



Role of convection and related effects on species crossover and capacity loss in vanadium redox flow batteries

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ABSTRACT

This study reports important observations regarding the convective transport through the membrane and related effects on the species crossover and the capacity loss in vanadium redox flow batteries (VRFBs). A 2-dimensional, isothermal, transient model is utilized to simulate several extended charge/discharge cycles with varying flow rates and electrolyte viscosities. The simulations indicate that osmotic and electro-osmotic convections in the membrane are major mechanisms contributing to species crossover. In addition, variations in electrolyte viscosity are observed to have a significant impact on the direction and magnitude of species crossover during VRFB operation. Finally, the simulations suggest that one potential approach to minimize the capacity loss in VRFBs would be to operate the system at constant pressure condition through the utilization of asymmetric flow rates (i.e. different flow rates in the '+' and '-' half-cells) to reduce the impact of osmotic convection.

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1. Introduction

Currently, the long-term performance of vanadium redox flow batteries (VRFBs) is limited by the significant loss of available stored energy in the electrolytes over time. The capacity loss occurs primarily due to the undesired transport of active vanadium species across the membrane [1]. Species crossover occurs as a result of three transport mechanisms in the membrane, namely; convection, diffusion, and migration. The rate of species transport across the membrane is primarily governed by the chemical composition of the membrane. In addition to membrane, electrolyte properties and operating conditions (e.g., flow rate) affect the spatial distribution of the potential and concentration inside the cell, which have a direct effect on the vanadium crossover [2–5]. To date, significant effort has been focused on the development of chemically stable membranes with low vanadium permeability [2–6]. However, identifying proper membrane architectures is currently hampered by the lack of understanding how these ion transport mechanisms are affected by the membrane composition and key operational parameters.

In a previous work by the authors, a comprehensive VRFB model was developed which incorporates, for the first time, the transport of all species through the membrane as a result of convection, diffusion and migration [7]. The model simulations suggested that diffusion and migration may *not* be the dominating mechanisms for species crossover in the membrane. Motivated by this observation, the objective of this study is to investigate the convective transport and related effects on the vanadium crossover. Several case studies

were conducted to examine the impact of i) electro-osmotic convection due to viscous interactions between the mobile ions and the electrolyte and ii) osmotic convection due to pressure gradients across the membrane [7]. In addition, the model was utilized to provide insight on how to select operating conditions to control the convection in the membrane and minimize the capacity loss in VRFBs.

2. Model description and case studies

In this study, four different case studies (that have different electrolyte viscosities and flow rates) were simulated to quantify the impact of convection on vanadium crossover. The main input parameters for these cases can be found in Table 1. The simulations were conducted using a 2-D, transient, isothermal model developed by the authors. The model incorporates the transport of all species (i.e., vanadium, water, hydrogen ions and bisulfate) across the membrane and accounts for all three transport mechanisms (i.e., convection, diffusion, and migration) [7]. The voltage is predicted using the Butler–Volmer equation along with a more complete version of the Nernst equation proposed for VRFBs [8]. To further improve the model accuracy, the key structural properties of the porous electrode material were captured using micro X-ray tomography and used as input in the model [9]. In addition, the model utilizes a set of boundary conditions based on the conservations of flux and current at the electrolyte/membrane interfaces to account for the side reactions associated with species crossover. All other sources of capacity loss (e.g. electrolyte leakage and irreversible reactions) are assumed to be negligible. In terms of validation, the model predictions were compared against a single charge/discharge cycle and a 45 cycle tests [4]. A very good agreement in cell voltage (less than 2% average error) and the capacity loss (less than 4% average error) due to the

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Table 1
Input parameters for simulated cases.

Parameters	Operating conditions		Viscosity effect	
	Case 1 (const flow rate)	Case 2 (const pressure)	Case 3	Case 4
Cell size [cm ²]	10	10	10	10
Current [mA]	500	500	500	500
Half-cell volume [ml]	25	25	25	25
Initial vanadium [mol l ⁻¹]	1.04	1.04	1.04	1.04
Total sulfate [mol l ⁻¹]	5.04	5.04	5.04	5.04
(+) viscosity [Pa s]	5×10^{-3}	5×10^{-3}	2.5×10^{-3}	2.5×10^{-3}
(-) viscosity [Pa s]	2.5×10^{-3}	2.5×10^{-3}	5×10^{-3}	25×10^{-3}
(+) flow rate [ml min ⁻¹]	20	40	20	20
(-) flow rate [ml min ⁻¹]	20	20	20	20

species crossover has been observed. The detailed description of the model formulation along with the model parameters, governing equations, boundary conditions, and assumptions can be found in [7].

3. Results and discussion

3.1. Constant flow rate vs. constant pressure

Osmotic convection occurs due to the pressure gradients across the membrane. These pressure gradients arise as a result of the electrolyte flow conditions (i.e., flow rate and electrolyte composition) within the system. Therefore, the first set of simulations (Cases 1 and 2) were selected to represent two flow conditions for a VRFB. Case 1 is a constant flow rate condition (i.e., same flow rate in each half-cell), and Case 2 represents a constant pressure condition (i.e., same pressure throughout each half-cell), where constant pressure was obtained by increasing the positive half-cell flow rate to account for variations in viscosity. In this study, simulations were performed for an electrolyte composition that has 1.04 M vanadium in 4 M H₂SO₄.

Fig. 1a shows the change in capacity after each cycle for both cases, where capacity was calculated with respect to the discharge time of the first cycle:

$$\text{capacity} = \left(\frac{t_{\text{dis},n}}{t_{\text{dis},1}} \right) \times 100\% \quad (1)$$

The capacity of a VRFB is limited by the amount of vanadium in the most vanadium deficient half-cell, which is the positive half-cell in this study due to crossover and the selected electrolyte composition for the simulation. As seen in Fig. 1a, the constant pressure operation appears to have a significantly reduced capacity loss (~96% capacity after 35 cycles) as compared to the constant flow rate operation (~87% capacity after 35 cycles). The amount of vanadium crossover in the constant pressure operation is observed to be relatively lower than the constant flow rate operation (Fig. 1b). This trend can be attributed to the smaller net vanadium transfer from the positive to the negative half-cell in the constant pressure condition. When the positive half-cells (i.e., deficient half-cells) of these two cases are compared, the constant pressure case has a consistently larger amount of vanadium in the positive half-cell over each cycle due to the slower rate of capacity loss.

The observed discrepancy in vanadium crossover between Cases 1 and 2 (Fig. 1b) can be explained through analysis of the magnitude and direction of the osmotic convection. Fig. 2 shows the average convection in the membrane at 50% state of charge (SOC) during the 35th cycle for both cases. Fig. 2a shows that the constant flow rate operating condition (Case 1) produces a constant osmotic convection from the '+' to '-' half-cell regardless of the direction of current, whereas the electro-osmotic convection is the same but occurs in a different

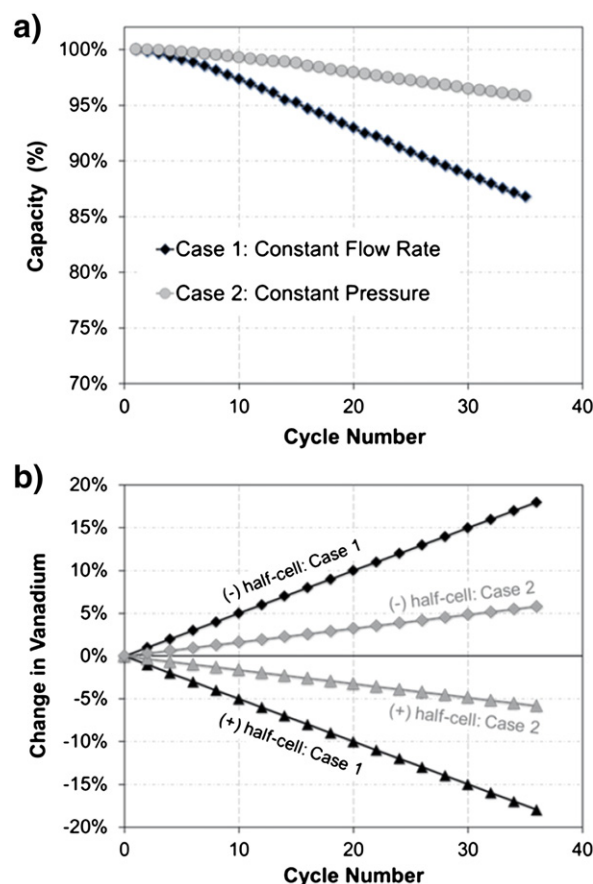


Fig. 1. Simulated results for constant pressure vs. constant flow rate case study: a) change in capacity loss (discharge time) after 35 cycles and b) change in vanadium in each half-cell at the end of each cycle.

direction during charge and discharge. This trend can be attributed to the difference in electrolyte viscosity between '+' and '-' half-cell (the positive electrolyte is more viscous than the negative electrolyte). The difference in electrolyte viscosities causes each half-cell to have a different pressure drop, which would result in a pressure difference (and osmotic convection) across the membrane.

In addition, Fig. 2a shows that the *net* rate of convection from the '+' to '-' half-cell during charge is 2× higher than the *net* rate of convection from the '-' to '+' half-cell during discharge. The difference in net convective transfer is governed by the osmotic convection, since electro-osmotic convection yields zero net effect for an entire cycle. Therefore, during constant flow rate operation, one would expect a net convection from the '+' to '-' half-cell, which yields a net vanadium transfer in the same direction.

In line with the analyses given above, Fig. 2b suggests that the constant pressure operating condition (Case 2) eliminates the osmotic convection, which results in a more balanced net convection between charging and discharging. Elimination of the pressure gradient across the membrane reduces the net vanadium transfer from the '+' to the '-' half-cell during a single cycle, which agrees with the trends in vanadium transfer observed for the 35 cycle simulation (Fig. 1b). However, it is important to note that despite the elimination of osmosis, a net crossover from the '+' to '-' half-cell is still observed for Case 2. This occurs for two reasons: i) electro-osmosis always facilitates vanadium transfer in the same direction as current (i.e. from '+' to '-' half-cell during charge and vice versa during discharge) and ii) the charge time is longer than the discharge time. Therefore, in a given cycle, the longer charge time results in more time for vanadium to transfer from the '+' to '-' half-cell, yielding a net crossover towards the '-' half-cell. Based on the simulation results of Cases 1 and 2, it can be concluded that one

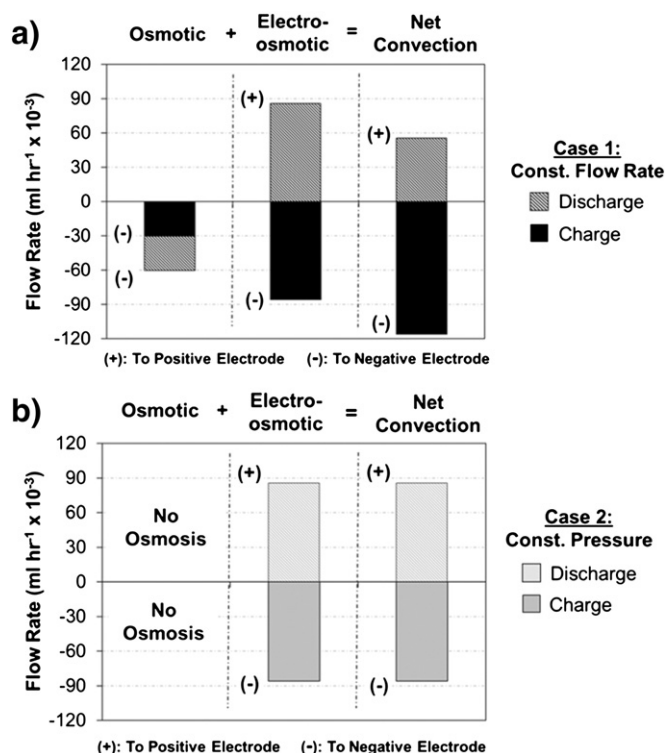


Fig. 2. Average convective flow rate across the membrane during the 35th cycle at 50% SOC for a) Case 1 (constant flow rate) and b) Case 2 (constant pressure).

potential approach to mitigate the capacity loss in a VRFB would be to operate the system at constant pressure condition through utilization of asymmetric flow rates (i.e., different flow rates in the '+' and '-' half-cells) to minimize the impact of osmotic convection on species crossover.

3.2. Influence of viscosity on vanadium crossover

In the previous section, it was suggested that the osmotic convection in the constant flow rate case occurs as a result of variations in the electrolyte viscosities, which yields a pressure gradient across the membrane. To further investigate the impact of electrolyte viscosity on the direction and magnitude of the vanadium crossover, three different cases (Cases 1, 3, and 4, see Table 1) were simulated with varying electrolyte viscosities that can be observed during VRFB operation. The viscosity values of the Case 1 were taken from [10] and selected as a baseline.

Fig. 3a shows the capacity loss over 20 cycles for these three cases. It was observed that the rate of capacity loss varies significantly depending on the variations in electrolyte viscosity. For example, a 5× increase in the negative electrolyte viscosity between Cases 3 and 4 results in an increase of capacity loss from ~0% to over 25% after 20 cycles. These variations in capacity loss can be attributed to the impact of the difference in electrolyte viscosities on the magnitude of the pressure gradient across the membrane.

In addition, Fig. 3b indicates that the direction and magnitude of net vanadium crossover also depend on the electrolyte viscosities, which vary based on electrolyte composition and SOC. The net direction of vanadium crossover is found to be towards the less viscous electrolyte regardless of the tested cases (e.g., '-' half-cell for Case 1 and '+' half-cell for Cases 3 and 4), which agrees with the fact that the direction of osmotic convection will always take place from a high pressure region (more viscous electrolyte) to a low pressure region (less viscous electrolyte).

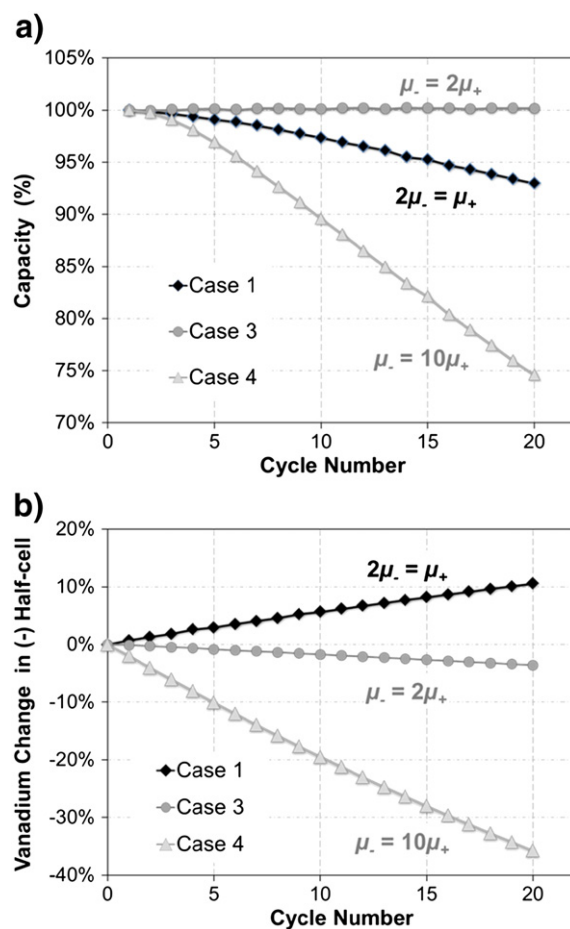


Fig. 3. Simulated results for viscosity case study: a) change in capacity loss (discharge time) after 20 cycles, and b) change in vanadium in '-' half-cell at the end of each cycle.

4. Conclusion

In this work, the convective transport in the membrane and related effects on vanadium crossover and capacity loss in VRFBs was investigated using a 2-D performance model developed by the authors. The model predictions indicate that convective transport across the membrane is a major mechanism contributing to the vanadium crossover. Model simulations suggest that the rate of vanadium crossover can be reduced through the use of asymmetric flow rates (different flow rates in the '+' and '-' half-cells) to control the pressure drop across the membrane and minimize the impact of osmotic convection. Furthermore, the direction and magnitude of the osmotic convection and resulting crossover are found to be highly dependent on the viscosity of the electrolytes in each half-cell.

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