



Simulation of the self-discharge process in vanadium redox flow battery

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ABSTRACT

A simple mathematical model is established to predict the self-discharge process in a kilowatt-class vanadium redox flow battery stack. The model uses basic mass transport theory to simulate the transfer of vanadium ions in the battery. The simulation results agree reasonably with the experimental values, confirming the validity of the model. It is found that the diffusion rate of vanadium ions depends on the diffusion coefficient, the partition coefficient and the concentration gradient of the vanadium ions between the two half cells. For the self-discharge process at the initial SOC of 0, the net transfer direction of vanadium ions is towards the negative electrolyte until the diffusion flux of V^{3+} becomes larger than that of VO^{2+} . For the self-discharge process at the initial SOC of 65%, the net transfer direction of vanadium ions is towards the positive electrolyte at the initial 20 h and then turns to the negative electrolyte. There are two obvious changes in the diffusion flux of vanadium ions at about 33 h and 43 h, corresponding to the vanishing time of VO_2^+ and V^{2+} respectively.

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1. Introduction

As a kind of rechargeable battery, the vanadium redox flow battery (VRFB) uses VO^{2+} and VO_2^+ vanadium ions as the positive electro-active species, and V^{2+} and V^{3+} as the negative electro-active species. Almost all the rechargeable batteries have the problem of energy capacity loss after long terms' charge–discharge operation. There are a variety of reasons resulting in the energy capacity loss in rechargeable batteries. For VRFB, the loss of energy capacity is mainly caused by self-discharge, i.e. the crossover of vanadium ions across the cation exchange membrane [1–5].

The transfer behavior of vanadium ions and water in VRFB has already been investigated by several groups. The diffusion coefficient of vanadium ions across the cation exchange membranes (CMS, CMV, CMX and Nafion) has been determined by Wiedemann et al. [1] and Sun et al. [2]. The transfer behavior of water across the commercial ion exchange membrane has been studied with a static dialysis cell by Sukkar and Skyllas Kazacos [3] and Mohammadi et al. [4], respectively. Moreover, Sun et al. [2] has investigated the transfer behavior of water and vanadium ions in self-discharge process and charge–discharge cycles by employing a kilowatt-class stack. However, most researches are focusing on the experimental studies and the conclusions are appropriate only for a certain condition. There is no research based on the math-

ematical model to study the self-discharge process of VRFB until now.

In this paper, a simple mathematical model is established to study the self-discharge process in VRFB. The model uses the basic mass transport theory and the parameters tested by Sun et al. [2] to simulate the transfer of vanadium ions in the battery. Based on the calculation of diffusion flux of vanadium ions, the self-discharge processes in a kilowatt-class stack at the initial state of charge (SOC) of 0 and 65% are simulated. The factors that influence the self-discharge rate are analyzed based on the calculated results.

2. Model development

2.1. Simulation of the transport of vanadium ions

The model domain together with a schematic concentration profile of species i (i denotes the vanadium ions) have been shown in Fig. 1. The modeled battery has been divided into three separated phases: the positive electrolyte, the membrane and the negative electrolyte. The species i is transported by diffusion and convection in the two liquid phases, whereas diffusion is the only transport mechanism in the membrane phase under self-discharge condition. The following mass transport equations can be used to describe the self-discharge process:

$$\nabla \cdot (-D_i \nabla C_i^p + C_i^p \vec{u}) = 0 \quad \text{in positive electrolyte} \quad (1)$$

$$\nabla \cdot (-D_i^m \nabla C_i^m) = 0 \quad \text{in membrane} \quad (2)$$

$$\nabla \cdot (-D_i \nabla C_i^n + C_i^n \vec{u}) = 0 \quad \text{in negative electrolyte} \quad (3)$$

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Nomenclature

<i>A</i>	area of the membrane (m ²)
<i>C</i>	concentration (mol m ⁻³)
<i>D</i>	diffusion coefficient (m ² s ⁻¹)
<i>F</i>	Faraday's constant (C mol ⁻¹)
<i>J</i>	diffusion flux (mol m ⁻² s ⁻¹)
<i>K</i>	partition coefficient (dimensionless)
<i>N</i>	number of cells (dimensionless)
Δn	change amount of vanadium ions (mol)
<i>P</i>	the liquid pressure (Pa)
<i>R</i>	universal gas constant (J mol ⁻¹ K ⁻¹)
<i>T</i>	temperature (K)
<i>U</i>	Nernst or equilibrium potential (V)
\vec{u}	velocity of the electrolyte flow (m s ⁻¹)
ΔV	change of electrolyte volume (L)

Greek

κ	permeability of the electrode (m ²)
μ	dynamic viscosity (Pa s)

Subscript

<i>i</i>	species $i \in \{V^{2+}, V^{3+}, VO_2^+, VO_2^+\}$
<i>in</i>	inlet value
<i>out</i>	outlet value
<i>p</i>	positive electrode quantity/property
<i>n</i>	negative electrode quantity/property

Superscript

<i>m</i>	membrane quantity/property
<i>p</i>	positive electrode quantity/property
<i>n</i>	negative electrode quantity/property

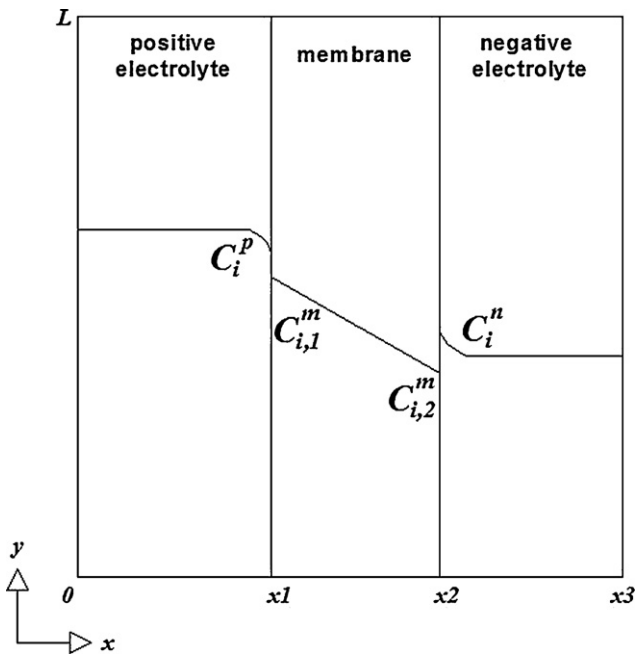


Fig. 1. Model domain together with a schematic concentration profile of species *i* (*i* denotes the vanadium ions).

where C_i represents the concentration of species *i* in the respective phases, D_i denotes the diffusion coefficient in the liquid phase, and D_i^m is the diffusion coefficient in the membrane, while \vec{u} denotes the velocity in the respective liquid phase. The velocity of the elec-

trolyte flowing through the porous electrode is described by Darcy's law:

$$\vec{u} = -\frac{\kappa}{\mu} \nabla P \tag{4}$$

where κ is the permeability of the porous media, and μ is the dynamic viscosity of the electrolyte. There are discontinuities in the concentration profile at the phase boundaries. The vanadium ions must dissolve into the membrane phase first in order to be transported through it. Therefore, the interface condition between the liquid and membrane phases for the concentration of species *i* can be described by the dimensionless partition coefficient, K_i [6]:

$$K_i = \frac{C_{i,1}^m}{C_i^p} = \frac{C_{i,2}^m}{C_i^n} \tag{5}$$

where $C_{i,1}^m$ denotes the concentration of species *i* in the membrane phase at the interface of positive electrolyte and membrane and $C_{i,2}^m$ denotes that at the interface of membrane and negative electrolyte.

It should be noted that the length of the battery is actually about 10 times longer than that is shown in the model. To avoid excessive amount of elements and nodes, the problem has been scaled. A new scaled coordinate y^* is introduced:

$$y^* = \frac{y}{\text{scale}} \tag{6}$$

In the mass transport equations (Eqs. (1)–(3)), *C* is differentiated twice in the diffusion term, which implies that the diffusion flux vector's *y* component must be multiplied by $(1/\text{scale})^2$. The convective term is only differentiated once, and therefore must be multiplied by a factor of $1/\text{scale}$. This leads to the following diffusion coefficient matrix:

$$\bar{D} = \begin{bmatrix} D & 0 \\ 0 & \frac{D}{\text{scale}^2} \end{bmatrix} \tag{7}$$

where *D* represents both D_i and D_i^m .

The concentration expression of the vanadium species at inlets is defined as:

$$C_i^{in} = C_i(t) \tag{8}$$

where $C_i(t)$ denotes the concentration of species *i* in the respective phase at time *t*. At the outlets ($y=L$), the diffusive fluxes of all species are set to zero:

$$-D \nabla C_i \cdot \vec{n} = 0 \tag{9}$$

At the boundaries between liquid and membrane phases, there are discontinuities in the concentration profile. To get continuous flux over the phase boundaries, apply a special type of boundary conditions:

$$(-D_i \nabla C_i^p + C_i^p \vec{u}) \cdot \vec{n} = C_i^m - K_i C_i^p \quad \text{at } x = x_1 \text{ for Eq. (1)} \tag{10}$$

$$(-D_i^m \nabla C_i^m) \cdot \vec{n} = K_i C_i^p - C_i^m \quad \text{at } x = x_1 \text{ for Eq. (2)} \tag{11}$$

$$(-D_i^m \nabla C_i^m) \cdot \vec{n} = K_i C_i^n - C_i^m \quad \text{at } x = x_2 \text{ for Eq. (2)} \tag{12}$$

$$(-D_i \nabla C_i^n + C_i^n \vec{u}) \cdot \vec{n} = C_i^m - K_i C_i^n \quad \text{at } x = x_2 \text{ for Eq. (3)} \tag{13}$$

All the other boundaries are set to walls, which mean the fluxes are zero:

$$(-D_i \nabla C_i + C_i \vec{u}) \cdot \vec{n} = 0 \tag{14}$$

Velocity boundary conditions are used at the inlets, pressure boundary conditions are used at the outlets and on all walls the

no-slip boundary condition is applied for the momentum equation (Eq. (4)). The detailed expressions are as follows:

$$\begin{cases} u = u_{in} (y = 0) \\ P = P_{out} (y = L) \\ \nabla P \cdot \vec{n} = 0 (x = 0, x_1, x_2, x_3) \end{cases} \quad (15)$$

where the outlet pressure P_{out} is usually set to zero.

2.2. Simulation of the self-discharge process at an initial SOC of 0

The self-discharge process at 0 SOC only involves the crossover of VO_2^+ and V^{3+} ions through the membrane. Therefore, the amount of species i transferred to the other side electrolyte through the membrane during Δt time can be calculated by the following equation:

$$\Delta n_i = N \cdot A \cdot \int_t^{t+\Delta t} J_i(t) dt \quad (16)$$

where $J_i(t)$ is the diffusion flux of species i through the membrane at time t , which can be calculated by solving the mass transport equations coupled with Darcy's law, N and A are the number of cells in the battery stack and the area of the membrane, respectively. On the assumption of no change in the diffusion flux J_i during a short time Δt , the above equation can be simplified as:

$$\Delta n_i = J_i(t) \cdot \Delta t \cdot A \cdot N \quad (17)$$

According to Sun et al. [2], the transfer of 1 mol VO_2^+ from +ve (the positive electrolyte) to -ve (the negative electrolyte) will result in a volume decrease of about 50 ml in the positive electrolyte, and the transfer of 1 mol V^{3+} from -ve to +ve will result in a volume decrease of about 16 ml in the negative electrolyte. Therefore, the volume change in the respective electrolyte can be estimated as:

$$\Delta V_p = -\Delta V_n = -0.05 \Delta n_{\text{VO}_2^+} + 0.016 \Delta n_{\text{V}^{3+}} \quad (18)$$

where ΔV_p and ΔV_n are the volume change of the positive and negative electrolyte respectively, $\Delta n_{\text{VO}_2^+}$ is the amount of VO_2^+ transferred from +ve to -ve and $\Delta n_{\text{V}^{3+}}$ is the amount of V^{3+} transferred from -ve to +ve. Therefore, the concentration of vanadium ions in the respective electrolyte can be calculated by:

$$C_i^p(t + \Delta t) = \frac{C_i^p(t) \cdot V_p(t) - \Delta n_{\text{VO}_2^+}}{V_p(t) + \Delta V_p} \quad (19)$$

$$C_i^p(t + \Delta t) = \frac{C_i^p(t) \cdot V_p(t) + \Delta n_{\text{V}^{3+}}}{V_p(t) + \Delta V_p} \quad (20)$$

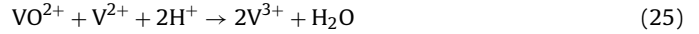
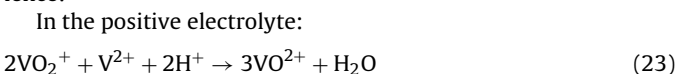
$$C_i^n(t + \Delta t) = \frac{C_i^n(t) \cdot V_n(t) + \Delta n_{\text{VO}_2^+}}{V_n(t) + \Delta V_n} \quad (21)$$

$$C_i^n(t + \Delta t) = \frac{C_i^n(t) \cdot V_n(t) - \Delta n_{\text{V}^{3+}}}{V_n(t) + \Delta V_n} \quad (22)$$

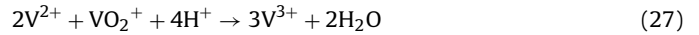
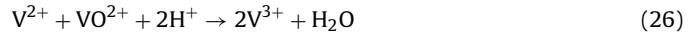
Then the diffusion flux $J_i(t + \Delta t)$ can be calculated by solving the mass transport equations introduced in Section 2.1. In this way, the self-discharge process at an initial SOC of 0 can be simulated. The results will be discussed in Section 4.1.

2.3. Simulation of the self-discharge process at an initial SOC of 65%

The self-discharge process at an initial SOC of 65% involves not only the crossover of the vanadium ions across the membrane but also the reactions between vanadium ions with different electrovalence:



In the negative electrolyte:



Assuming that the reaction rate is much quicker than the diffusion rate of vanadium ions, the change amount of the vanadium ions during Δt time can be calculated by the following equations:

$$\Delta n_{\text{VO}_2^+} = (-J_{\text{VO}_2^+}(t) + 2J_{\text{V}^{3+}}(t) + 3J_{\text{V}^{2+}}(t)) \cdot \Delta t \cdot A \cdot N \quad (29)$$

$$\Delta n_{\text{VO}^{2+}} = (-J_{\text{VO}_2^+}(t) - J_{\text{V}^{3+}}(t) - 2J_{\text{V}^{2+}}(t)) \cdot \Delta t \cdot A \cdot N \quad (30)$$

$$\Delta n_{\text{V}^{2+}} = (-J_{\text{V}^{2+}}(t) - J_{\text{VO}_2^+}(t) - 2J_{\text{VO}^{2+}}(t)) \cdot \Delta t \cdot A \cdot N \quad (31)$$

$$\Delta n_{\text{V}^{3+}} = (-J_{\text{V}^{3+}}(t) + 2J_{\text{VO}_2^+}(t) + 3J_{\text{VO}^{2+}}(t)) \cdot \Delta t \cdot A \cdot N \quad (32)$$

The volume change of electrolyte during self-discharge process at 65% SOC is much more complicated than that at 0 SOC. To simplify the problem, we assume that the transfer of the water is to balance the concentration of the total vanadium ions in the respective electrolyte. Therefore, the volume change of the respective electrolyte can be approximately calculated by:

$$\Delta V_p = -\Delta V_n = \frac{\Delta n_{\text{VO}_2^+} + \Delta n_{\text{VO}^{2+}}}{C_{\text{VO}_2^+}^p(t) + C_{\text{VO}^{2+}}^p(t)} = -\frac{\Delta n_{\text{V}^{2+}} + \Delta n_{\text{V}^{3+}}}{C_{\text{V}^{2+}}^n(t) + C_{\text{V}^{3+}}^n(t)} \quad (33)$$

According to the reactions (23)–(28), there will be no V^{3+} in +ve until the concentration of VO_2^+ decreases to zero, and there will be no VO_2^+ in -ve until the concentration of V^{2+} decreases to zero. Therefore, before the vanishing of VO_2^+ and V^{2+} , the concentration of vanadium ions in the respective electrolyte can be calculated by:

$$C_{\text{VO}_2^+}^p(t + \Delta t) = \frac{C_{\text{VO}_2^+}^p(t) \cdot V_p(t) + \Delta n_{\text{VO}_2^+}}{V_p(t) + \Delta V_p} \quad (34)$$

$$C_{\text{VO}_2^+}^p(t + \Delta t) = \frac{C_{\text{VO}_2^+}^p(t) \cdot V_p(t) + \Delta n_{\text{VO}_2^+}}{V_p(t) + \Delta V_p} \quad (35)$$

$$C_{\text{V}^{2+}}^n(t + \Delta t) = \frac{C_{\text{V}^{2+}}^n(t) \cdot V_n(t) + \Delta n_{\text{V}^{2+}}}{V_n(t) + \Delta V_n} \quad (36)$$

$$C_{\text{V}^{3+}}^n(t + \Delta t) = \frac{C_{\text{V}^{3+}}^n(t) \cdot V_n(t) + \Delta n_{\text{V}^{3+}}}{V_n(t) + \Delta V_n} \quad (37)$$

According to Sun et al. [2], the concentration of VO_2^+ decreases to zero first. After the vanishing of VO_2^+ , the change amount of the vanadium ions during Δt time will be:

$$\Delta n_{\text{VO}_2^+} = (-J_{\text{VO}_2^+}(t) - J_{\text{V}^{2+}}(t)) \cdot \Delta t \cdot A \cdot N \quad (38)$$

$$\Delta n_{\text{V}^{3+}}^p = (J_{\text{V}^{3+}}(t) + 2J_{\text{V}^{2+}}(t)) \cdot \Delta t \cdot A \cdot N \quad (39)$$

$$\Delta n_{\text{V}^{2+}} = (-J_{\text{V}^{2+}}(t) - J_{\text{VO}_2^+}(t)) \cdot \Delta t \cdot A \cdot N \quad (40)$$

$$\Delta n_{\text{V}^{3+}}^n = (-J_{\text{V}^{3+}}(t) + 2J_{\text{VO}_2^+}(t)) \cdot \Delta t \cdot A \cdot N \quad (41)$$

Then the volume change of the electrolyte can be approximately calculated by:

$$\Delta V_p = -\Delta V_n = \frac{\Delta n_{\text{VO}_2^+} + \Delta n_{\text{V}^{3+}}^p}{C_{\text{VO}_2^+}^p(t) + C_{\text{V}^{3+}}^p(t)} = -\frac{\Delta n_{\text{V}^{2+}} + \Delta n_{\text{V}^{3+}}^n}{C_{\text{V}^{2+}}^n(t) + C_{\text{V}^{3+}}^n(t)} \quad (42)$$

Therefore, the concentration of V^{3+} in +ve can be calculated by:

$$C_{\text{V}^{3+}}^p(t + \Delta t) = \frac{C_{\text{V}^{3+}}^p(t) \cdot V_p(t) + \Delta n_{\text{V}^{3+}}^p}{V_p(t) + \Delta V_p} \quad (43)$$

Table 1
Properties of the vanadium ions in the respective electrolyte.

Parameter	Positive electrolyte		Negative electrolyte		Origin
	VO ²⁺	VO ₂ ⁺	V ²⁺	V ³⁺	
$D_i/m^2 s^{-1}$	4.54×10^{-10}	3.82×10^{-10}	1.05×10^{-10}	2.54×10^{-10}	Ref. [2]
$D_i^m/m^2 s^{-1}$	6.825×10^{-12}	5.9×10^{-12}	8.768×10^{-12}	3.222×10^{-12}	Ref. [2]
K_i	0.6 ^a	0.77 ^b	1.15 ^b	0.76 ^a	a—tested b—estimated

Table 2
Properties of the VRFB system together with operational conditions.

VRFB stack	Number of cells	15
	Electrode's area	875 cm ²
	Electrode's permeability	9.35×10^{-11} m ²
	Membrane	Nafion 115
Electrolyte's properties	Volume	+ve: 23 L, -ve: 23 L
	Concentration	+ve: 1.5 M VOSO ₄ + 3 M H ₂ SO ₄ ; -ve: 0.75 M V ₂ (SO ₄) ₃ + 2.25 M H ₂ SO ₄
	Dynamic viscosity	4.928×10^{-3} Pa s
Operational conditions	Temperature	298 K
	Volumetric flow rate	3.6 L min ⁻¹

The concentration of the other vanadium ions can be calculated by Eqs. (34), (36) and (37). After the disappearance of V²⁺, there will be only VO²⁺ and V³⁺ left in each electrolyte. The self-discharge process will be the same as that at 0 SOC. Therefore, the concentration of vanadium ions during self-discharge process at an initial SOC of 65% can be simulated. The electrode potential can be determined by the following equations:

$$U_p(t) = U_p^{eq} + \frac{RT}{F} \ln \left(\frac{C_O^p(t)}{C_R^p(t)} \right) \quad (44)$$

$$U_n(t) = U_n^{eq} + \frac{RT}{F} \ln \left(\frac{C_O^n(t)}{C_R^n(t)} \right) \quad (45)$$

where U_p and U_n are the positive and negative electrode's potential, respectively; U_p^{eq} and U_n^{eq} are the positive and negative electrode's equilibrium potential, respectively; C_O^p and C_R^p are the concentration of the oxidized and reduced species in the positive electrolyte, respectively; C_O^n and C_R^n are the concentration of the oxidized and reduced species in the negative electrolyte, respec-

tively. The battery's open circuit potential is equal to U_p minus U_n , i.e. $OCV = U_p(t) - U_n(t)$.

3. Simulation procedure and parameters

The mass transport equations were discretized using a finite-element method and solved using the commercial package COMSOL Multiphysics®. The diffusion flux of the vanadium ions across the membrane at time t can be obtained by post-processing of the simulation results. Taking 1 h as the time interval, the amount of the transferred vanadium ions through the membrane Δn_i and the concentration of vanadium ions at time $t + \Delta t$ can be calculated by the equations listed in Sections 2.2 and 2.3. Then the diffusion flux of the vanadium ions at time $t + \Delta t$ can be obtained by solving the mass transport equations. In this way, the self-discharge processes at the initial SOC of 0 and 65% can be simulated.

The properties of the vanadium ions and the characteristic of the battery system together with initial and operational conditions are listed in Tables 1 and 2, respectively.

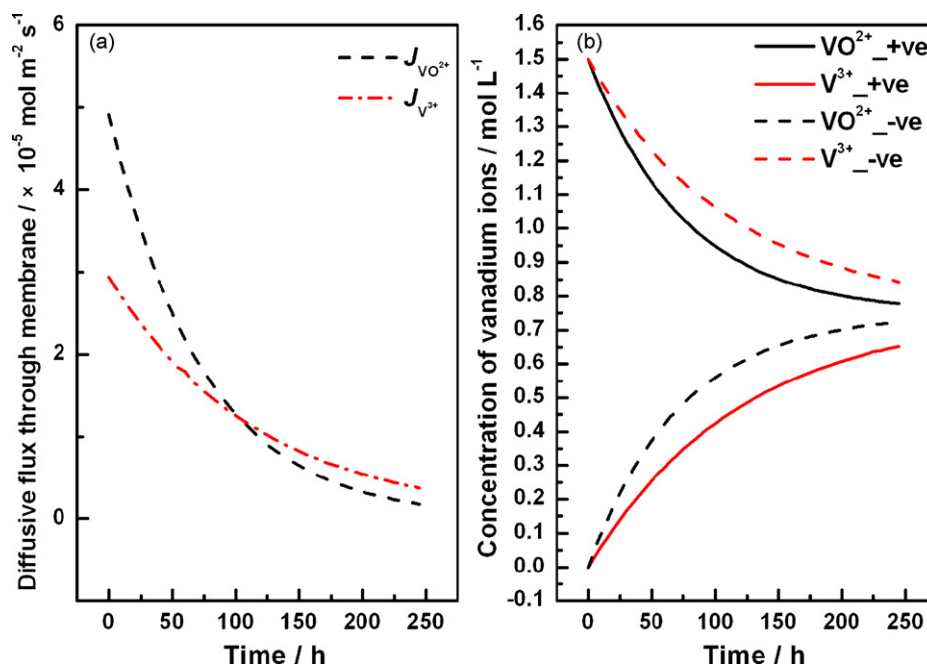


Fig. 2. Change of diffusion flux (a) and concentration (b) of vanadium ions with time during the self-discharge process at the initial SOC of 0.

4. Results and discussion

The self-discharge process depends on the state of charge of the electrolyte, i.e. the ratio between different vanadium ions in the respective electrolyte. Therefore, two typical SOC data points were chosen as the initial state of the self-discharge process, i.e. 0 SOC and 65% SOC. The simulation results are as follows:

4.1. Simulation results of the self-discharge process at an initial SOC of 0

As mentioned above, the self-discharge process at an initial SOC of 0 only involves the crossover of VO^{2+} and V^{3+} ions through the membrane. The diffusion rate depends on the diffusion coefficient, the partition coefficient and the concentration gradient of the vanadium ions between the two half cells. Fig. 2 shows the change behavior of diffusion flux (a) and concentration (b) of vanadium ions as a function of time. The initial diffusion rate of VO^{2+} is much quicker than that of V^{3+} due to a higher diffusion coefficient of VO^{2+} . Therefore, the decrease of the concentration of VO^{2+} in the positive electrolyte is greater than that of V^{3+} in the negative electrolyte, and the increase of the concentration of VO^{2+} in the negative electrolyte is greater than that of V^{3+} in the positive electrolyte. However, this leads to a smaller concentration gradient of VO^{2+} between the positive and negative electrolyte compared to that of V^{3+} . As a result, the decrease rate of the diffusion flux of VO^{2+} is much quicker than that of V^{3+} . After about 100 h, the diffusion rate of V^{3+} becomes larger than that of VO^{2+} .

Fig. 3 shows the change of the concentration of VO^{2+} in the battery at different times. It can be seen from Fig. 3 that there is a drop in the concentration profile at the phase boundaries due to the ion-exchange between the membrane and the electrolyte. The extent of the drop in the concentration depends on the partition coefficient and the concentration of the electrolyte. As time goes on, the concentration of VO^{2+} decreases in the positive electrolyte and increases in the negative electrolyte, and the concentration gradient of VO^{2+} decreases in the membrane. Finally, the concentration

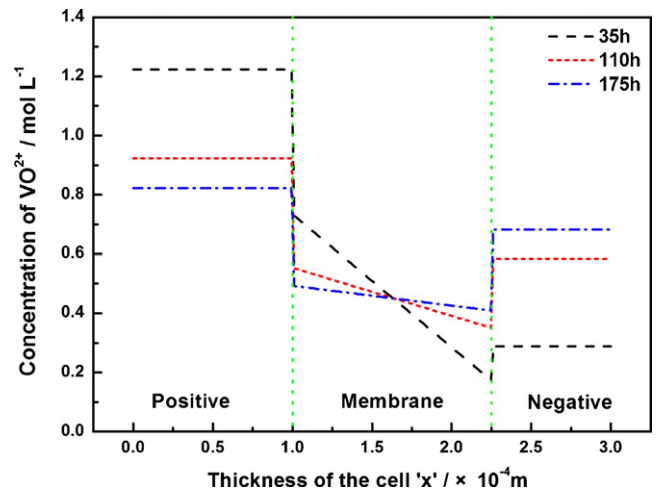


Fig. 3. Change in the concentration of VO^{2+} in the battery at different times during the self-discharge process at the initial SOC of 0.

of VO^{2+} in the respective electrolyte will be equal and there will be no net mass transfer in the battery. This is corresponding to the change of diffusion flux and concentration of VO^{2+} with time as shown in Fig. 2.

The calculated data of the amount of vanadium ions in the respective electrolyte are compared with the experimental values. The results are shown in Fig. 4. It shows that the calculated values match well with the experimental data, indicating the validity of the model. The simulated curves predict much longer time of self-discharge than the experimental results tested by Sun et al. [2]. Fig. 5 shows the simulated results of the change of the total vanadium amount in the respective electrolyte (a) and the change of electrolyte volume (b). It can be seen from Fig. 5(a) that there is an inflexion at each curve. The appearance time of the inflexion is corresponding to the time when the diffusion rate of V^{3+} becomes

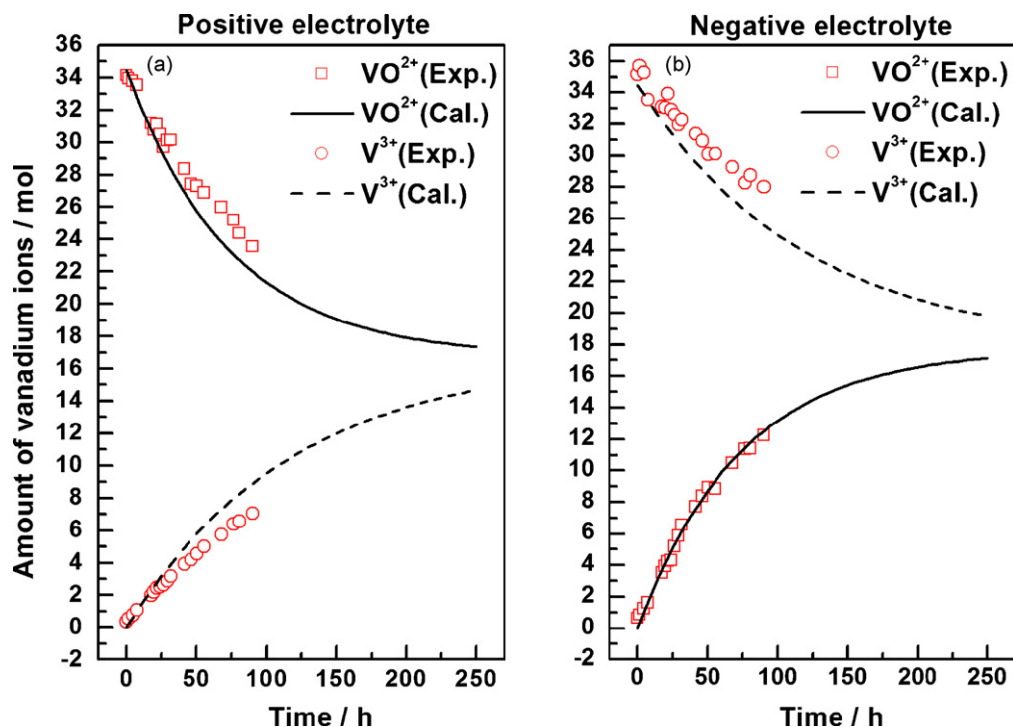


Fig. 4. (a and b) Calculated (lines) and experimental (dots) data of the amount of vanadium ions in the respective electrolyte during the self-discharge process at the initial SOC of 0.

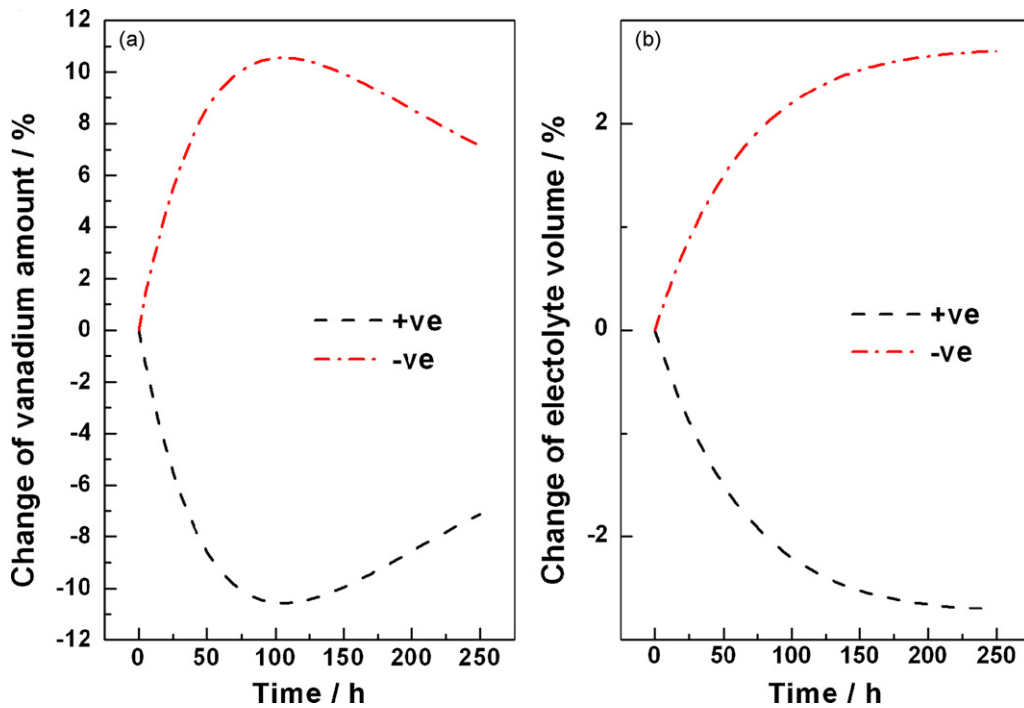


Fig. 5. Simulated results of the change of the total vanadium amount in the respective electrolyte (a) and the electrolyte volume (b) during the self-discharge process at the initial SOC of 0.

larger than that of VO^{2+} as shown in Fig. 2. That is to say, the net transfer direction of vanadium ions is towards $-ve$ during the initial 100 h and then turns to $+ve$. The transfer direction of water is always from $+ve$ to $-ve$ as shown in Fig. 5(b). It also shows that the volume of the negative electrolyte increases about 2.5% after 100 h. However, the experimental result of that value is about 10%. The difference may be attributed to the assumption that water transfer is caused only by the transfer of vanadium ions. The transfer of

water caused by osmosis is not taken into account, because of the difficulty of simulation in the current model.

4.2. Simulation results of the self-discharge process at an initial SOC of 65%

Fig. 6 shows the simulated results of the concentration of vanadium ions during the self-discharge process at an initial SOC of

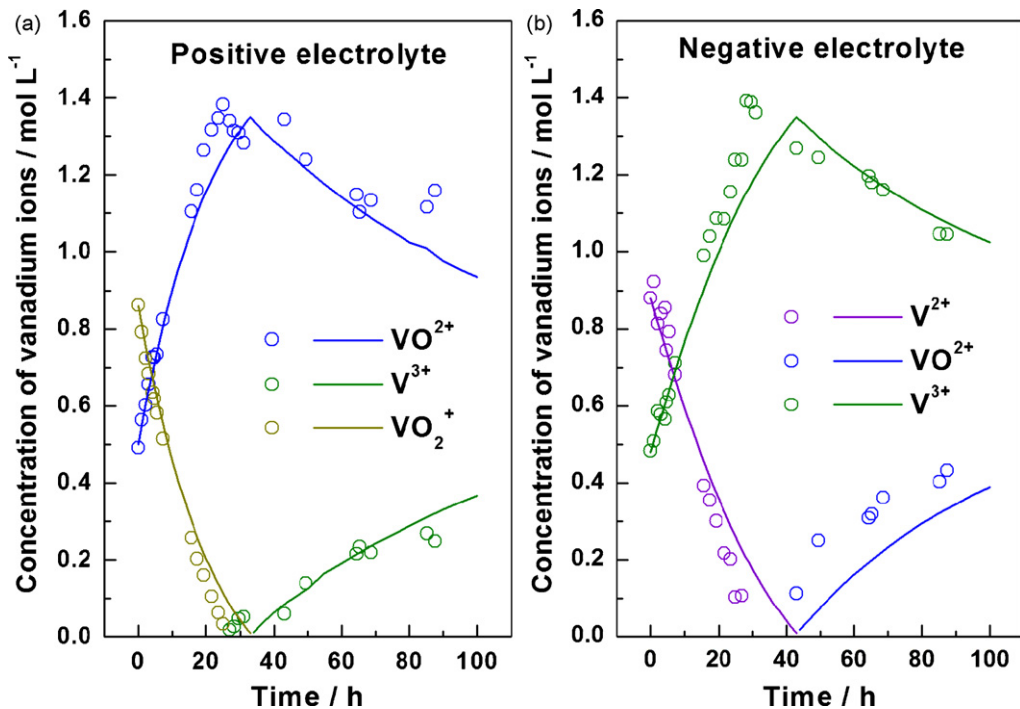


Fig. 6. (a and b) Simulated results of the concentration of vanadium ions during the self-discharge process at an initial SOC of 65% (lines represent calculated data and dots represent experimental values).

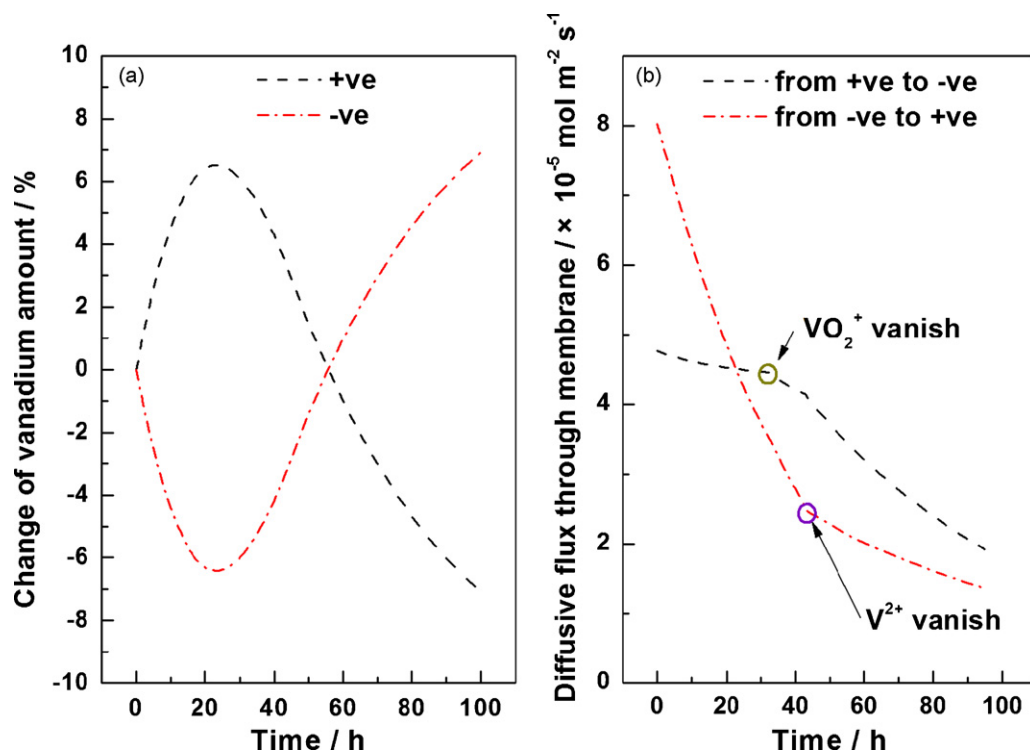


Fig. 7. Change behavior of the vanadium amount (a) and the diffusive flux through the membrane (b) as a function of time during the self-discharge process at an initial SOC of 65%.

65%. In the figure, the lines represent the simulation results and the dots represent the experimental values. It shows that the simulated data predict the experimental values well for the initial 20 h. However, the deviation between calculated and experimental values becomes larger as the self-discharge time gets longer. It also shows that the inflexion of the simulation curves appear latterly compared with the experimental one, and the difference in the appearance time of the inflexion between experimental and calculated values for the negative electrolyte is much greater than that for the positive electrolyte. The deviation between calculated and experimental values may be related to the inappropriate assumption of water transfer. Only the water transferred to balance the concentration of the total vanadium ions is considered in this model. However, the actual water transfer is more complicated and cannot be estimated by a single equation. The reason for the difference in the vanishing time of VO₂⁺ and V²⁺ between calculated and experimental values is simple. Because the V²⁺ ions are very unstable, it is easily oxidized by the oxygen in the air during sampling and testing process. But the model is in an ideal condition. Therefore, the simulated vanishing time of V²⁺ and VO₂⁺ is latter than the experimental results. Besides, there is difference between the calculated and experimental results of the volume change in the respective electrolyte due to the assumption of water transfer. It is another reason for the difference of the vanishing time.

Fig. 7 shows the change of the vanadium amount with time (a) and the change of the diffusive flux through the membrane with time (b). From Fig. 7(a), it can be seen that the net transfer direction of vanadium ions is towards +ve during the initial 20 h and then turns to -ve. The time of the inflexion point is corresponding to the intersection point as shown in Fig. 7(b), which represents the time when the diffusion flux towards -ve becomes larger than that towards +ve. However, the experimental results tested by Sun et al. [2] show that the transfer direction of vanadium ions changes at about 7 h, which is much earlier than the simulation results. The reason may be attributed to the inappropriate assumption of water

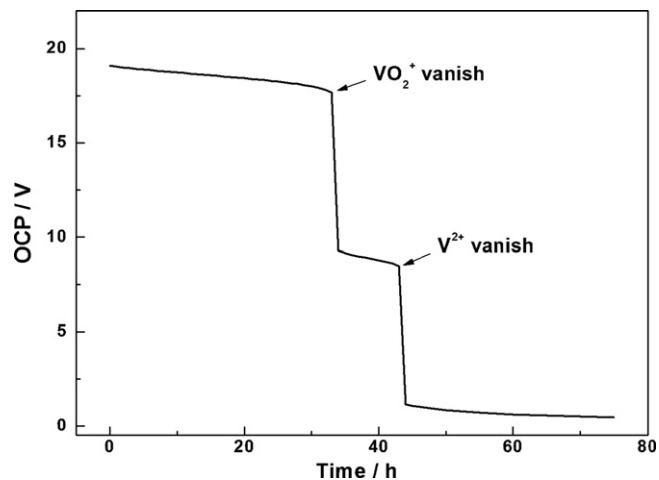


Fig. 8. Change behavior of the calculated open circuit potential (OCP) of the battery stack as a function of time during the self-discharge process at an initial SOC of 65%.

transfer, which has been discussed above. Fig. 7(b) also shows an inflexion point at each curve, which is corresponding to the vanishing time of VO₂⁺ and V²⁺ respectively. Fig. 8 shows the change of the calculated open circuit potential (OCP) of the battery stack with time. There are two obvious decreases of the OCP value at about 33 and 43 h, corresponding to the vanishing time of VO₂⁺ and V²⁺, respectively.

5. Conclusion

In this paper, the self-discharge process in VRFB at the initial SOC of 0 and 65% has been simulated. The model uses the mass transport equations to describe the transfer of vanadium ions in the respective phases. The simulation results agree reasonably with

the experimental values, confirming the validity of the model. It is found that the diffusion rate of vanadium ions depends on the diffusion coefficient, the partition coefficient and the concentration gradient of the vanadium ions between the two half cells. For the self-discharge process at the initial SOC of 0, the net transfer direction of vanadium ions is towards the negative electrolyte until the diffusion rate of V^{3+} becomes quicker than that of VO^{2+} . Both the diffusion rate of V^{3+} and VO^{2+} decrease with time due to the decrease in the concentration gradient between the two half cells. For the self-discharge process at the initial SOC of 65%, the net transfer direction of vanadium ions is towards the positive electrolyte during the initial 20 h. As the diffusion flux of vanadium ions towards the negative electrolyte becomes larger than that towards the positive electrolyte, the net transfer direction of vanadium ions turns to the negative electrolyte. There are two obvious changes in the diffusion flux of vanadium ions and in the OCP at about 33 and 43 h, corresponding to the vanishing time of VO_2^+ and V^{2+} respectively.

Although the model predicts the self-discharge process well, there are still some divergences between the calculated and experimental values. The main reason of the divergence is the inap-

propriate assumption of water transfer, which is too complicated to be predicted by a single model. Therefore, dynamic model would be used to simulate the crossover of both water and vanadium ions in the next paper and the cycling performance will be predicted.

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References

- [1] E. Wiedemann, A. Heintz, R.N. Lichtenthaler, *J. Membr. Sci.* 141 (1998) 215–221.
- [2] C.X. Sun, J. Chen, H.M. Zhang, et al., *J. Power Sources* 195 (2010) 890–897.
- [3] T. Sukkar, M. Skyllas Kazacos, *J. Membr. Sci.* 222 (2003) 235–247.
- [4] T. Mohammadi, S.C. Chieng, M. Skyllas Kazacos, *J. Membr. Sci.* 133 (1997) 151–159.
- [5] E. Wiedemann, A. Heintz, R.N. Lichtenthaler, *J. Membr. Sci.* 141 (1998) 207–213.
- [6] M. Mulder, *Basic Principles of Membrane Technology*, 2nd ed., Kluwer Academic Publishers, 1998.