



## Reducing capacity fade in vanadium redox flow batteries by altering charging and discharging currents



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### HIGHLIGHTS

- Asymmetric current operation is explored as a technique to reduce capacity loss.
- Diffusion-dominated and convection-dominated membranes.
- Capacity loss of a VRFB is found to decrease with increasing charging current.
- The decrease in capacity loss is greater for the diffusion-dominated membrane.
- Voltage efficiency is found to decrease with an increase in the charging current.

### ARTICLE INFO

#### Article history:

Received 8 May 2013

Received in revised form

27 July 2013

Accepted 5 August 2013

Available online 15 August 2013

#### Keywords:

Asymmetric current

Capacity fade

Crossover

Energy storage

Membrane

Vanadium flow battery

### ABSTRACT

In this study, the operation of a vanadium redox flow battery (VRFB) under asymmetric current conditions (i.e., different current densities during charge and discharge) was investigated as a technique to reduce its capacity loss. Two different membrane types (a convection-dominated membrane and a diffusion-dominated membrane) were analyzed. In these analyses, the charging current density was varied while the discharging current was held constant. For both membranes, it was found that increasing the charging current decreases the net convective crossover of vanadium ions, which reduces the capacity loss of the battery. When the tested membranes were compared, the improvement in capacity retention was found to be larger for the diffusion-dominated membrane (12.4%) as compared to the convection-dominated membrane (7.1%). The higher capacity retention in the diffusion-dominated membrane was attributed to the reduction in the cycling time (and hence, suppressed contribution of diffusion) due to the increased charging current. While asymmetric current operation helps reduce capacity loss, it comes at the expense of a reduction in the voltage efficiencies. Increasing the charging current was found to increase the ohmic losses, which lead to a decrease of 6% and 4.3% in the voltage efficiencies of the convection-dominated and diffusion-dominated membranes, respectively.

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### 1. Introduction

Vanadium redox flow batteries (VRFBs) hold great promise for use in grid-scale energy storage due to their flexible design and ability to efficiently store large amounts of energy. Unlike conventional electrochemical systems (e.g., closed-cell batteries and supercapacitors), VRFBs have a unique system architecture which allows them to decouple energy storage capacity from power output [1–5]. Although this architecture offers a number of key advantages, one major issue that hinders the long-term

performance of these systems is the loss of available capacity over time. Typically, VRFBs experience significant capacity fade during cycling, which occurs primarily due to the undesired transport of vanadium ions through the membrane (known as ‘crossover’). Species crossover during operation initiates side reactions which reduce the system capacity, lower the device voltage, and increase the operating cost [6].

One main approach to alleviate the crossover problem in these systems is to employ a membrane that has high ion selectivity for ion conduction versus vanadium crossover. To date, a majority of the studies in this field have been largely focused on exploring new membranes that can effectively suppress vanadium crossover while providing reasonable proton conductivity. Various types of membranes, including: proton exchange membranes (PEMs) [7,8], anion exchange membranes [9–11], nanoporous membranes [12] and

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amphoteric membranes [13,14] have been investigated. While significant progress has been achieved, one major issue limiting the implementation of these membranes is the conductivity/permeability trade-off. In most cases, raising the conductivity of the membrane results in an increase in the vanadium permeability, and vice versa. For instance, increasing the ion exchange capacity improves the proton conductivity; however this improvement often results in an increase in vanadium permeability and water uptake, which increases the crossover [15]. Although with the help of recent efforts, significant advances with regards to performance and capacity fade have been achieved with new membranes as compared to Nafion® (which has been widely accepted as a benchmark membrane for VRFBs), the performance trade-off between conductivity and vanadium permeability in these systems is not well understood at present. The lack of a breakthrough in the conductivity/permeability trade-off is largely due to the lack of understanding of the multi-ionic transport mechanisms and how they are related to the membrane properties. Studies are still underway to better understand this trade-off and explore new membranes that are inexpensive and possess the desired performance characteristics required for long-term VRFB operation.

In addition to tailoring membrane properties, our recent studies [16–18] indicate that one potential approach to reduce the crossover during VRFB operation is altering the operating conditions (e.g., flow type, flow rate) to take advantage of the membrane properties. The idea behind this approach is that by adjusting the operating conditions, it is possible to minimize the driving forces that are responsible for species crossover in the membrane. In our previous studies [16–18], we investigated the transport of vanadium species ( $V^{2+}$ ,  $V^{3+}$ ,  $V^{4+}$ ,  $V^{5+}$ ) through the membrane as a result of diffusion, convection, and migration. For diffusion-dominated membranes such as Nafion®, we observed that osmotic convection (which occurs due to the difference in viscosities of the electrolytes in positive and negative half-cell giving rise to a pressure gradient across the membrane) has a significant effect on the magnitude and direction of net crossover flux [16]. Accordingly, it was shown that by controlling the pressure gradient across the membrane, the net osmotic convection in a charge/discharge cycle can be minimized, and the net species crossover (and thus capacity fade) can be significantly reduced [17]. This was also experimentally observed in Ref. [19]. Similarly, in a more recent study [18], we compared the species transport mechanisms governing capacity loss in Nafion® 117 and sulfonated Radel (s-Radel) membranes [6]. The goal of this study was to quantify how the differences in key membrane properties affect the dominance of specific species transport mechanisms within the membrane. When compared to Nafion®, s-Radel (composed of post-sulfonated polyphenylsulfone resin – Radel) has been shown to possess superior ion selectivity, high coulombic efficiency, and low capacity fade rate (almost half that of Nafion®) [6]. Our analysis indicated that the transport of vanadium ions across s-Radel is primarily dominated by electro-osmotic convection, which depends on the magnitude and direction of the current [18]. Accordingly, it was suggested that varying the applied current during charging and discharging (i.e., using different current during charge and discharge) can potentially balance the convective crossover (osmosis and electro-osmotic convection) during cycling, which would reduce the capacity fade.

Motivated by the findings in our previous work, in this study, we further explored the effectiveness of altering the charge and discharge current as a potential technique to reduce the capacity loss in VRFBs. Two types of membranes, namely a diffusion-dominated and a convection-dominated membrane, were investigated to assess the effectiveness of the proposed technique with respect to membrane type/properties. Analyses were conducted by using an experimentally-validated VRFB model that was developed

**Table 1**

Side reactions incorporated at membrane|electrolyte interface in the model due to crossover [20].

Mobile species <sup>a</sup>	Reaction location	Side reaction
$VO^{2+}$	Negative half-cell	$VO^{2+} + V^{2+} + 2H^+ \rightarrow 2V^{3+} + H_2O$
$VO_2^+$	Negative half-cell	$VO_2^+ + 2V^{2+} + 4H^+ \rightarrow 3V^{3+} + 2H_2O$
$V^{2+}$	Positive half-cell	$V^{2+} + 2VO_2^+ + 2H^+ \rightarrow 3VO^{2+} + H_2O$
$V^{3+}$	Positive half-cell	$V^{3+} + VO_2^+ \rightarrow 2VO^{2+}$

<sup>a</sup> Indicates species which crosses over and initiates the side reaction.

by our group [16]. Several studies, including the long-term cycling performance under symmetric (i.e., same current during charge/discharge) and asymmetric current operations (i.e., different currents during charging and discharging) were performed for these two membrane types. The changes in specific transport modes and resulting crossover with respect to tested operating conditions were quantified and linked to the membrane properties to measure the effectiveness of the approach and provide guidance for future optimization efforts.

## 2. Model formulation and method of approach

### 2.1. Assumptions and governing equations

The proposed asymmetric current operation technique was evaluated using a 2-D, transient, isothermal VRFB model previously developed by the authors [16]. The model has five domains (i.e., positive/negative current collector plates, negative/positive electrode, and membrane) and was constructed based on the assumptions that i) the electrolyte flow is incompressible, ii) the mass and charge transfer properties of the electrode, electrolyte and membrane (i.e., diffusion coefficients, resistivity, etc.) are isotropic, iii) hydrogen and oxygen evolution are neglected, iv) all domains in the cell are isothermal and v) variations in concentration, potential, and pressure in the z-direction are neglected (i.e., 2-dimensional). Detailed information about this model, including governing equations, boundary and initial conditions for each domain, can be found in our previous studies [16–18]. However, for the sake of the readers, a brief description regarding how the species transport is modeled in the membrane (the key domain for the current study) is provided below.

The model incorporates the transport of all vanadium species, water, protons and sulfate ions across the membrane as a result of convection, diffusion, and migration. The transport of species through the electrodes and membrane is modeled using the Nernst–Planck equation:

$$\vec{N}_i^m = -D_i^m \nabla c_i^m - z_i \frac{F}{RT} D_i^m c_i^m \nabla \phi_i^m + \vec{v}^m c_i^m \quad (1)$$

where  $c_i^m$  is the bulk concentration of species  $i$  in the membrane,  $\vec{N}_i^m$  is the flux of the species  $i$  in the membrane,  $D_i^m$  is the diffusion coefficient of species  $i$  in the membrane,  $c_i^m$  is the diffusion coefficient of species  $i$  in the membrane,  $z_i$  is the valence for species,  $R$  is the universal gas constant and  $T$  is temperature,  $F$  is Faraday's constant, and  $\phi_i$  is the ionic potential. The velocity term,  $v$  is given by an alternate form of Schlogl's equation for describing the convective transport of bulk electrolyte:

$$\vec{v}^m = -\frac{\kappa_p}{\mu_w} \nabla p - \frac{\kappa_\phi}{\mu_w} c_f F \left( \nabla \phi_1^m + \frac{RT \sum z_i D_i^m \nabla c_i^m}{F \sum z_i^2 D_i^m c_i^m} \right) \quad (2)$$

where  $\mu_w$  is the viscosity of bulk electrolyte,  $\kappa_p$  is the electrokinetic permeability and  $\kappa_\phi$  is the hydraulic permeability. This equation accounts for i) the osmosis of electrolyte through the membrane as

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