An improved model of ion selective adsorption in membrane and its application in vanadium redox flow batteries

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HIGHLIGHTS

- We propose an accurate model for ion selective adsorption (ISA).
- The Donnan effect is considered for mobile ions in membrane pores only.
- ISA is considered to accurately predict the ion transport through the membrane.
- Effect of membrane properties and electrolytes on performance is captured.
- The improved VRFB model is a good tool to help membrane optimization.

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ABSTRACT

An accurate prediction of ion selective adsorption in ion exchange membranes is essential to reflect the role of fixed charges on ion transport through the membrane in vanadium redox flow batteries (VRFB). Unlike those empirical models reported in the literature, this work reports on a new ion selective adsorption model with the Donnan effect considered for mobile ions distributed in the membrane pores only. This model, no longer relying on empirical coefficients, is then applied to the calculation of ion transport through membranes in VRFBs. The model shows a more accurate prediction of vanadium crossover and membrane conductivity, and enables to capture the effect of key membrane properties on battery performance. It is found that (i) an increase in H2SO4 concentration reduces the electrolyte imbalance and improves the coulombic efficiency; (ii) an increase in membrane porosity significantly improves the membrane effective conductivity; (iii) the change of fixed charges should be careful to balance all performances. Therefore, membrane properties and operating conditions need proper adjustment to improve the battery performance, and our VRFB model is a good tool to help membrane optimization.

1. Introduction

Vanadium redox flow battery (VRFB) has received widespread attentions as an attractive technology for large-scale energy storage systems since it demonstrates the following advantages: independence of capacity and power, long lifetime and high safety [1–13]. Although promising, the VRFB commercialization is restricted by several pragmatic issues, one of which is the crossover of vanadium ions through membranes [14–21]. Prior to the study of reducing crossover, we should first be able to predict the ion transport through an ion exchange membrane accurately. However, the process of ion transport through an ion exchange membrane differs from that in bulk solution, due to that the fixed charges on the membrane matrix directly affect the ion selective adsorption in the membrane. Hence, it is clear that an accurate prediction of ion selective adsorption is our top priority.

To study the ion selective adsorption in VRFBs, the ion exchange membranes are immersed in different vanadium solutions, composed of vanadium sulfate and sulfuric acid. Typically, researchers use the membrane volume-averaged ion concentrations to study the ion selective adsorption, considering that the neglect of distinction between the membrane matrix and pores does not affect the results [22,23]. However, the results of ion selective adsorption, obtained by using the electrochemical potential conservation or its alternative form at the membrane/solution interfacial region [24–26], are often largely deviated from the experimental results. To eliminate this deviation, researchers introduce empirical coefficients without solid physical
meaning in the model, such as the selectivity coefficient and equilibrium constant. Since these empirical coefficients are irregular, it is difficult to obtain a unified expression for the use in VRFB models. Hence, we consider establishing a new model for ion selective adsorption in the membrane that exhibits good accuracy and no longer relies on the empirical coefficients. It is found that, in many cases, the membrane volume-averaged concentration of counter-ions measured in ion exchange membranes is lower than that in the external solution, different from our previous understanding about the Donnan effect [22,23]. This result implies that the ion concentration obtained by this averaging method may not be directly related to the Donnan effect. Considering that the movable ions are distributed in the membrane pores only, we establish a new model for ion selective adsorption, with the membrane pore volume-averaged concentration introduced for describing the Donnan effect. The newly established ion selective adsorption model is then applied to the modeling of ion transport through the membrane. Since the diffusion, migration and convection largely depend on the ion concentration or its gradient, it is of critical importance to consider the ion selective adsorption when predicting the ion transport through the membrane in different vanadium solutions. Accordingly, for flow batteries restricted by crossover, the prediction of battery performance should be improved by considering ion selective adsorption.

In this work, we focused on an accurate prediction of ion selective adsorption in ion exchange membranes to improve the prediction of ion transport through the membrane. Firstly, we measured and analyzed the ion selective adsorption in the membrane. Then, we established an ion selective adsorption model with the Donnan effect considered for movable ions distributed in membrane pores only. Thirdly, we applied the new ion selective adsorption model to the calculation of ion transport through the membrane. Finally, we modified the transient VRFB model by considering the ion selective adsorption and predicted the effect of key membrane properties and operating conditions on the battery performance.

2. Experiment and model

2.1. Ion selective adsorption experiment

2.1.1. Preparation

$5 \times 5 \text{ cm}^2$ Nafion 117 samples were prepared in the experiment. The samples were sequentially pretreated with 5% H$_2$O$_2$, deionized water, 0.5 M H$_2$SO$_4$ and deionized water. Each step lasted 2 h at 80 °C. Then, membrane samples were dried in a drying oven at 80 °C for 3 days and finally preserved in laboratory environment. A series of tetravalent vanadium solutions were prepared, with a composition of $[x \text{ M VOSO}_4 + 1 \text{ M H}_2\text{SO}_4]$ or $[y \text{ M VOSO}_4 + 0.2 \text{ M H}_2\text{SO}_4]$, where $x = 0.1-0.9$ and $y = 0.1-0.3$. The purity of VOSO$_4$·5H$_2$O is 96%. All other reagents used in experiment are of analytical grade.

2.1.2. Measurement

At the room temperature, we first immersed Nafion 117 samples in a series of $[\text{VOSO}_4 + \text{H}_2\text{SO}_4]$ solutions for three days to reach an equilibrium state, then rinsed the membrane surfaces with deionized (DI) water to remove the remains, later immersed each membrane sample in 1 M NaCl solution for three days to soak out all ions in the membrane, and finally measured the amounts of VO$^{2+}$, SO$_4^{2−}$, HSO$_4^{−}$ and H$^+$ in NaCl solution.

The concentrations of VO$^{2+}$ and [SO$_4^{2−}$ + HSO$_4^{−}$] in NaCl solutions were separately measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Optima 7000DV, PerkinElmer) and Ion Chromatography (IC, 930 Compact IC Flex, Metrohm). Both correlation coefficients reached 0.9999. It should be noted that, based on the measuring principle of IC instrument, we cannot distinguish between SO$_4^{2−}$ and HSO$_4^{−}$ concentrations. Consequently, [H$^+$ + HSO$_4^{−}$] concentration is obtained from the electroneutrality:

$$c_{[\text{H}^+ + \text{HSO}_4^{−}]} = c_{\text{M}} + 2c_{[\text{SO}_4^{2−} + \text{HSO}_4^{−}]} - 2c_{\text{VO}^{2+}}$$

(1)

where $c_{\text{M}}$ denotes the membrane volume-averaged concentration when immersed in vanadium solutions, subscript M represents the fixed charges. $c_{\text{M}}$ is obtained from $c_{\text{M}} = c_{\text{M}}/c_{\text{m,sv}}$, where $c_{\text{m,sv}}$ is the membrane volume expansion coefficient that changes from 23 °C, 50% relative humidity (RH) to soaked solution. Subscript r denotes 23 °C, 50% RH. Then, the membrane pore volume-averaged concentration $c_{\text{m,sv}}$ is obtained by $c_{\text{m,sv}} = c_{\text{m,sv}}/c_{\text{m,sv}}$, where $c_{\text{m,sv}}$ is the membrane porosity in soaked solution, expressed as:

$$c_{\text{m,sv}} = \frac{V_{\text{m},d} - V_{\text{m},r}}{V_{\text{m},r}} = \frac{V_{\text{m},d} - V_{\text{m},r}}{V_{\text{m},r}} = \frac{(1 - \epsilon_{m,sv})V_{\text{m},r}}{V_{\text{m},d}} = 1 - \frac{1 - \epsilon_{m,sv}}{\epsilon_{m,sv}}$$

(2)

where, $V_{\text{m},d}$, $V_{\text{m},r}$ are the membrane volume in soaked solution and that at 23 °C, 50% (RH) environment, respectively. $V_{\text{m,sv}}$ is the volume of the membrane matrix, assumed to be constant when the membrane sample is immersed in different solutions. $\epsilon_{m,sv}$ represents the membrane porosity at 23 °C, 50% RH. The properties of Nafion 117 are presented in Table 1.
As an ion exchange membrane is immersed in the solution and reaches equilibrium, we consider that the ion distribution in the bulk membrane is uniform. Then, the ion selective adsorption is described by using the electrochemical potential conservation of every species between the membrane phase and external solution phase, with the electroneutrality satisfied in each bulk phase. Based on the fact that the movable ions and fixed charges are distributed in membrane pores only, we introduce the membrane pore volume-averaged quantities to describe the electrochemical potential:

\[ \mu_i = \mu_i^{m,s} + RT\ln c_i + z_i F \Phi_{i,m} = \mu_i^{m,s} + RT\ln c_i + z_i F \Phi_{i,m} \]  \hspace{1cm} (3)

where subscript \( i \) denotes movable ions, including both counter-ions and co-ions; \( \mu_i^{m,s}, c_i, z_i \) are the standard electrochemical potential, concentration and valence of species \( i \) respectively; \( R \) and \( F \) are the universal gas constant and Faraday constant; \( T \) is the temperature; \( \Phi_i \) is the electric potential of solution; subscript \( m \) and \( s \) represent the external solution phase and the membrane phase separately. With the assumption that \( \mu_i^{m,s} = \mu_i^{m,s} \), the Boltzmann distribution is derived from Eq. (3):

\[ c_{i,m} = c_{i,m}^0 \exp \left[ -\frac{z_i F (\Phi_{i,m} - \Phi_{i,m}^\alpha)}{RT} \right] \]  \hspace{1cm} (4)

In the meantime, electroneutrality conditions in the external solution and membrane pore are expressed as:

\[ \sum_i z_i c_{i,s} = 0 \quad \text{External solution} \]
\[ \sum_i z_i c_{i,m} + z_m c_m = 0 \quad \text{Membrane pore} \]  \hspace{1cm} (5)

where \( z_m \) is the valence of fixed charge. Membrane volume-averaged concentration \( c_{i,m} \) and \( c_m \) are then achieved by:

\[ c_{i,m} = c_{i,m}^0 c_{i,m} \quad c_m = c_m^0 c_m \]  \hspace{1cm} (6)

where \( c_{i,m}^0 \) is the membrane porosity immersed in the solution.

### 2.2. Ion selective adsorption model

As an important transport mechanism in crossover, the diffusion of vanadium ions through the membrane should be reconsidered due to its dependence on ion selective adsorption. Here, we suppose a dialysis cell that Nafion 117 is used to separate \( \{x \text{ M V}(\text{SO}_4)_{x/2} + y \text{ M H}_2\text{SO}_4\} \) and \( \{x \text{ M MgSO}_4 + y \text{ M H}_2\text{SO}_4\} \) solutions [26], where \( \text{V}^{2+}, \text{VO}^{2+}, \text{V}_2\text{O}_7^{2-} \) and \( \text{VO}^{2+} \) separately. The flux of \( \text{V}^{2+} \) through the membrane is caused by the diffusion only, since the migration and convection are minimized when using the \( \{\text{MgSO}_4 + \text{H}_2\text{SO}_4\} \) solution. Then, the ion diffusion through the membrane with the ion selective adsorption (ISA) is considered is shown in Eq. (7). As a comparison, the ion diffusion with ISA neglected is also given:

\[ D_{i,m}^0 \Delta c_{i,m}/L_{i,m}, \text{ with ISA} \]
\[ D_{i,m}^0 \Delta c_{i,m}/L_{i,m}, \text{ without ISA} \]  \hspace{1cm} (7)

where \( \Delta \) is the flux through the membrane, \( L_{i,m} \) is the membrane thickness, \( c_{i,m} \) is the concentration in the membrane, \( c_{i,m}^0 \) is the concentration in the external solution, \( \Delta \) is the concentration difference between the two solutions of the dialysis cell; while, \( \Delta c_{i,m} \) is the concentration difference between the two boundaries of bulk membrane, where the Donnan effect has been considered at the solution/membrane interface. At the \( \{\text{MgSO}_4 + \text{H}_2\text{SO}_4\} \) solution side, \( c_{i,m} \) of vanadium ions is zero; at the vanadium solution side, \( c_{i,m} \) at the boundary of bulk membrane is obtained by using the ion selective adsorption model described in Section 2.2. This is because the solution/membrane interfacial region where Donnan effect occurs is very narrow and the concentration jump in this region is very steep, so that the change in concentration at the interfacial region caused by ion transport can be neglected. The conditions and properties are listed in Table 2.

### 2.2.1. Diffusion

As an important transport mechanism in crossover, the diffusion of vanadium ions through the membrane should be reconsidered due to its dependence on ion selective adsorption. Here, we suppose a dialysis cell that Nafion 117 is used to separate \( \{x \text{ M V}(\text{SO}_4)_{x/2} + y \text{ M H}_2\text{SO}_4\} \) and \( \{x \text{ M MgSO}_4 + y \text{ M H}_2\text{SO}_4\} \) solutions [26], where \( \text{V}^{2+}, \text{VO}^{2+}, \text{V}_2\text{O}_7^{2-} \) and \( \text{VO}^{2+} \) separately. The flux of \( \text{V}^{2+} \) through the membrane is caused by the diffusion only, since the migration and convection are minimized when using the \( \{\text{MgSO}_4 + \text{H}_2\text{SO}_4\} \) solution. Then, the ion diffusion through the membrane with the ion selective adsorption (ISA) is considered is shown in Eq. (7). As a comparison, the ion diffusion with ISA neglected is also given:

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where \( \Delta \) is the flux through the membrane, \( L_{i,m} \) is the membrane thickness, \( c_{i,m} \) is the concentration in the membrane, \( c_{i,m}^0 \) is the concentration in the external solution, \( \Delta \) is the concentration difference between the two solutions of the dialysis cell; while, \( \Delta c_{i,m} \) is the concentration difference between the two boundaries of bulk membrane, where the Donnan effect has been considered at the solution/membrane interface. At the \( \{\text{MgSO}_4 + \text{H}_2\text{SO}_4\} \) solution side, \( c_{i,m} \) of vanadium ions is zero; at the vanadium solution side, \( c_{i,m} \) at the boundary of bulk membrane is obtained by using the ion selective adsorption model described in Section 2.2. This is because the solution/membrane interfacial region where Donnan effect occurs is very narrow and the concentration jump in this region is very steep, so that the change in concentration at the interfacial region caused by ion transport can be neglected. The conditions and properties are listed in Table 2.

### 2.2.2. Membrane effective conductivity

The expression of membrane effective conductivity \( \sigma_{eff} \), an important transport property in flow batteries, is revised by considering the ion selective adsorption:

\[ \sigma_{eff} = \frac{\varepsilon^2}{RT} \sum_i z_i^2 c_{i,m} D_{i,m}^0 \]  \hspace{1cm} (8)

where \( \varepsilon \), \( c_{i,m} \), \( D_{i,m}^0 \) are the valence, concentration and revised diffusion coefficient of species \( i \) in the membrane respectively. For the situation that Nafion 117 samples are immersed in vanadium solutions or sulfuric acid solutions and reaches equilibrium, \( c_{i,m} \) in Eq. (8) is determined with our new ion selective adsorption model. At the same time, by using \( \sigma_{eff} \) measured in the pure water from Ref. [28], \( D_{i,m}^0 \) is derived to be 2.867 × 10^{-9} m^2 s^{-1}, where \( c_{i,m} \) is equal to \( c_m \).

### 2.4. VRFB model

To further study the effect of ion crossover on battery performance, we improve our one-dimensional VRFB model reported in Ref. [21] with a reconsideration of the ion selective adsorption. The ion selective adsorption model established in this work is used to replace the previous mathematical description at the membrane/electrolyte interfacial regions. In the membrane, the concentration of movable ions is membrane pore volume-averaged and the diffusion coefficient of ions is modified as described in Sections 2.2 and 2.3. Tables 1 and 2 list the values of the properties and parameters; the rest are the same as that in Ref. [21]. The governing equations were solved using the software COMSOL Multiphysics with the relative tolerance set to 1 × 10^{-6}.
3. Results and discussion

3.1. Ion selective adsorption analysis

The ion selective adsorption in ion exchange membranes is experimentally studied by immersing Nafton 117 samples in various tetravalent vanadium solutions. Fig. 1 presents the membrane volume-averaged ion concentration \( c_{i,m} \) and membrane pore volume-averaged ion concentration \( c_{i,m} \) for \( \text{VO}^{2+} \), \( [\text{SO}_4^{2-} + \text{HSO}_4^-] \) and \( [\text{H}^+ + \text{HSO}_4^-] \), respectively. For each case, the \( [\text{SO}_4^{2-} + \text{HSO}_4^-] \) concentration is significantly lower than the \( [\text{H}^+ + \text{HSO}_4^-] \) concentration, so the proportion of \( \text{HSO}_4^- \) in \( [\text{H}^+ + \text{HSO}_4^-] \) is very small. Therefore, the concentration of \( [\text{H}^+ + \text{HSO}_4^-] \) can be approximated as that of \( \text{H}^+ \). From Fig. 1, it is observed that for all ions, \( c_{i,m} \) at 1 M \( \text{H}_2\text{SO}_4 \) is lower than the external solution concentration \( c_{i,s} \), which appears to be contrary to the Donnan effect that the counter-ion is “adsorbed” in the membrane. For \( [\text{H}^+ + \text{HSO}_4^-] \) at 0.2 M \( \text{H}_2\text{SO}_4 \), \( c_{i,m} \) is not always greater than \( c_{i,s} \), as shown in Fig. 1b. Therefore, the ion selective adsorption represented by the membrane volume-averaged ion concentration cannot be explained by the Donnan effect. This may be due to neglect the role of membrane porosity. To find out the reason, we also analyze the membrane pore volume-averaged ion concentration \( c_{i,m} \). It is observed that the concentration of counter-ions (\( \text{VO}^{2+} \), \( \text{H}^+ \)) in the membrane is enhanced and that of co-ions (\( \text{SO}_4^{2-} + \text{HSO}_4^- \)) is reduced in all cases. This result follows the Donnan effect and can be explained by that the movable ions affected by the fixed charges are distributed in the membrane pores only. Accordingly, the membrane porosity should be taken into account in the description of ion selective adsorption.

In addition, the effect of solution components on ion selective adsorption is studied. We divide the membrane pore volume-averaged ion concentration \( c_{i,m} \) into two parts: one is the known concentration \( c_{i,s} \) of external solution; the other is the amount of ion selective adsorption defined as the difference between \( c_{i,m} \) and \( c_{i,s} \). From Fig. 1, it is found that the amount of ion selective adsorption increases with (i) the concentration \( c_{i,s} \) of external solution, (ii) the proportion of \( c_{i,s} \) in the total solution concentration as well as (iii) the valence of the ion. In addition, for mixed solutions of the same ionic proportion, the amount of ion adsorption or repulsion is not always the same due to the limitation of co-ion, which concentration can only be reduced to zero at most.

3.2. Ion selective adsorption model

To clarify the accuracy of the model in section 2.2, we calculate the ion selective adsorption of all ions in Nafton 117 samples immersed in \( [\text{VOSO}_4 + \text{H}_2\text{SO}_4] \) solutions, and compare the results with the experimental results. The calculated results with the membrane porosity neglected are also given. Fig. 2a–f shows the results of \( c_{i,m} \) for \( \text{VO}^{2+} \), \( [\text{H}^+ + \text{HSO}_4^-] \) and \( [\text{SO}_4^{2-} + \text{HSO}_4^-] \) at 1 M and 0.2 M \( \text{H}_2\text{SO}_4 \), respectively. The dissociation degree \( \alpha_{\text{HSO}_4^-} \) of bisulfate ion is taken into account. It is obvious that, for each ion, the results of considering the membrane porosity \( \varepsilon_m \) are clearly closer to the experimental results, where the results are more accurate when \( \text{HSO}_4^- \) is assumed to be completely dissociated (\( \alpha_{\text{HSO}_4^-} = 1 \)) in the cation exchange membrane.

Fig. 1. Experimental results of the membrane volume-averaged and membrane pore volume-averaged ion concentrations: (a) \( \text{VO}^{2+} \), (b) \( [\text{H}^+ + \text{HSO}_4^-] \) and (c) \( [\text{SO}_4^{2-} + \text{HSO}_4^-] \). \( c_{i,m} \) and \( c_{i,s} \) denote \( c_{i,m} \) and \( c_{i,s} \), respectively.
The complete dissociation of \( \alpha_{\text{HSO}_4^-} \) may be explained by the fact that a large amount of protons are adsorbed in the membrane due to the presence of fixed charges, and thus the bisulfate ion has a tendency to dissociate. In summary, considering the membrane porosity and the dissociation degree of \( \text{HSO}_4^- \) will greatly improve the accuracy of the ion selective adsorption model. Importantly, our model eliminates the dependence on the empirical coefficients and maintains high accuracy under various operating conditions. Hence, it is quite suitable for applying to the transient VRFB model.

3.3. Ion transport through membranes

3.3.1. Diffusion

By incorporating our ion selective adsorption model, we calculate the diffusion of vanadium ions through the Nafion 117 in a dialysis cell, described in section 2.3.1. As a comparison, the ion diffusion without the consideration of ion selective adsorption is also given. The solution component is \( [x \text{ M V(SO}_4)_{n/2} + y \text{ M H}_2\text{SO}_4] \), where \( x \) ranges from 0.3 to 1.5 and \( y \) is set to 0.2, 1, 3, respectively. The diffusions of \( \text{V}^{3+}, \text{V}^{2+} \) and \( \text{VO}_2^+ \) through Nafion 117 are separately shown in Fig. 3a–c. It is found that (i) the diffusion of each vanadium ion increases with the external \( V^{n+} \) concentration for both models; (ii) When the external \( V^{n+} \)
concentration is fixed, with an increase in external H$_2$SO$_4$ concentration, the diffusions almost coincide for the model with ISA neglected, while the diffusion largely decreases for the model with ISA considered. It means that H$_2$SO$_4$ has a great influence on vanadium ion transport through membranes, and only our model can capture this effect. Based on this, it can be inferred that the additives in the electrolytes would also affect the vanadium crossover. This is since the diffusion is proportional to $c_i$ at the membrane boundary of vanadium solution side, increasing with the proportion of vanadium ion in the external solution as concluded in Section 3.1. Accordingly, the diffusion of vanadium ion is not linear to the external vanadium concentration $c_{%iV_{out}}$. Take the result of VO$_{2}^{+}$ diffusion in Fig. 3b as an example. By comparing the VO$_{2}^{+}$ diffusions between 1.5 M and 0.3 M VO$_{2}^{+}$, the diffusion ratios at 0.2 M, 1 M, 3 M H$_2$SO$_4$ are 1.77, 2.79, 3.53 respectively, far from 5. Fig. 3d shows the relative difference of the ion diffusions obtained with and without the ion selective adsorption considered. It is observed that for all vanadium ions, the relative difference is enhanced as the external solution deviates from the measurement condition [1 M V(SO$_4$)$_2$ + 2.5 M H$_2$SO$_4$] for diffusion coefficients. For 0.2 M H$_2$SO$_4$, the relative difference of VO$_{2}^{+}$ is even up to 400% at low $c_{%iV_{out}}$. For 3 M H$_2$SO$_4$, this value also reaches 20–30%. In summary, the effect of key electrolyte parameters on ion transport can be obtained by considering Fig. 3.

![Fig. 3](image_url)

Fig. 3. Diffusions of (a) V$_{3}^{3+}$, (b) VO$_{2}^{+}$ and (c) VO$_{2}^{+}$ through Nafion 117 with and without the ion selective adsorption (ISA) considered, and (d) the relative differences.
the ion selective adsorption. Moreover, since the ion selective adsorption is associated with the membrane porosity and fixed concentration, the effect of key membrane properties on ion transport is also available, not discussed in detail here.

3.3.2. Membrane effective conductivity

After a discussion on ion diffusion through the membrane, we study the membrane effective conductivity $\sigma^{eff}_{mem}$ of Nafion 117 immersed in $\pi$ M H$_2$SO$_4$ solution or [x M VOSO$_4$ + y M H$_2$SO$_4$] solution, as shown in Fig. 4, where $z$ is 0–3, $x$ is 0–1.5, and $y$ is equal to 1 and 3. Since $c_{\sigma_{\infty}}$ of H$^+$ and VO$_2^+$ is much higher than that of SO$_4^{2-}$ and that $D_{\sigma^{eff}_{mem}}$ is much larger than $D_{\sigma^{eff}_{m}}$ in Eq. (8) is simplified as:

$$\sigma^{eff}_{mem} \approx \frac{p^2}{RT} \varepsilon_{c m s}^{eff} D_{\sigma^{eff}_{mem}}$$

(9)

where $D_{\sigma^{eff}_{mem}}$ is 2.867 $\times$ 10$^{-9}$ m$^2$ s$^{-1}$ for Nafion 117. Then, $\sigma^{eff}_{mem}$ in different solutions is only a function of $\varepsilon_{c m s}^{eff}$. As shown in Table 3, $\varepsilon_{c m s}^{eff}$ is determined in a variety of ways, including two main aspects: (1) the membrane porosity is considered or not; (2) the fixed charges are compensated only by anions or protons, or by the ions obtained from the Donnan effect. Fig. 4a shows the membrane effective conductivities $\sigma^{eff}_{mem}$ calculated with different $\varepsilon_{c m s}^{eff}$, compared with the measured value in Ref. [28]. For cases 1–3 that neglect the membrane porosity, the calculated results of $\sigma^{eff}_{mem}$ are much larger than the experimental results, and this deviation is enhanced sharply with an increase in the external H$_2$SO$_4$ concentration. But for cases 4–6 of considering the membrane porosity or assuming $\varepsilon_{c m s}^{eff}$ to be $c_{\sigma_{\infty}}$, the prediction accuracy of $\sigma^{eff}_{mem}$ is improved. Among them, the result of $\sigma^{eff}_{mem}$ calculated by considering the ion selective adsorption is better. For case 4, the good accuracy of $\sigma^{eff}_{mem}$ is specific since in sulfuric acid solution only H$^+$ is adsorbed in the membrane and co-ions are largely repulsed. To compare the accuracy of cases 4–6, the membrane effective conductivity of Nafion 117 in [VOSO$_4$ + H$_2$SO$_4$] solutions is discussed as shown in Fig. 4b, where $\varepsilon_{c m s}^{eff}$ in Eq. (9) is from cases 4–6. It is found that, for both 1 M and 3 M H$_2$SO$_4$, the value of $\sigma^{eff}_{mem}$, determined with the ion selective adsorption considered (case 5), is significantly reduced with the addition of vanadium ion in the external solution. This phenomenon was mentioned in Ref. [28], where $\sigma^{eff}_{mem}$ measured in 5 M H$_2$SO$_4$ and [1 M VOSO$_4$ + 5 M H$_2$SO$_4$] are 7.3 and 5.0 5, respectively. Although the H$_2$SO$_4$ concentration is different, the extent of reduction in $\sigma^{eff}_{mem}$ we calculated is similar to the experimental result. But for cases 4 and 6, the predicted $\sigma^{eff}_{mem}$ remains stable or decreases slightly with an increase in the external VOSO$_4$ concentration. In conclusion, by incorporating our ion selective adsorption model, the prediction accuracy of the membrane effective conductivity in VRFB systems is greatly enhanced.

3.4. VRFB model

3.4.1. Vanadium crossover and membrane conductivity

Since the ion selective adsorption has a great influence on the ion transport through the membrane, we propose a modified VRFB model that incorporates the ion selective adsorption to predict battery performance, as described in Section 2.4. The crossover rate of vanadium ions through the Nafion 117 under different operating conditions in VRFBs is discussed, where the current density is 400 A m$^{-2}$ and the external vanadium concentration is 1 M. Fig. 5 shows the crossover of VO$_2^+$, including the diffusion, convection, migration, and the total ion flux. The ion flux from the negative electrode to the positive electrode is defined as positive. The results show that, the consideration of ion selective adsorption greatly affects the calculated VO$_2^+$ crossover under various operating conditions. The change in the total flux has been shown in each figure, even up to 239% in Fig. 5c. This is due to the change in diffusion and convection terms, since these two terms are directly related to the ion concentration in the membrane. In addition, the change in the total flux is also related to the directions of diffusion and convection. In the same direction, the amount and extent of this change is promoted; whereas in the opposite direction, the effects of diffusion and convection on the total flux are partially offset. For each ion, the direction of diffusion is fixed during cycles; the direction of convection is determined by the direction of the current density, provided that the pressure difference across the membrane is set to 0 Pa. Therefore, the influence of ion selective adsorption on crossover of vanadium ions in VRFBs is significant and complicated under different operating conditions.

Fig. 6a–c shows the crossover rates of all vanadium ions in the VRFB, obtained with and without the ion selective adsorption considered. The current density is set to 400 A m$^{-2}$ and the external vanadium concentration is 1 M. It is found that under each operating condition, considering the ion selective adsorption in the model results in a great change in the flux of vanadium ions and the direction of this change is consistent for all vanadium ions. At the charging state, this direction is from positive electrode to negative electrode; while, at the discharging state, the direction is opposite; that is, the direction of flux change is determined by the current density. Besides, it is found that the vanadium crossover is dominated by VO$_2^+$, V O$_2$ at the charging state of SOC = 0.5 while that is dominated by V$^{3+}$, V$^{3+}$ at the discharging state. The dominant extent may be related to the magnitude of current density. Therefore, it is essential to consider the ion selective adsorption in the calculation, which helps to improve our understanding of vanadium crossover in VRFBs.

Furthermore, Fig. 6d shows the membrane effective conductivity $\sigma^{eff}_{mem}$ of Nafion 117 at the charging state of SOC = 0.5, where the current density is set to 400 A m$^{-2}$ and the external vanadium concentration is 1 M. It is found that, due to the neglect of ion selective adsorption, the membrane effective conductivity is seriously overestimated, especially at larger H$_2$SO$_4$ concentration in electrolytes. Therefore, it is very important to consider the ion selective adsorption in the model, which can largely improve the prediction accuracy of membrane effective conductivity during charging-discharging processes in VRFBs.

3.4.2. Battery performance

After a discussion on the vanadium crossover and membrane effective conductivity in VRFBs, the battery performance including the electrolyte imbalance and coulombic efficiency is studied. The current density is set to 400 A m$^{-2}$ and the external vanadium concentration is 1 M. As a comparison, the result of VRFB model with ion selective adsorption neglected is also given. Fig. 7a shows the electrolyte imbalance of five cycles at different external H$_2$SO$_4$ concentrations. Taking the positive electrolyte as an example, the results of electrolyte imbalance are almost the same at different H$_2$SO$_4$ concentrations for the model with ISA neglected (dotted line); while, when the ISA is considered (solid line), the results of electrolyte imbalance at 1 M and 3 M H$_2$SO$_4$ are much different. With an increase in the H$_2$SO$_4$ concentration of electrolytes from 1 M to 3 M, the electrolyte imbalance is reduced by

<table>
<thead>
<tr>
<th>Case</th>
<th>$\varepsilon_{c m s}^{eff}$ Expression</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>$c_{\sigma_{\infty}}$</td>
<td>Membrane porosity is neglected; $c_{\sigma_{\infty}}$ is compensated by anions</td>
</tr>
<tr>
<td>2</td>
<td>$c_{\sigma_{\infty}} + c_{\sigma}$</td>
<td>Membrane porosity is neglected; $c_{\sigma}$ is compensated by protons</td>
</tr>
<tr>
<td>3</td>
<td>$c_{\sigma_{\infty}} = c_{\sigma_{\infty}} e^{-\left(-\frac{\varepsilon_{\sigma_{\infty}}}{\varepsilon_{\sigma_{\infty}} + \varepsilon_{\sigma_{\infty}}}</td>
<td></td>
</tr>
</tbody>
</table><p>ight)}$ | Membrane porosity is neglected; Donnan effect is considered |
|      | $\sum z_{\sigma_{\infty}} x_{\sigma_{\infty}} = \sum z_{\sigma_{\infty}} x_{\sigma_{\infty}} + c_{\sigma} c_{\sigma}$ | |
| 4    | $c_{\sigma}$ | Membrane porosity and Donnan effect are considered |
| 5    | $\varepsilon_{c m s}^{eff} = \exp\left[-\frac{\varepsilon_{\sigma_{\infty}}}{\varepsilon_{\sigma_{\infty}} + \varepsilon_{\sigma_{\infty}}}ight]$ | $\varepsilon_{c m s}^{eff}$ is assumed to be $c_{\sigma}$ |
| 6    | $\sum z_{\sigma_{\infty}} x_{\sigma_{\infty}} + c_{\sigma}$ | Membrane porosity is considered; $c_{\sigma}$ is compensated by protons |</p>

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34.1%. For the coulombic efficiency, the situation is similar, as shown in Fig. 7b. For the model with ISA considered, the coulombic efficiency is lower at a smaller H2SO4 concentration; while, for the model with ISA neglected, the coulombic efficiencies are almost the same. In conclusion, the transient VRFB model must be improved by incorporating the ion selective adsorption, which enables to reflect the effect of key parameters of membrane and electrolytes on battery performance.

With the improved VRFB model, the effects of membrane properties and operating conditions on battery performance are investigated. In each electrolyte, the vanadium and H2SO4 concentrations are 1 M and 3 M, respectively. Fig. 8a and b separately show the electrolyte imbalance and the coulombic efficiency during five cycles, with different membrane porosities and fixed concentrations. The electrolyte imbalance is characterized by the total vanadium ions in negative electrolyte. For a certain fixed concentration, as the membrane porosity increases from 0.135 to 0.22 and 0.3, the total vanadium ions in negative electrolyte decreases by 10% and 25% respectively, that is, the electrolyte imbalance is slightly worse; the coulombic efficiency is almost unchanged. When the membrane porosity is fixed, as the fixed concentration increases from 1063 to 2000 and 3000 mol m\(^{-3}\), the total vanadium ions in negative electrolyte decreases by 98% and 210% respectively, that is, the electrolyte imbalance is severely deteriorated; the coulombic efficiency is also significantly reduced. It should be noted that the change in membrane pore size is not in our consideration. In addition, the effect of membrane properties on membrane effective conductivity is investigated, as shown in Table 4. It should be explained that for any membrane type in the table, the results of membrane effective conductivity cover the entire battery operating range, and this conductivity increases with the state of charge SOC. By comparing the results of these membranes, it shows that the membrane effective conductivity increases with both the membrane porosity and the fixed concentration, where the effect of membrane porosity is more significant. Combining the above discussions on the electrolyte imbalance, coulombic efficiency and membrane effective conductivity, it is concluded that (i) an appropriate increase in the membrane porosity helps to overall improve the battery performance; (ii) the fixed concentration should be carefully changed to avoid a serious deterioration of electrolyte imbalance and a drastic reduction of coulombic efficiency.

Fig. 8c shows the capacity decay of the battery cycling with SOC = 0.05–0.30 and SOC = 0.70–0.95, respectively, where the current density is 1600 A m\(^{-2}\). It is found that the battery capacity decays more seriously at SOC = 0.70–0.95, inferred that it is better to avoid the battery overcharging at high current density. Fig. 8d shows the capacity decay for various current densities. When the abscissa is the cycle number, the battery capacity decays more seriously at lower current density; while, when the abscissa is the running time, the situation is different, which truly reflects the impact of vanadium crossover rate on the battery capacity. It shows that the battery capacity curves almost coincide at current densities of 200 and 400 A m\(^{-2}\). When the current density is larger than 400 A m\(^{-2}\), the capacity decays more seriously as the current density increases. It implies that operating at high current densities would shorten the replacing interval of battery electrolytes.

4. Conclusion

In the present work, an improved model of ion selective adsorption in ion exchange membranes is proposed and applied in vanadium redox flow batteries. Since movable ions are distributed in the membrane pores only, a membrane pore volume-averaged concentration is...
introduced in the ion selective adsorption model that incorporates the Donnan effect, thereby eliminating the dependence on the empirical coefficients and improving the model accuracy. The results are in good agreement with the experiment data. Then, the model is applied to the calculation of ion transport through membranes in VRFBs. The model shows a more accurate prediction of vanadium crossover and membrane effective conductivity, and enables to capture the effect of key parameters of membrane and electrolytes on the battery performance. The results show that (i) an increase in H₂SO₄ concentration from 1 M to 3 M improves the coulombic efficiency and reduces the electrolyte imbalance by 34%; (ii) an increase in membrane porosity from 0.135 to 0.3 approximately doubles the membrane effective conductivity, with a slight worse in the electrolyte imbalance and no decrease in the coulombic efficiency; (iii) however, the change in the fixed concentration should be careful. As it increases, the membrane effective conductivity is improved, while the electrolyte imbalance is severely deteriorated and the coulombic efficiency is greatly reduced. Furthermore, at high current densities, the replacing interval for two electrolytes is shortened and the battery overcharging needs be avoided. These results suggest that both key membrane parameters and operating conditions need proper adjustment to improve the battery performance, and our VRFB model with the incorporation of ion selective adsorption is a good tool for these applications.

Fig. 6. (a–c) The crossover rates of all vanadium ions and (d) the membrane effective conductivity in the VRFB, with and without ISA considered. The current density is 400 A m⁻² and the external vanadium concentration is 1 M. Each operating condition is shown in the figure.

Fig. 7. The comparison of (a) electrolyte imbalance and (b) coulombic efficiency, with and without ISA considered at various H₂SO₄ concentrations. The current density is 400 A m⁻² and the external vanadium concentration is 1 M.
for designing and optimizing membranes.

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