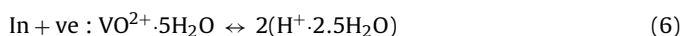
Table 2

The net diffusion rate of vanadium ions across Nafion 115.

Time/h	Diffusion rate of VO ²⁺ and VO ₂ ⁺ from +ve to -ve/ × 10 ⁻³ mol min ⁻¹	Diffusion rate of V ²⁺ and V ³⁺ from -ve to +ve/ × 10 ⁻³ mol min ⁻¹	The net diffusion rate/ × 10 ⁻³ mol min ⁻¹
0	5.35	5.84	-4.94
2.1	5.31	5.73	-4.20
3	5.40	5.81	-4.11
4.2	5.52	5.87	-3.49
5.5	5.34	5.65	-3.12
7.2	5.48	5.21	2.72
15.6	5.72	4.18	1.54
17.3	5.75	4.07	1.68
19.3	6.04	3.87	2.17
21.7	6.06	3.40	2.66
23.6	6.03	3.46	2.57
25	6.07	3.09	2.98

The minus value means the net transfer of vanadium ions is from -ve to +ve.

[4]). And the transfer of 1 mol V³⁺ from -ve to +ve will result in a weight decrease of 21 g in -ve, corresponding to a volume decrease of 16 mL.



In the experiment, the initial concentration of V³⁺ in -ve and VO²⁺ in +ve was similar. The unequal transfer of the vanadium ions across Nafion 115 will lead to the concentration difference of vanadium ions between +ve and -ve. In such cases, the water will transfer to the side of higher vanadium concentration driven by osmotic pressure. For example, if the concentration of vanadium increases in +ve, the water will transfer from -ve to +ve, and vice versa. Thus, the direction of water transfer driven by osmotic pressure will be the same as the net transfer direction of the vanadium ions. In summary, in the process of self-discharge at the initial SOC of 0, the water transfer across Nafion 115 is mainly caused by the transfer of vanadium ions and protons with the bound water, and the pressure difference of osmosis between the two sides of the membrane.

The transfer of water caused by osmosis can be estimated by subtracting the volume change caused by the transfer of vanadium ions and protons calculated as mentioned above from the total volume change. The results are shown in Fig. 7. The ratio of water transfer caused by the transfer of the vanadium ions and the corresponding protons and osmosis can be estimated. The percentage of water transfer caused by osmosis is about 75%.

3.3. Transfer of water and vanadium ions in the self-discharge process at an initial SOC of 65%

The transfer of water and vanadium ions in self-discharge process was investigated as described in Section 2. In this experiment, the electrolytes were at an initial SOC of 65%.

The changes of electrolyte volume during the self-discharge process were tested. As shown in Fig. 8, the volume of +ve increased and the volume of -ve decreased during the initial 7 h, indicating the water transfer direction was towards +ve. Afterwards the electrolyte volume of +ve decreased and that of -ve increased, indicating the reversal of the water transfer direction. The change of the total vanadium amount was the same as that of the electrolyte volume, indicating the transfer direction of vanadium ions was the same as that of water.

The changes of concentration of vanadium ions with the self-discharging time are shown in Fig. 9. It can be seen, after charging the stack to 23.25 V, the concentration of VO₂⁺ and V²⁺ in +ve and -ve was about 0.9 mol L⁻¹, respectively, and the concentration of VO²⁺ and V³⁺ in +ve and -ve was about 0.5 mol L⁻¹, respectively, corresponding to SOC value of 65%. When the self-discharge starting, both the concentration of VO₂⁺ and V²⁺ decreased linearly. Contrarily, both the concentration of VO²⁺ and V³⁺ increased linearly. The decrease of VO₂⁺ and V²⁺ concentration and the increase of VO²⁺ and V³⁺ concentration was not only due to the crossover of the vanadium ions but also related to the reactions involved in the electrolytes:

In +ve:

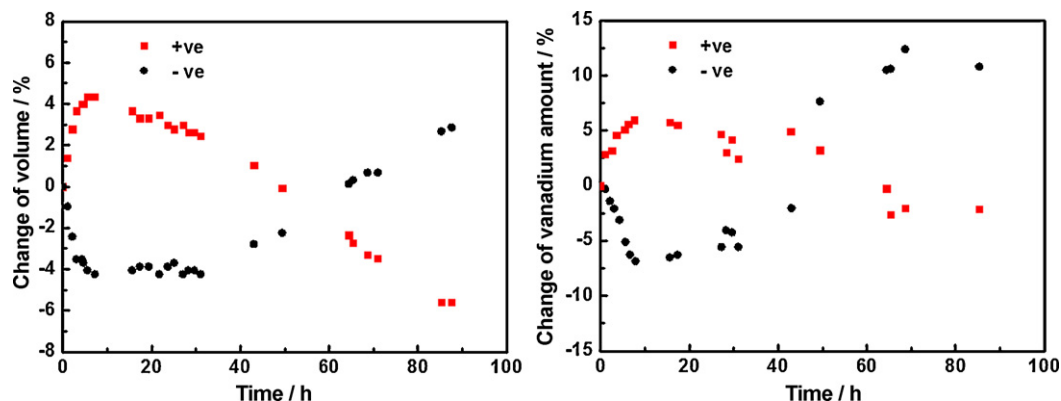


Fig. 8. Change of volume and vanadium amount in +ve and -ve in the self-discharge process (the electrolytes were at an initial SOC of 65%).

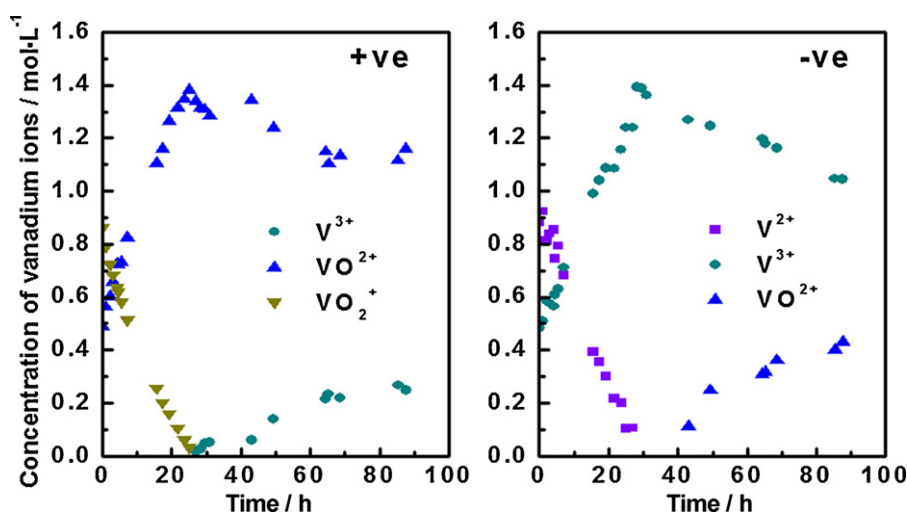


Fig. 9. Change of vanadium concentration in +ve and -ve in the self-discharge process (the electrolytes were at an initial SOC of 65%).



In -ve:



According to reactions 1 and 2, VO_2^+ in +ve reacted with V^{3+} and V^{2+} that transferring from -ve to generate VO^{2+} . This led to the decrease of VO_2^+ concentration and the increase of VO^{2+} concentration in +ve. Besides, according to reaction 3, V^{3+} appeared in +ve only when the concentration of VO_2^+ decreased to zero. For the similar reasons, according to reactions 4 and 5, V^{2+} in -ve reacted with VO_2^+ and VO^{2+} that transferring from +ve to generate V^{3+} . This caused the decrease of V^{2+} concentration and the increase of V^{3+} concentration in -ve. Besides, VO^{2+} appeared in -ve only when the concentration of V^{2+} decreased to zero according to reaction 6. As shown in Fig. 9, after discharging the battery for about 25 h, VO_2^+ exhausted in +ve; and after about 30 h, V^{2+} exhausted in -ve. And then V^{3+} and VO^{2+} appeared in +ve and -ve, respectively. After that, only VO^{2+} and V^{3+} coexisted in +ve and -ve. The decrease of the concentration of VO^{2+} and V^{3+} respectively in +ve and -ve was caused by the crossover of the vanadium ions.

The values of OCV measured during the self-discharging of the battery are shown in Fig. 10. As can be seen, there were two obvious decreases of the OCV value appearing at about 25 and 30 h, corresponding to the disappear of VO_2^+ in +ve and V^{2+} in -ve as discussed above.

According to Eq. (1), the transfer rate of vanadium ion across the membrane from the enrichment side to the deficiency side is determined by the concentration difference of the vanadium ion between +ve and -ve and the corresponding diffusion coefficient. Thus, the transfer rate of VO_2^+ and VO^{2+} from +ve to -ve, and that of V^{2+} and V^{3+} from -ve to +ve at a certain self-discharge time can be calculated by employing Eq. (1) and the data of vanadium concentration as shown in Fig. 9. The results are listed in Table 2. It can be seen that the transfer rate of V^{2+} and V^{3+} from -ve to +ve was larger than that of VO_2^+ and VO^{2+} from +ve to -ve when the self-discharge time was less than 7 h. After the initial 7 h, the transfer rate of VO_2^+ and VO^{2+} from +ve to -ve was larger than that of V^{2+} and V^{3+} from -ve to +ve. This means that after discharging the battery for 7 h, the total amount of V^{2+} and V^{3+} transferring from -ve to +ve was less than that of VO^{2+} and VO_2^+ from +ve to -ve. It is necessary to be indicated that in fact the transfer rate

of vanadium ions across the membrane at a certain time is determined by the value of SOC at that time. Thus, the net transfer of vanadium ions is determined by the value of SOC at the certain time. According to Eq. (1), in this experiment, when the value of SOC is 55%, the transfer amount of V^{2+} and V^{3+} from -ve to +ve is equal to the transfer amount of VO^{2+} and VO_2^+ from +ve to -ve. At this time, the net transfer amount of vanadium ions is zero. When the value of SOC is larger than 55%, the net transfer of vanadium ions across Nafion 115 is from -ve to +ve, and when it is less than 55%, the net transfer of vanadium ions is conversely from +ve to -ve.

The reason causing the transfer of water in the self-discharge process at the initial SOC of 65% is similar to that in the self-discharge at the initial SOC of 0. The transfer of water includes the transfer of vanadium ions with the bound water caused by the concentration difference and the corresponding transfer of protons with the dragged water to balance the charges, and the transfer of water driven by osmosis (as shown in Fig. 11). It can be easily understood that the transfer of water caused by the osmosis are also related to the value of SOC which is decreased due to the crossover of the vanadium ions during the self-discharge process, and the transfer direction of water is the same as the net transfer direction of vanadium ions.

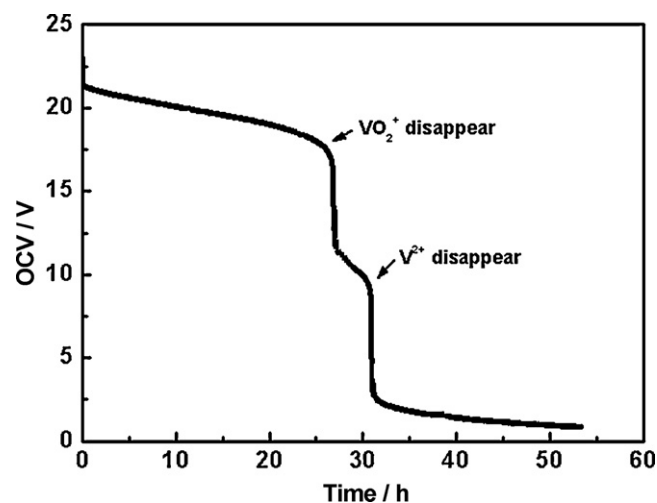


Fig. 10. The relationship between OCV and self-discharge time (the electrolytes were at an initial SOC of 65%).

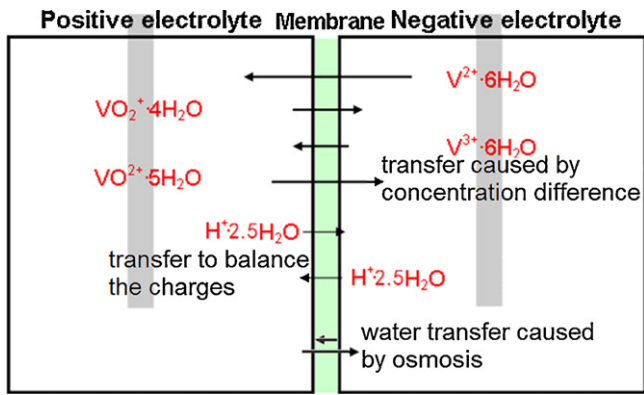


Fig. 11. Illustration of transfer of water and vanadium ions in self-discharge process.

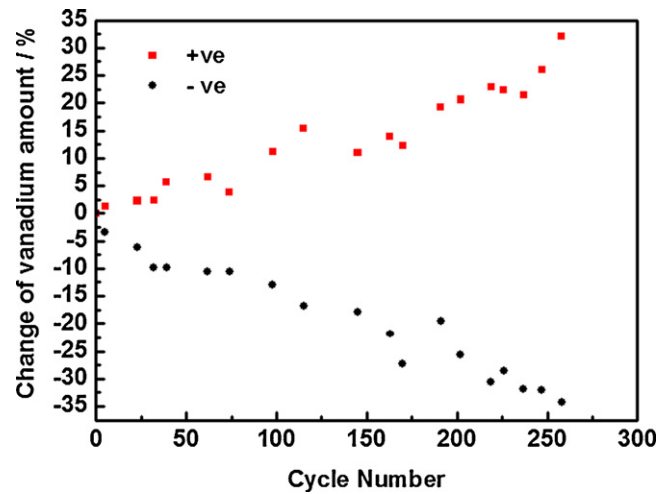


Fig. 12. Change of total amount of vanadium ions in the long-term cycles of charge–discharge.

3.4. Transfer of water and vanadium ions in charge–discharge process

The transfer of water and vanadium ions across the membrane occurs not only in self-discharge process, but also in charge–discharge cycles, which leads to the imbalance of the electrolytes and capacity loss. But the situations in the long-term cycles of charge–discharge are different from that in the self-discharge process, because during charge–discharge cycles there are always electrode reactions occurring.

3.4.1. Vanadium transfer in charge–discharge process

The changes of vanadium amount in both +ve and –ve during the successive 300 cycles of charge–discharge were measured and recorded as shown in Fig. 12. It can be seen that the amount of vanadium ions increased in +ve while decreased in –ve. In a charge–discharge cycle, due to the electrode reactions, V^{2+} and V^{3+} always exist in –ve and VO_2^+ and VO_2^+ always exist in +ve if the value of SOC and SOD is not 100%. Thus, VO_2^+ and VO_2^+ transfer across the membrane from +ve to –ve, and V^{2+} and V^{3+} transfer across the membrane from –ve to +ve during charge–discharge cycles. According to the experimental data shown in Fig. 12, the net transfer of vanadium is from –ve to +ve, indicating that the amount of vanadium ions transferring from –ve to +ve is larger than that of vanadium transferring from +ve to –ve. The experiments for further understanding the vanadium transfer mechanism in the process of charge–discharge are undergoing.

3.4.2. Water transfer in charge–discharge process

The volume changes of the electrolytes during the successive 300 cycles of charge–discharge are shown in Fig. 13a. As can be seen, the volume increased in +ve and decreased in –ve in the long-term cycles of charge–discharge. In Fig. 13b, the volume changes of the electrolytes during the successive 8 cycles of charge–discharge are presented. Within a single charge–discharge cycle, the volume of +ve decreased in the charge process and that of –ve decreased in the discharge process. It indicates that the water transferred from +ve to –ve during the charge process, and transferred from –ve to +ve during the discharge process. Besides, Fig. 13a and b also shows that the amount of water transferring to +ve is larger than that transferring to –ve in each cycle of charge–discharge. The net amount of water transferring to +ve is 24 mL on average in each charge–discharge cycle. But in the long-term cycles of charge–discharge of a VRFB, the direction of net transfer of water is similar to that of vanadium ions, indicating that the direction of water transfer is also the same as that of net vanadium transfer.

The transfer of water across the membrane in a charge–discharge cycle includes the transfer of vanadium ions with the bound water and the corresponding transfer of the protons with the dragged water to balance the charges, the transfer of water driven by osmosis, and the transfer of the protons with the dragged water across membrane for the formation of the internal

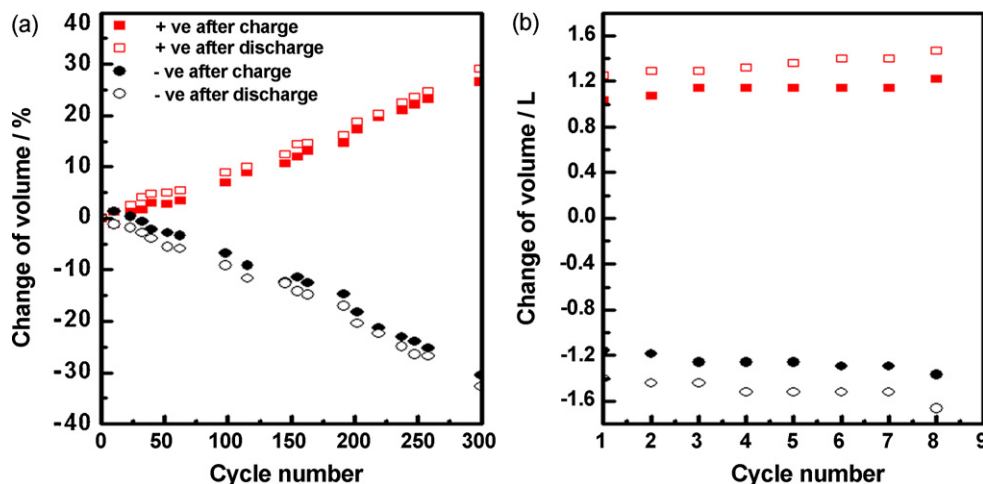


Fig. 13. Change of volume in the long-term cycles of charge–discharge.

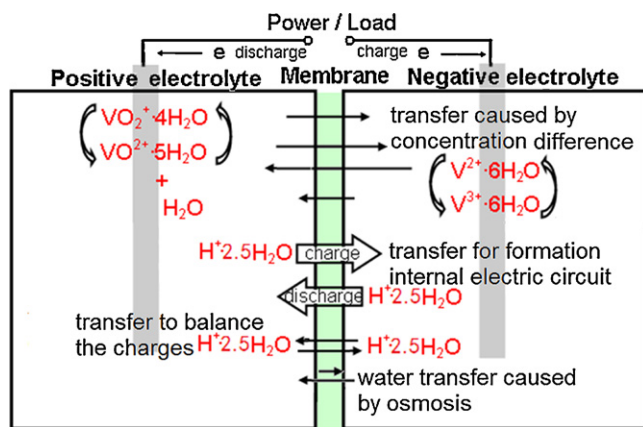


Fig. 14. Illustration of transfer of water and vanadium ions in charge–discharge cycles.

electric circuit in the electrolytes, among which the last one is the most important difference between the processes of self-discharge and charge–discharge.

In a charge process, the positive electrode is served as the anode, and the electrons transfer from positive electrode to negative electrode via the external circuit, thus there should be an equal amount of protons with the dragged water transferring from +ve to –ve for the formation of the internal electric circuit, resulting in the water transfer towards –ve. In a discharge process, the electrons transfer from negative electrode to positive electrode, thus causing the transfer of protons with the dragged water from –ve to +ve, and leading to the water transfer towards +ve.

All the factors causing the water transfer are shown in Fig. 14. According to the experimental data as shown in Fig. 13, although the transfer of protons with the dragged water for the formation of the internal electric circuit during the electrode reaction plays the important role in water transfer, in the long-term cycles of charge–discharge, the net transfer of water towards +ve is caused by the transfer of vanadium ions with the bound water and the transfer of water driven by osmosis.

4. Conclusion

Diffusion coefficients of four kinds of vanadium ions across Nafion 115 were measured and found to be in the order of $\text{V}^{2+} > \text{VO}^{2+} > \text{VO}_2^+ > \text{V}^{3+}$.

In both self-discharge process and charge–discharge cycles, the transfer of vanadium ions is caused by the concentration difference of the vanadium ions between +ve and –ve.

As for water transfer, in the case of self-discharge, the water transfer is caused by the transfer of vanadium ions with the bound water and the corresponding transfer of protons with the dragged water to balance the charges in the solution, and the water transfer driven by osmosis. It is calculated that about 75% of the net transfer of water is caused by osmosis. Furthermore, in self-discharge process, the transfer of vanadium ions and water at a certain time is determined by the instant value of SOC.

In the case of charge–discharge process, except the factors which caused water transfer in self-discharge process, the water transfer is also caused by the transfer of protons with the dragged water across Nafion 115 during the electrode reaction for the formation of the internal electric circuit in solution, which plays the key role in the water transfer in charge or discharge process. But in the long-term cycles of charge–discharge, the transfer of vanadium ions with the bound water and water transfer driven by osmosis are the main reasons leading to the net water transfer towards +ve.

Acknowledgements

Financial support from “863” project of MOST (Ministry of Science and Technology of China) (2006AA05Z255) is gratefully acknowledged.

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