In Situ Potential Distribution Measurement and Validated Model for All-Vanadium Redox Flow Battery

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An in situ, local potential measurement technique was further developed and applied to all-vanadium redox flow batteries to determine the potential distribution within multilayer electrodes of the battery. Micro-scale potential probes enabled in situ measurement of local potential in electrode layers between the cell flow field and membrane. The local redox potentials were recorded for different operating conditions and states of charges. To further analyze the behavior of potential distribution in the through-plane direction, a mathematical model was developed and the species distribution as well as the flux density of any individual component was modeled in terms of contributions from convective, diffusive and electrophoretic fluxes at each operating condition. Good agreement was achieved between the mathematical model prediction and experimental data with maximum error of 8%. Both mathematical simulation and experimental data confirmed the distribution of potential in the through plane direction as a function of discharge current density, predicting the lowest potential in a region close to the flow plate.

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Redox flow batteries have many benefits including energy efficiency, capital cost, and life cycle costs compared with other grid-scale energy storage technologies.1 Multiple chemistries have been developed for redox flow batteries such as iron-chromium,2 all-vanadium,3 bromine-poly sulfide4 and zinc-bromine.5 Among these, the all-vanadium redox flow battery (VRFB) has been studied in great detail and is relatively mature with several full-size systems in operation around the world. The VRFB employs the VO2+/VO2 redox couple at the negative side and the V4+/V3+ redox couple at the positive side, in the form of VOs2+1 and VO42−. The kinetics associated with reduction and oxidation of vanadium species are known to be very complex6,7 in this paper, the following simplified set of global half-reactions are adopted for the negative and positive electrodes.

\[
V^{3+} + e^- \leftrightarrow V^{2+} \quad E^0 = -0.26 \text{ V vs. RHE} 
\]

\[
VO_2^{2+} + H_2O \leftrightarrow VO_4^{3-} + 2H^+ + e^- \quad E^0 = 1.00 \text{ V vs. RHE} 
\]

One advantage of VRFBs is that in utilizing the same element, vanadium, as active species in both negative and positive electrolytes, crossover of active species does not foul the electrolyte, and results only in decreased coulombic efficiency. Storage capacity can be regained through electrolyte rebalancing. The VRFB also has a wide operating temperature range from -5 °C to 50 °C8 and fast response (around 350 μs) for start-up and switching between charging and discharging processes, using a sulfuric and hydrochloric acid mixture.9 Cost is still the major barrier to VRFB commercialization. Zhang et al.10 estimated that the cell stack is one of the highest cost components with 31% of capital cost from a base case VRFB. One way to decrease the stack cost is to increase the power density of the VRFB during charge-discharge cycles, allowing for smaller stacks for the same power.11 In order to achieve high power density, the cells should operate at high current density with decreased polarization losses (activation, ohmic and concentration).12 Among the components of the VRFB, electrode materials significantly contribute to activation and concentration overpotentials.13 Many prior efforts have focused on electrode material development and modification to improve performance.14–16 Along with better materials, there is also a need to develop an in situ diagnostic of the physicochemical phenomena happening within the electrodes during cell operation. Therefore, in this work, a diagnostic technique is established based on the implementation of a dynamic hydrogen electrode (DHE) for in situ measurement of the local potential distribution within the multilayer electrodes of the VRFB. Additionally, a mathematical model is presented that simulates the concentration distribution and local potential distribution within the VRFB electrode layers at different operating conditions. Finally, a comparison of experimental data and mathematical simulation has been provided.

Experimental

In situ potential distribution set-up.— Potential distribution measurements have been described in polymer electrolyte membrane fuel cell literature that include a reference electrode in the cell design.17–18 Kjeang et al.19 placed reference electrodes in the reservoirs of an operating microfluidic flow battery where the reference electrodes’ positions in the reservoirs resulted in large separation between the working electrode and the reference electrodes. Generally, sandwich-type and edge-type reference electrodes are commonly used for the study of thin layer cells. In the sandwich-type configuration, a fine wire reference electrode is inserted between two membranes.20,21 For this configuration, since two membranes are used, the membrane resistance increases by a factor of two or more. In the edge-type configuration, the reference electrode is attached to a region of the ion-exchange membrane that is well outside the active area between the two electrodes.22,23 For this configuration, membrane dehydration outside the active region is possible,24 thus the cell should be designed appropriately to prevent this.25 Also, much work has been described regarding the placement of reference electrodes inserted through the thickness of electrodes for secondary batteries and fuel cells. Ng et al. investigated inhomogeneity in current density distribution for lithium-ion batteries by designing an electrochemical cell
that utilized multiple working electrodes to measure the current density distribution across the electrode thickness.\(^{24}\) K. C. Hess et al. measured the electrolyte potential distribution through the thickness of a polymer electrolyte fuel cell electrode.\(^{25}\) This work utilized a cell equipped with a micro-structured electrode scaffold to analyze the transport through the porous electrodes, allowing estimation of the ionic conductivity in the electrodes. The same group utilized the electrode scaffold to measure the electrode potential through the negative electrode of an electrochemical double layer capacitor negative electrode of the VRFB.\(^{26}\) Charging/discharging rates were modeled. The electrode scaffold was further developed by the same group to measure electrolyte phase potential within an electric double layer capacitor negative electrode of the aqueous hybrid battery.\(^{27}\) The potential distribution data were used to identify the areas of the electrode that were underutilized and then investigate the cumulative charge storage distribution. In situ voltage measurement has also been applied to flowable electrode systems in which the behavior of the suspension electrodes has been investigated both static and flowing conditions.\(^{28}\)

In this work, a dynamic hydrogen electrode (DHE) has been used as the reference electrode. Usually, platinum (Pt) or palladium (Pd) serves as the working electrode for the DHE architecture where a small cathodic current produces hydrogen gas at the reference electrode location. Constant coverage of hydrogen on the electrode is required for the DHE to provide a stable potential. Due to the simplicity of the DHE set-up, not only does it minimize contamination risk to the measured system, but it also avoids the need of a bulky salt bridge.\(^{29}\) The DHE utilized two platinum wires sandwiched between two membranes; one wire served as the working electrode (WE) after forming a thin layer of hydrogen bubbles on its surface while the other electrode functioned as the counter electrode (CE).\(^{30}\) The equilibrium potential between the protons and hydrogen on a platinum wire can then serve as in situ reference electrode. Equation 3 includes the forward and reverse reactions associated with the DHE for the WE and CE respectively.\(^{31}\)

\[
2H^+ + 2e^- \leftrightarrow H_2 \quad E^0 = 0 \text{ vs. } RHE
\]  

Equation 3

It is critical to place the DHE in a uniform potential region of the cell in order to ensure uniform current density at the working electrode.\(^{32}\) Also, the distance between the reference electrode and the cell electrodes should be carefully selected so that the measurements are independent of the reference electrode location.\(^{33}\) Finally, uneven current distribution was avoided via precise alignment of the anode and cathode electrodes.\(^{31,32}\) These location-dependent considerations were met by ensuring that the distance between the tips of the reference electrode wires was ∼1 mm; this was also the distance from the tips of the electrode wires to the active electrode area. The reference electrode was installed in the vertical position as depicted in Fig. 1. Furthermore, the DHE was connected to the 9 V battery at least 30 minutes before any measurement to give time for potential stabilization.

In this work, the VRFB architecture was based on the acid-proof, modified fuel cell architecture (Fuel Cell Technologies, Inc.) with 5 cm\(^2\) active area, which includes no-gap construction.\(^{34,35}\) The 10AA carbon paper electrodes (SGL Group) were sandwiched between a flow plate and the membrane. On both sides, three layers of carbon paper were stacked to provide suitable surface area for electrode reactions. All measurements were performed on the positive half-cell. At the positive side, potential probes were placed between each layer of carbon paper. The tip of each probe was fixed to the center point on the surface of the carbon paper. The probes (125 μm diameter) were made of platinum wire covered by a layer of polytetrafluoroethylene (PTFE). Only the tip of Pt probe was exposed to electrolyte and was in direct electrical contact with the carbon paper. At the negative side, the same number of carbon papers as the positive side was used, but no potential probes were installed. Two pieces of Nafion 117 proton-exchange membrane (Ion Power, Inc) were used, between which was the reference electrode.\(^{36}\) PTFE gaskets were used to seal the cell and ensure even compression across the carbon paper electrode surface; gasket thickness resulted in ∼25% compression of the carbon paper electrodes. A schematic of the construction and placement of the DHE and Pt probes within the layers of the VRFB electrodes is shown in Fig. 1.

The electrolyte for all the experiments was 1 M\(\text{VOS}_2\cdot\text{H}_2\text{O}\) (20.87 wt% vanadium, 99.9% purity, Alfa Aesar, U.S.) dissolved in 5 M sulfuric acid (\(\text{H}_2\text{SO}_4\)). The initial volume of electrolyte was 50 and 100 ml at the negative and positive sides, respectively; after fully charging the battery, half of the positive electrolyte was removed so that both sides of the VRFB had 50 mL of electrolyte. Fully charging was assumed when the cell current was less than 20 mA (4 mA cm\(^{-2}\)) at an imposed voltage of 1.8 V. A two-channel peristaltic pump (Cole Parmer, U.S.) was used to circulate the electrolyte within the cell during testing. Nitrogen gas constantly purged the negative electrolyte to prevent oxidation of \(\text{V}^2+\).

In order to obtain the potential distribution experimental data, each potential probe was connected with the DHE through a multichannel potentiostat (Arbin Instruments, U.S.), and the potential differences between each probe and DHE were simultaneously recorded during single-cell operation for different operating conditions according to the procedure explained elsewhere.\(^{37}\) In order to conduct the experiments, replicate cells were assembled and the fully charged solution discharged at different current densities until the cell potential reached the cutoff voltage. The potentials referenced to the DHE from the 4 probes were simultaneously recorded at each SoC value.

**Mathematical Model**

Mathematical modeling aids in analyzing the VRFB system behavior since the presence of four different vanadium cations (\(\text{V}^{2+}\))/\(\text{V}^{3+}\))/\(\text{V}^{4+}\)/\(\text{V}^{5+}\)) on the negative side and \(\text{V}^{3+}\)/\(\text{V}^{4+}\)/\(\text{V}^{5+}\)) on the positive side) complicate interpretation of the experimental data. Several mathematical models have been developed for VRFBs, with varying levels of complexity. Li and Hikihara\(^{38}\) developed the first 0-D model for a VRFB to predict the dynamic performance of the battery. Shah et al.\(^{39}\) developed a 2-D transient model and simulated the distribution of current density, over-potential and reactant concentration during operation. The same group later expanded the model and simulated the effect of parasitic reactions including hydrogen and oxygen evolution.\(^{40,41}\) The model developed by Vynnycky\(^{42}\) was based on the asymptotic analysis that offered a significant simplification of the model already developed by Shah et al. The first 3-D model was developed by Ma et al.\(^{43}\) and further analyzed in greater depth by Xu et al.\(^{44,45}\) Oh et al.\(^{44,46}\) and Wang et al.\(^{47}\) The modeling of species crossover through the ion-exchange membrane originated with the work of Skyllas-Kazacos and co-workers\(^{48,49}\), in which they modeled the species crossover considering diffusion as the only mechanism for crossover. Knehr et al. simulated the crossover rate of active species through the membrane using a model based on dilute solution
approximation. Further analyses of crossover based on the dilute solution approximation have been recently performed.51,52 Models based on the resistor-and pore-network methodology53 and concentrated solution theory54–57 have also been developed to simulate the transport of species through the ion-exchange membranes.

In this work, a mathematical model has been developed consisting of the porous electrodes, electrolytes and the membrane as shown in Fig. 2. In the negative electrolyte, V(II), V(III), H⁺, HSO₄⁻, SO₄²⁻ ions and in the positive electrolyte V(IV), V(V), H⁺, HSO₄⁻, SO₄²⁻ ions have been considered. The goal of this model is not to develop a sophisticated comprehensive mathematical simulation, rather it is to develop a tool to analyze the experimental data obtained via the potential distribution apparatus. The following assumptions have been adopted within the model:

1. The geometry is two-dimensional
2. The cell is isothermal
3. The membrane is fully hydrated
4. H⁺ ions can cross the membrane, but other ions cannot
5. The dilute solution approximation is applicable for species transport within the porous media
6. Side reactions are negligible

**Model formulation.**—The model geometry is sketched in Fig. 2, which consists of three domains: negative electrode, ion-exchange membrane, and positive electrode. The geometric, material, and kinetic properties are summarized in Table I and the properties of the electrolyte are given in Table II.

**Porous carbon electrodes.**—Adopting the transport equations in dilute solution,58 the molar flux, \( N_j \), of ionic species \( j \) in the porous medium of porosity \( \varepsilon \) can be expressed via the Nernst-Planck equation. The Nernst-Planck equation represents ionic transport due to diffusive, electrophoretic and convective fluxes.

\[
N_j = -D_{ij}^{eff} \nabla c_j - z_j u_j c_j F \nabla \phi_e + v_{a_j c_j} c_j \tag{4}
\]

where \( c_j \) denotes the concentration of species \( j \), \( \phi_e \) is the electric potential in the electrolyte, \( v_{a_j c_j} \) is the superficial molar-averaged velocity of the electrolyte in the anode or cathode electrode, \( z_j \) is the charge number for species \( j \), and \( D_{ij}^{eff} \) is the effective diffusion coefficient in porous media for species \( j \), which can be related to the bulk diffusion

![Figure 2. 2-D Schematic of the computational domain.](image-url)

<table>
<thead>
<tr>
<th>Table I. Geometric, material and kinetic properties.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>Length of cell, ( l_{cell} ), [m]</td>
</tr>
<tr>
<td>Thickness of one layer of electrode, ( w_e ), [m]</td>
</tr>
<tr>
<td>Thickness of membrane, ( w_m ), [m]</td>
</tr>
<tr>
<td>Porosity of electrode, ( \varepsilon ), [-]</td>
</tr>
<tr>
<td>Width of electrode, ( t_e ), [m]</td>
</tr>
<tr>
<td>Specific surface area of the electrode, ( \sigma_s ), [m⁻¹]</td>
</tr>
<tr>
<td>Electronic conductivity of electrode, ( \sigma_e ), [S m⁻¹]</td>
</tr>
<tr>
<td>Mean fiber diameter, ( d_f ), [μm]</td>
</tr>
<tr>
<td>Kozeny-Karman constant, ( K ), [-]</td>
</tr>
<tr>
<td>Concentration of fixed-charge in the membrane, ( c_{f_r} ), [mol m⁻³]</td>
</tr>
<tr>
<td>Valence of fixed-charge in the membrane, ( z_f ), [-]</td>
</tr>
<tr>
<td>Hydraulic permeability of membrane, ( k_w ), [m²]</td>
</tr>
<tr>
<td>Electrokinetic permeability of membrane, ( k_e ), [m²]</td>
</tr>
<tr>
<td>Negative electrode reaction rate constant, ( k_{a_+} ), [s⁻¹]</td>
</tr>
<tr>
<td>Positive electrode reaction rate constant, ( k_{c_+} ), [s⁻¹]</td>
</tr>
<tr>
<td>Negative charge transfer coefficient, ( a_{-} ), [-]</td>
</tr>
<tr>
<td>Positive charge transfer coefficient, ( a_{+} ), [-]</td>
</tr>
</tbody>
</table>
Coefficient, \( D_j \), by the Bruggeman relation.

\[
D_j^{(1/2)} = \frac{D_j}{\varepsilon^{1/2}}
\]

The application of the Nernst-Planck equation in the form of Eq. 4 allows for the elimination of the ion mobility \( u_j \) as an independent parameter.

\[
u_j = \frac{D_j}{RT}
\]

If \( a \) is the specific interfacial area (surface area of the pore walls per unit volume of the total electrode \((m^2/m^3)\)), then the conservation of mass for the homogeneous reactions can be adopted for the heterogeneous reaction taking place at the electrode/electrolyte interface and formulated as:

\[
\frac{\partial}{\partial t}(a c_j) + \nabla \cdot J_j = a \sigma_j
\]

Where \( c_j \) is the bulk concentration and \( \sigma_j \) is the pore-wall flux density of species \( j \) averaged over the interfacial area (Table III). Three different averages within Eq. 7 are used: \( c_j \) is an average over the volume of the solution in the pores, \( \bar{c}_j \) is an average over the interfacial area between the matrix and the pore solution, and \( N_j \) is an average over a cross section through the electrode, dividing the matrix and pore. Equation 7 states that the concentration at a point within the porous electrode can change due to divergence of the flux density \( N_j \), which forces the species to move away from a point, or because the species undergoes an electrode process (faradaic electrochemical reactions or double-layer charging) or simple dissolution of a solid material. Equation 7 applies to all charged species except \( SO_4^{2-} \) which is calculated from the condition of electroneutrality within the electrolyte.

\[
\sum_j \bar{c}_j c_j = 0
\]

It is a consequence of the assumption of electroneutrality that the divergence of the total current density is zero. Therefore, the charge leaving the matrix phases must enter the pore solution. For the macroscopic model,

\[
\nabla i_e + \nabla i_s = 0
\]

where \( i_e \) and \( i_s \) are the ionic and electronic current densities that can be calculated using the following equations:

\[
i_e = F \sum_j \bar{c}_j N_j
\]

\[
i_s = -\sigma_j^{ff} \nabla \phi_i
\]

Where \( \sigma_j^{ff} \) is the effective electronic conductivity of the porous electrodes, which is related to the electronic conductivity of solid material, \( \sigma_s \), through Eq. 12.

\[
\sigma_j^{ff} = (1 - \varepsilon)^{3/2} \sigma_s
\]

Eq. 10 can now be used to solve for the divergence of the ionic current.

\[
\nabla i_e = \nabla F \sum_j \bar{c}_j N_j = F \sum_j \bar{c}_j \nabla N_j
\]

From the continuity equation substitution yields:

\[
\nabla i_e = \nabla F \sum_j \bar{c}_j - \frac{\partial}{\partial t} \sum_j \bar{c}_j c_j
\]

The last term within Eq. 14 vanishes due to electroneutrality within the solution. Let \( j_n \) be the transfer current per unit volume of the electrode \((A/m^3)\):

\[
j_n = \nabla i_e = a F \sum_j \bar{c}_j j_n = a_i_n
\]

Here \( i_n \) is the average transfer current density \((A/m^2)\). The Butler-Volmer expressions are used to formulate the transfer currents as a function of overpotentials. For the set of equations below, it is assumed that \( f = \frac{RT}{k T} \).

\[
j_{na} = a F k_a (c_{V_i})^{(1-a)} (c_{V_{O2}^+})^{(1+\alpha_+)} \left[ \frac{c_{V_{O2}^+}}{c_{V_i}} \right] \exp((1 - a) \ f \ \eta_a)
\]

\[
- \frac{c_{V_{O2}^+}}{c_{V_i}} \exp((-a) \ f \ \eta_a)
\]

\[
j_{nc} = a F k_a (c_{V_{O2}^+})^{(1+\alpha_+)} (c_{V_i})^{(1-a)} \left[ \frac{c_{V_i}}{c_{V_{O2}^+}} \right] \exp((1 - a) \ f \ \eta_n)
\]

\[
- \frac{c_{V_i}}{c_{V_{O2}^+}} \exp((-a) \ f \ \eta_n)
\]

Here, \( j_{na} \) and \( j_{nc} \) are the transfer current per unit volume of the electrode of anode and cathode side respectively, \( k_a \) and \( k_a \) are reaction rate constants for heterogeneous reaction, \( \alpha_+ \) and \( \alpha_- \) are the anodic and cathodic transfer coefficients for reactions 1 and 2, respectively, and \( \eta_a \) and \( \eta_n \) are the overpotentials, given by:

\[
\eta_a = \phi_i - \phi_e - E_a
\]

\[
\eta_n = \phi_i - \phi_e - E_c
\]

where \( E_a \) and \( E_c \) are the equilibrium potentials that can be calculated using the Nernst equation in which the proton activity in the positive half-cell due to participation of the protons in reaction has been taken into account.

\[
E_a = E_{0,a} + \frac{RT}{F} \ln \left( \frac{c_{V_{O2}^+}}{c_{V_i}} \right)
\]

\[
E_c = E_{0,c} + \frac{RT}{F} \ln \left( \frac{c_{V_i}}{c_{V_{O2}^+}} \right)
\]

where \( E_{0,a} \) and \( E_{0,c} \) denote the equilibrium potentials for negative and positive electrodes’ reactions at standard conditions. Furthermore,

### Table II. Electrolyte properties.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V(II) ) diffusion coefficient in the electrode, ( \text{[cm}^2\text{s}^{-1}\text{]} )</td>
<td>( 2.4 \times 10^{-10} )</td>
</tr>
<tr>
<td>( V(III) ) diffusion coefficient in the electrode, ( \text{[cm}^2\text{s}^{-1}\text{]} )</td>
<td>( 2.4 \times 10^{-10} )</td>
</tr>
<tr>
<td>( V(IV) ) diffusion coefficient in the electrode, ( \text{[cm}^2\text{s}^{-1}\text{]} )</td>
<td>( 3.9 \times 10^{-10} )</td>
</tr>
<tr>
<td>( V(V) ) diffusion coefficient in the electrode, ( \text{[cm}^2\text{s}^{-1}\text{]} )</td>
<td>( 3.9 \times 10^{-10} )</td>
</tr>
<tr>
<td>( H^+ ) diffusion coefficient in the electrode, ( \text{[cm}^2\text{s}^{-1}\text{]} )</td>
<td>( 9.3 \times 10^{-9} )</td>
</tr>
<tr>
<td>( HSO_4^- ) diffusion coefficient in the electrode, ( \text{[cm}^2\text{s}^{-1}\text{]} )</td>
<td>( 1.3 \times 10^{-9} )</td>
</tr>
<tr>
<td>( SO_4^{2-} ) diffusion coefficient in the electrode, ( \text{[cm}^2\text{s}^{-1}\text{]} )</td>
<td>( 1.1 \times 10^{-9} )</td>
</tr>
<tr>
<td>Density of negative electrolyte, ( \text{[cm}^3\text{kg}^{-1}\text{]} )</td>
<td>( 1300 )</td>
</tr>
<tr>
<td>Density of positive electrolyte, ( \text{[cm}^3\text{kg}^{-1}\text{]} )</td>
<td>( 1350 )</td>
</tr>
<tr>
<td>Dynamic viscosity of negative electrolyte, ( [Pa.s] )</td>
<td>( 1.0025 )</td>
</tr>
<tr>
<td>Dynamic viscosity of positive electrolyte, ( [Pa.s] )</td>
<td>( 0.0051 )</td>
</tr>
<tr>
<td>Dissociation reaction rate constant, ( k_a , [s^{-1}] )</td>
<td>( 10^5 )</td>
</tr>
<tr>
<td>( HSO_4^- ) degree of dissociation, ( \beta , [-] )</td>
<td>( 0.25 )</td>
</tr>
</tbody>
</table>

### Table III. Reaction source term.

<table>
<thead>
<tr>
<th>Term</th>
<th>Negative electrode</th>
<th>Positive electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \xi_{V^{2+}} )</td>
<td>( \frac{\partial}{\partial t} )</td>
<td>-</td>
</tr>
<tr>
<td>( \xi_{V^{3+}} )</td>
<td>( \frac{\partial}{\partial t} )</td>
<td>-</td>
</tr>
<tr>
<td>( \xi_{V^{O2+}} )</td>
<td>( \frac{\partial}{\partial t} )</td>
<td>( \frac{-k_a}{2} )</td>
</tr>
<tr>
<td>( \xi_{V^{O3+}} )</td>
<td>( \frac{\partial}{\partial t} )</td>
<td>( \frac{k_a}{2} )</td>
</tr>
<tr>
<td>( \xi_{H^{+}} )</td>
<td>( \frac{k_a}{2} )</td>
<td>( \frac{3k_a}{2} - \frac{k_a}{2} )</td>
</tr>
<tr>
<td>( \xi_{HSO_4^-} )</td>
<td>( \frac{3k_a}{2} )</td>
<td>-</td>
</tr>
</tbody>
</table>
there is a Donnan potential across the membrane due to the difference in proton activities across both half-cells.\(^{50}\)

\[
E_m = \frac{RT}{F} \ln \left( \frac{c_{H_2O_s}^V}{c_{H_2O_s}^e} \right)
\]  

[22]

Therefore, the full description of the open-circuit potential (OCP) for the VRFB can be formulated as the following:

\[
E_{corr} = E_e - E_a + E_m = E_{0,e} - E_{0,a} + \frac{RT}{F} \ln \left( \frac{c_{V_2+} c_{O_2^{2-}} c_{H_2O_s}^V}{c_{V_2+} c_{O_2^{2-}} c_{H_2O_s}^e} \right)
\]

[23]

The modified Butler-Volmer relations expressed in Eqs. 16 and 17 include the mass transfer effects from bulk solution to the solid-matrix/electrolyte interface. It is commonly assumed that there exists a linear concentration gradient within the Nernst diffuse layer.\(^{61}\)

Therefore the mass transfer flux \(Q_{m}^e\), \(\left(\frac{\mu}{\rho}\right)\) to the solid-matrix/electrolyte interface is obtained through the following:

\[
Q_{m}^e = \frac{D_0}{b_0} (c^e - c^v)
\]

[24]

In Eq. 24, \(c^e\) is the bulk concentration and \(c^v\) is the concentration in the solid-matrix/electrolyte interface. Since the Nernst diffuse layer thickness \(b_0\) is often unknown, it is convenient to combine it with the diffusion coefficient to produce the mass-transfer coefficient \(\theta_{0}\) \(\left(\frac{\mu}{\rho}\right)\) and re-write the Eq. 24 in the form of following equation.\(^{61}\)

\[
Q_{m} = \theta_{0} (c^e - c^v)
\]

[25]

Equation 25 needs to be written for the anode and cathode sides and for the species undergoing faradaic reaction; the mass transport flux is balanced by the flux of species consumption/production according to Butler-Volmer equation.\(^{62}\)

\[
\begin{align*}
\Phi_{V_2^+} = & \theta_{V_2^+} \left( c_{V_2^+} - c_{V_2^+}^v \right) = k_3 (c_{V_2^+})^3 (c_{V_2^+})^{1-a_2} \\
& \times \left[ \left( \frac{c_{V_2^+}}{c_{V_2^+}} \right) \exp \left( (1-a_2) f \eta_{pa} \right) - \left( \frac{c_{V_2^+}}{c_{V_2^+}} \right) \exp \left( (-a_2) f \eta_{pa} \right) \right] \\
\Phi_{V_2^+} = & \theta_{V_2^+} \left( c_{V_2^+} - c_{V_2^+}^v \right) = k_3 (c_{V_2^+})^3 (c_{V_2^+})^{1-a_2} \\
& \times \left[ \left( \frac{c_{V_2^+}}{c_{V_2^+}} \right) \exp \left( (-a_2) f \eta_{pa} \right) - \left( \frac{c_{V_2^+}}{c_{V_2^+}} \right) \exp \left( (1-a_2) f \eta_{pa} \right) \right] \\
\Phi_{V_2^+} = & \theta_{V_2^+} \left( c_{V_2^+} - c_{V_2^+}^v \right) = k_3 (c_{V_2^+})^3 (c_{V_2^+})^{1-a_2} \\
& \times \left[ \left( \frac{c_{V_2^+}}{c_{V_2^+}} \right) \exp \left( (1-a_2) f \eta_{pa} \right) - \left( \frac{c_{V_2^+}}{c_{V_2^+}} \right) \exp \left( (-a_2) f \eta_{pa} \right) \right] \\
\end{align*}
\]

[26]  

[27]  

[28]

Now, Eqs. 26 through 29 can be solved to correlate the bulk concentration of species to surface concentration.\(^{62}\)

\[
\begin{align*}
c_{V_2^+}^v &= \frac{U_1 c_{V_2^+} + (1 + U_1) c_{V_2^+}}{1 + U_1 + U_2} \\
c_{V_2^+}^v &= \frac{U_1 c_{V_2^+} + (1 + U_1) c_{V_2^+}}{1 + U_1 + U_2} \\
\end{align*}
\]

[30]  

[31]

where \(U_1\), \(U_2\), \(U_3\), \(U_4\), \(U_5\), \(U_6\), \(U_7\), \(U_8\) are calculated using the following equations.

\[
\begin{align*}
U_1 &= \left( \frac{k_a}{\theta_{V_2^+}} \right) \left( \frac{(c_{V_2^+})^{1+a_2-3}}{(c_{V_2^+})^{1-a_2}} \right) \exp \left( (1-a_2) f \eta_{pa} \right) \\
U_2 &= \left( \frac{k_a}{\theta_{V_2^+}} \right) \left( \frac{(c_{V_2^+})^{1-a_2}}{(c_{V_2^+})^{1-3}} \right) \exp \left( (-a_2) f \eta_{pa} \right) \\
U_3 &= \left( \frac{k_e}{\theta_{V_2^+}} \right) \left( \frac{(c_{V_2^+})^{1+a_2}}{(c_{V_2^+})^{3}} \right) \exp \left( (1-a_2) f \eta_{pa} \right) \\
U_4 &= \left( \frac{k_e}{\theta_{V_2^+}} \right) \left( \frac{(c_{V_2^+})^{1-a_2}}{(c_{V_2^+})^{3}} \right) \exp \left( (-a_2) f \eta_{pa} \right) \\
\end{align*}
\]

[32]  

[33]

For the set of equations formulated above, the key parameter to determine is the mass-transfer coefficients \(\theta_{V_2^+}, \theta_{V_2^+}, \theta_{V_2^+}, \theta_{V_2^+}\). This parameter has been determined as a function of electrolyte velocity in the work of Schmal et al.\(^{63}\) the results of that work are adopted here in the form of following equation.

\[
\theta_{0} = 1.6 \times 10^{-4} \nu_{ave}^{0.4}
\]

[34]  

[35]  

[36]  

[37]

Equation 38 as well as Eq. 4 requires the velocity field to be determined. To solve for the velocity field, Darcy’s law is used:

\[
\nu_{ave} = - \frac{d}{K \mu} \left( \frac{1}{1 - \epsilon^2} \right) \nabla p_{ave}
\]

[38]  

[39]

where \(p_a\) and \(p_r\) are the liquid pressures in the anode and cathode electrodes respectively, \(\mu\) is the dynamic viscosity of the liquid, \(d\) is the mean fiber diameter and \(K\) is the Kozeny-Carman constant. The application of Darcy’s law for the transport through the porous electrodes is justified because the Reynolds number is less than unity. Reynolds number for porous carbon papers is defined based on the pore-size length scale, \(d\), according to the following equation.

\[
Re = \frac{\rho d U}{\mu}
\]

[40]

The negative and positive electrolytes are incompressible solutions; therefore, the continuity equation simplifies to the following equation:

\[
\nabla \cdot \nu_{ave} = 0
\]

[41]

Inserting Eq. 39 into Eq. 41, we derive:

\[
\nabla \cdot \nabla p_{ave} = 0
\]

[42]

It is worth mentioning that \(\nu_{ave}\) is the mass-averaged velocity, rather than the molar-averaged velocity that was shown in Eq. 4. However, within the limit of infinite dilution, these values are equal. 

Membrane.—The electroneutrality condition must hold within the membrane. This condition dictates that:

\[
z_{m} c_{m} + z_{j} c_{j} = 0
\]

[43]

where \(z_f\) is the charge of the fixed sites and \(c_f\) is their concentration. The velocity of the liquid water in the membrane is obtained using Schrögl’s equation.

\[
\nu_{m} = - \frac{k_{m} F c_{H_2O_s}^V}{\epsilon} \nabla \Phi_{H_2O_s} - \frac{k_{m} \mu}{\epsilon} \nabla p_{m}
\]

[44]
Where $p_m$ is the liquid pressure, $\phi_m$ is the ionic potential, $k_q$ is the electrokinetic permeability and $k_m$ is the hydraulic permeability. The continuity equation within the membrane for water (incompressible) results in the following equation:

$$\nabla \cdot \mathbf{v}_m = 0 \quad [45]$$

Within the membrane, the conservation of current holds. Therefore,

$$\nabla \cdot \mathbf{j}_m = 0 \quad [46]$$

Since it is assumed that the protons are the only charge carriers within the membrane; the current density is formulated as:

$$i_m = zH^+F N_{H^+} \quad [47]$$

The flux of the protons within the membrane can be calculated using the following equation.

$$N_{H^+} = c_{H^+} \mathbf{v}_m - \frac{zH^+ F}{RT} D_{H^+,m} c_{H^+} \nabla \phi_m \quad [48]$$

where the $D_{H^+,m}$ is the proton diffusion coefficient in the membrane. Substituting Eqs. 47 and 48 into Eq. 46 we derive:

$$\nabla \left[ zH^+ F \left( c_{H^+} \mathbf{v}_m - \frac{zH^+ F}{RT} D_{H^+,m} c_{H^+} \nabla \phi_m \right) \right] = 0 \quad [49]$$

Equation 49 can be simplified to:

$$\nabla \cdot (zH^+ F c_{H^+} \mathbf{v}_m) - \nabla \left( \frac{zH^+ F^2}{RT} D_{H^+,m} c_{H^+} \nabla \phi_m \right) = 0 \quad [50]$$

According to Eq. 43, the proton concentration within the membrane is constant and therefore the first term in Eq. 51 vanishes due to conservation of mass and we derive:

$$\nabla \cdot (\sigma_m \nabla \phi_m) = 0 \quad [51]$$

where $\sigma_m$ is the ionic conductivity of the membrane and is described below.

$$\sigma_m = \frac{zH^+ F^2}{RT} D_{H^+,m} c_{H^+} \quad [52]$$

According to Eq. 52, constant ionic conductivity for the membrane is assumed and therefore:

$$\nabla \nabla \phi_m = 0 \quad [53]$$

Now, if Eq. 44 is inserted into Eq. 45 and Eq. 53 is adopted as well, we obtain:

$$\nabla \nabla p_m = 0 \quad [54]$$

**Boundary conditions.**—Definition of the boundary conditions at the outer surfaces is required in order to adopt the single-domain modeling approach. However, in this work, a multi-domain approach is used, requiring boundary conditions at all the boundaries of the computational domain, as well as internal interfaces.

**Boundary conditions for the conservation of mass.**—The battery is operated in potentiostatic mode; thus, the electronic potentials have been incorporated as boundary conditions.

$$\phi_e = 0 \quad (X = 0) \quad [55]$$

$$\phi_e = \phi_e \quad (X = X_3) \quad [56]$$

where $\phi_e$ is the applied electronic potential at the positive electrode/current collector interface. The membrane is not electronically conductive and the current (electronic and ionic) does not spread outside the computational domain.

$$i_e, n = 0 \quad (X = X_1, X_2) \quad [57]$$

$$i_e, n = 0 \quad (Y = 0, l_{cell}) \quad [58]$$

$$i_e, n = 0 \quad (X = X_3) \quad [59]$$

$$i_e, n = 0 \quad (Y = 0, l_{cell}) \quad [60]$$

**Boundary conditions for the conservation of momentum.**—At the inlets, the inlet velocity ($v_{inlet}$) is determined using the volumetric flow rate and used as the boundary condition. At the outlets the exit pressure is applied as the boundary condition. Also, no-slip boundary conditions are used at the interfaces of electrodes with current collectors and the membrane.

$$v_y = v_{in} \quad (Y = 0) \quad [61]$$

$$p = p_{out} \quad (Y = l_{cell}) \quad [62]$$

$$\nabla p \cdot n = 0 \quad (X = 0, X_1, X_2, X_3) \quad [63]$$

The inlet velocity is determined using the following equation:

$$v_{inlet} = \frac{Q}{\varepsilon A_{in}} \quad [64]$$

where $Q$ is the volumetric flow rate and $A_{in}$ is the cross-sectional area.

**Boundary conditions for the conservation of mass.**—Circulation of the electrolytes through their respective reservoirs alters the concentrations of all species entering the electrodes. To model this circulation, the inlet concentration for each species is simulated using the conservation of mass as follows:

$$\frac{\partial c_i^{in}}{\partial t} = \frac{\varepsilon_{el}}{V_{res}} \left( \int v^{out} c_i^{out} dl - \int v^{in} c_i^{in} dl \right) \quad [65]$$

Here, $V_{res}$ refers to the volume of the reservoir and $t_e$ is the width of the electrode as shown in Table I. The superscripts $in$ and $out$ are used for the value at the inlet and outlet of the electrodes. In a similar fashion, the changes in electrolyte volume can be calculated as follows:

$$\frac{\partial V_{res}}{\partial t} = \varepsilon A_{in} \left( v^{out} - v^{in} \right) = \varepsilon A_{el} \left( v^{out} - v^{in} \right) \quad [66]$$

There are also mechanical design considerations for the reservoirs that are function of $V_{res}$, but they are not considered in this model. The initial concentrations for the simulations are given in Table IV. The initial concentrations in the electrolytes represent the concentration.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Initial description</th>
<th>Value (mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1^{in}$</td>
<td>Initial concentration of $V(II)$</td>
<td>950</td>
</tr>
<tr>
<td>$c_{II}^{in}$</td>
<td>Initial concentration of $V(I)$</td>
<td>50</td>
</tr>
<tr>
<td>$c_{IV}^{in}$</td>
<td>Initial concentration of $V(IV)$</td>
<td>50</td>
</tr>
<tr>
<td>$c_1^+$</td>
<td>Initial concentration of $V(V)$</td>
<td>950</td>
</tr>
<tr>
<td>$c_{H^+,neg}$</td>
<td>Initial concentration of $H^+$ in negative electrolyte</td>
<td>3967</td>
</tr>
<tr>
<td>$c_{H^+,pos}$</td>
<td>Initial concentration of $H^+$ in positive electrolyte</td>
<td>4963</td>
</tr>
<tr>
<td>$c_{HSO_4^{neg}}^0$</td>
<td>Initial concentration of $HSO_4^-$ in negative electrolyte</td>
<td>5989</td>
</tr>
<tr>
<td>$c_{HSO_4^{pos}}^0$</td>
<td>Initial concentration of $HSO_4^-$ in positive electrolyte</td>
<td>5987</td>
</tr>
<tr>
<td>$c_{SO_4^{neg}}^0$</td>
<td>Initial concentration of $SO_4^2^-$ in negative electrolyte</td>
<td>16.6</td>
</tr>
<tr>
<td>$c_{SO_4^{pos}}^0$</td>
<td>Initial concentration of $SO_4^2$ in positive electrolyte</td>
<td>13.3</td>
</tr>
</tbody>
</table>

**Table IV. Initial species concentration.**

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of the species at 95% state of charge (SoC). SoC is defined using the following equation:

$$\text{SoC} = \frac{c_{V(V)} - c_{V(V)}}{c_{V(V)} + c_{V(V)}}$$  \[67\]

It is worth mentioning that it is critical to maintain electroneutrality within the negative and positive electrolytes while calculating the initial concentrations of the species as the input for the model. In some earlier modeling works, this fact was neglected, resulting in unrealistic initial concentrations to keep the solutions electrically neutral. In this work, a subroutine was developed to calculate the initial concentrations for the species to ensure electroneutrality within the solutions, taking into account the fact that the second step of sulfuric acid dissociation is incomplete according to Eq. 69.

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-, K1 = 2.4 \times 10^6$$  \[68\]

$$HSO_4^- + H_2O \leftrightarrow H_3O^+ + SO_4^{2-}, K2 = 1.1 \times 10^{-2}$$  \[69\]

According to Eq. 68, complete dissociation for the first step of sulfuric acid dissociation occurs and, for the second step, the dissociation happens according to the following manner.50

$$S_d = k_d \left( \frac{c_{H^+} - c_{HSO_4^-}}{c_{H^+} + c_{HSO_4^-}} - \beta \right)$$  \[70\]

where $S_d$ is the dissociation source term, $k_d$ is the dissociation reaction coefficient, and $\beta$ is the degree of dissociation for bisulfate ion and assumed to be constant.66 Table IV summarizes the initial concentration for the species at SoC of 95%.

**Numerical modeling approach.**— The governing equations formulated above, subjected to specific boundary conditions for the battery geometries, operating parameters, and electrolyte properties presented in Table I and II are solved numerically using the finite-element software COMSOL Multiphysics.

### Results and Discussion

For the model simulations, mesh sensitivity analysis was performed to ensure that the results were independent of the mesh size. In order to capture steep gradients within the model, the mesh size was refined for the intersections where different domains meet ($X = X_1, X_2$). The final model consisted of 15202 elements after which increasing the number of elements did not change the accuracy of the numerical data. Figure 3 includes the schematic of the cross-sectional areas used for comparison between the model and experiment. $Y_1$ simulates the data at the cell height of $l_{cell}/4$, $Y_2$ simulates the data at the cell height of $l_{cell}/2$ and finally $Y_3$ simulates the data at the cell height of $(31/32) \times l_{cell}$.

**The effect of convective mass transport on the species distribution.**— During operation of the VRFB, the species concentration constantly changes within the electrodes, resulting in concentration gradients for both in-plane and through-plane directions. As a
The concentration of both ions is higher at the cathode side. Both experimental and theoretical work has been performed to measure the partitioning factor of the membrane exposed to different concentrations of sulfuric acid solutions. An early theoretical and experimental work by Verbrugge et al. observed severe de-swelling for the Nafion exposed to sulfuric acid; due to ionic cluster channel compression which led to decreased membrane porosity. Acid uptake by membranes can also result in significant water loss after equilibration with concentrated sulfuric acid solution. According to Fig. 4b when the membrane was exposed to solutions with varying concentration of protons at the anode and cathode sides, proton uptake will vary according to Eq. 23 and the Donnan potential across the membrane.

It is important to quantify the convective, diffusive, and electrohydrodynamic fluxes at different operating conditions in order to evaluate the portion of each flux density. Figure 5 includes the different sources of mass transport flux at a volumetric flow rate of 20 mL min$^{-1}$ and cell discharge current density of 200 mA cm$^{-2}$. As shown in Figs. 5a and 5b, the diffusive flux density is relatively pronounced at the interface between the electrode/current collector and slightly pronounced at the electrode/membrane interface. This is clearly supported by the results shown in Fig. 4. Also, the electrohydrodynamic and diffusive fluxes are on the same order and almost 4 orders of magnitude lower than the convective flux. Comparing the fluxes for protons, the convective flux is 3 orders of magnitude higher than the diffusive and electrohydrodynamic fluxes, primarily due to greater diffusivity of protons versus vanadium ions. Also, the dissimilar proton convective fluxes in the anode and cathode are due to the difference in proton concentration at each cell location along the flow stream.

Figure 6 includes the simulation results for 20 mL min$^{-1}$ flow rate and discharge at 800 mA cm$^{-2}$. Along the flow direction, charged species consumption occurs resulting in a severe concentration gradient adjacent to the current collectors, suggesting that the reaction location is toward the flow-plate side. The species distribution profile clearly shows that along the flow path, species starvation occurs toward the current collectors at the cell exit port; as a result, mass transport limitations are the primary source of the cell starvation at high current density. Figure 6b illustrates that the Donnan potential is more pronounced at high current density. Also, comparing the concentration distribution of protons and bisulfate ions from Figs. 6b and 5b indicates that a large concentration gradient occurs adjacent to the membrane during high current discharge, resulting in the high rate of proton flux. However, even at high discharge current density, the concentrations of protons and bisulfate ions do not change to a great extent along the flow direction.

To further understand the concentration gradients in Fig. 6, it is important to quantify the mass flux for the vanadium species the same way as shown in Fig. 5. Figure 7 shows the different flux components for the vanadium species. The convective flux decreased greatly compared to Fig. 5 for $V(II)/V(V)$ due to high rate of consumption along the flow direction. The same pattern is observed for $V(III)/V(IV)$ where the increase in convective flux density is significant. Of particular importance is the difference in diffusive flux in the electrode/current collector interface for $V(II)$ and $V(III)$ versus $V(V)$ and $V(IV)$. This difference is primarily due to the difference in diffusion coefficients tabulated in Table II. The increased discharge current for this case is apparent in its impact on the electrohydrodynamic flux. Clearly, increased overpotential has resulted in greater electrohydrodynamic flux for the species. Also, the difference for electrohydrodynamic flux of the species for anode versus cathode is due to the difference in the mobility values for $V(II)$ versus $V(V)$ and $V(III)$ versus $V(IV)$.

Figure 8 includes the simulation result for 90 mL min$^{-1}$ flow rate and discharge at 200 mA cm$^{-2}$. In this case, the concentration gradients adjacent to the current collectors are decreased considerably due to increased convective flow within the porous media. However, the concentration of species undergoing faradaic reactions has not changed to a great degree along the flow direction. Finally, the concentrations of the bisulfate ions and protons change to a greater degree along the flow direction compared to Fig. 4 and Fig. 6. Along the flow...
Figure 5. Species flux densities at 20 mL.min\(^{-1}\) and 200 mA.cm\(^{-2}\) discharge; (a) \(V^{(II)}/V^{(V)}\), (b) \(V^{(III)}/V^{(IV)}\), (c) \(H^{+}_{\text{anode}}/H^{+}_{\text{cathode}}\), (d) \(HSO_{4}^{\text{anode}}/HSO_{4}^{\text{cathode}}\).

Figure 6. Species distribution at 20 mL.min\(^{-1}\) and 800 mA.cm\(^{-2}\) discharge; (a) Vanadium species, (b) Protons and bisulfate.

path, the concentration of protons increased; conversely, the concentration of the bisulfate ions decreased due to higher rate of dissociation and convective flux.

Figure 9 shows the different components of the mass flux for the conditions in Figure 8 (90 mL.min\(^{-1}\) flow rate and 200 mA.cm\(^{-2}\) discharge current). In this case, the diffusive and electrophoretic fluxes are six orders of magnitude lower than the convective flux for \(V^{(II)}\) and \(V^{(V)}\). Also, as expected, the increased convective mass flux decreased the rate of charged species (\(V^{(II)}\) and \(V^{(V)}\)) utilization along the flow direction. The difference in the concentration of protons and bisulfate ions observed along the flow direction in Fig. 8b can further be explained through Figs. 9c and 9d. In this case the convective mass transport is different at varying cell location along the flow stream, causing the significant change in the concentration of the protons and bisulfate ions along the flow direction. This behavior was not observed at lower volumetric flow rate (Fig. 5).

Figure 10 includes the simulation results for operation at 90 mL.min\(^{-1}\) and 800 mA.cm\(^{-2}\) discharge. Among the observations is the cell’s ability to operate without starving at the exit port. Contrary to operations with high discharge rate and lower volumetric flow rate (Fig. 6), increased convective mass flux prevents the depletion of \(V^{(II)}\) and \(V^{(V)}\) at the exit port. As expected from previous results, the concentration gradient is higher toward the electrode/current-collector interface. Due to different diffusivity values for \(V^{(II)}\) and \(V^{(V)}\), somewhat different concentration gradients are observed. Therefore, increased convective flux of the species improves mass transport and therefore enables the cell to operate at high current density without starvation at the exit ports of the electrodes. Similar to the previous case, the concentration of protons increased along the flow direction while the bisulfate ion concentration decreased concurrently.

Figure 11 compares the different components of the mass flux. It is clear that the electrophoretic flux has increased compared to Fig. 9 due to increased overpotential for the vanadium species. The asymmetry observed for the electrophoretic fluxes of \(V^{(II)}\) versus \(V^{(V)}\) and \(V^{(III)}\) versus \(V^{(IV)}\) is due to differences in ion mobility in the solution. Compared to Fig. 9, the convective mass transport for \(V^{(II)}\) and \(V^{(V)}\) has decreased along the flow direction due to high discharge rate. Also, due to high current discharge, the diffusive mass flux increased compared to Fig. 9 but is still five orders of magnitude lower than the convective flux. The difference in concentration of protons.
and bisulfate ions for anode and cathode has imposed asymmetry for the electrophoretic flux.

Analysis of overpotential on the species distribution.— It was shown earlier that there exists a concentration difference for protons and bisulfate ions between the anode and cathode compartments. As a result, it is important to analyze the change in electrolyte potential as well as solid phase potential at different operating conditions. Figure 12 compares the electrolyte and solid phase potentials for the cases analyzed earlier: discharge at 200 mA.cm$^{-2}$ and 800 mA.cm$^{-2}$ at a flow rate of 90 mL.min$^{-1}$.

The solid-phase and electrolyte potentials, as well as overpotentials, have been compared for both anode and cathode side at different discharge current densities in the through-plane direction of the VRFB in Fig. 12. The model predicts much higher overpotential in the anode than in the cathode, confirming more sluggish kinetic behavior for the anode side, agreeing with in situ kinetics measurements. However, this is contrary to the experimental data of some who have found slower electrochemical reactions at the cathode side. As shown in Fig. 12, the model simulates the lower solid-phase and electrolyte-phase potential for the cathode side for higher discharge current density (Fig. 12b versus Fig. 12a).

Experimental validation of the potential-distribution simulation data.— The micro-probes installed at the location of $Y = Y_2$ (according to Fig. 3) of the cathode side enable direct measurement of potential for comparison with simulated results at the center of the cell model. Figure 13 summarizes the measured potentials at the cell location of $Y = Y_2$ at different operating conditions. Figures 13a–13d include the potential data for discharge current densities in the through-plane direction of the VRFB. According to the experimental data, at a given SoC, the potentials from all the probes behaved in a similar manner as a function of SoC and exhibited lower potential (corresponding to greater overpotential) at decreased SoC. Also, for all measurements, measured potentials decreased with increasing discharge currents. As shown in Fig. 13, the experimental data are in good agreement with the numerical results. The discrepancy between the model prediction and experimental results is greatest at lower SoC and higher discharge rate where the maximum error is 8% for the discharge rate of 800 mA.cm$^{-2}$.

Figure 14 compares data from different probes at the beginning of discharge for 95% SoC and different discharge currents as well as open-circuit voltage (OCV). To obtain the experimental data, three
different cells were built and tested. The experimental data shown here for each probe are the average of all builds while the error bars were calculated based on the standard deviation from the average data.

Fig. 14 shows measured potentials for all probes at OCV and during the constant current discharge at 200 mA·cm$^{-2}$, 400 mA·cm$^{-2}$, 600 mA·cm$^{-2}$, and 800 mA·cm$^{-2}$. When current was drawn from the cell, the probe potentials decreased relative to OCV with the lowest potential measured at probe #1 (current-collector side) and the maximum value at probe #4 (membrane side). Greater discharge current increased the potential difference between probe #1 and probe #4, indicating that the reaction is more uniform across the electrode layers at low current density; and as the current density increased, the reaction shifted toward the flow plate side. The observed behavior among the potential probes have been compared with the model simulation for the solid-phase potential shown within Fig. 12 and this comparison has been provided in Fig. 14. As shown Fig. 14, good agreement was achieved between the model prediction and experimental results.

**Conclusions**

During operation of all-vanadium redox flow batteries (VRFB), several gradients form in the in-plane and through-plane directions of the cell. In order to quantify these gradients, an in situ potential distribution technique was developed. Micro potential probes were installed within the layered porous carbon electrode at the positive side of the VRFB. The experimental results revealed that the reaction locations within the porous electrode shifted toward the flow plate side with increasing current density during discharge, indicating a mass transfer limited system. To describe the experimental results, a mathematical model was developed that quantified the species concentration distribution, multiple mass flux components, and solid-phase and electrolyte-phase potentials. The mathematical model agreed with the experimental data, with a maximum error of 8%. The lowest predicted and measured potential occurred close to the electrode/current-collector interface, indicating the dominant reaction location in the through-plane direction. In addition, the model simulated the diffusive, convective and electrophoretic mass fluxes at different operating conditions. The model simulation showed that the convective mass transport flux is at least 4 orders of magnitude higher than the diffusive and electrophoretic fluxes at the corresponding cell location along the flow stream. The concentration gradient not only occurs along the
Figure 11. Species flux densities at 90 mL min⁻¹ and 800 mA cm⁻² discharge; (a) $V^{(II)}/V^{(V)}$, (b) $V^{(III)}/V^{(IV)}$, (c) $H^+_{\text{anode}}/H^+_{\text{cathode}}$, (d) $HSO_4^{−}_{\text{anode}}/HSO_4^{−}_{\text{cathode}}$.

Figure 12. Potential distribution in the through-plane direction of an operando VRFB; (a) 200 mA cm⁻² discharge, (b) 800 mA cm⁻² discharge.
flow direction, but also in the through-plane direction with the highest concentration gradient at the electrode/flow plate interface. If the cell is to be operated at high current density (800 mA cm\(^{-2}\) and higher), starvation of active species (V(II)/V(V)) needs to be prevented at the electrode/current-collector interface. This goal is achieved partially by increased convective mass flux (which was shown in this work). Mass transport can further be increased by improved electrode design such that the mass transport resistance in the in-plane direction decreases along the flow direction. This would enable increased diffusion flux from the main stream of the flow toward the electrode/current-collector interface. Also, it was shown that when the cell is operating at high volumetric flow rate, a large concentration gradient of protons and bisulfate ions forms along the flow direction, resulting in varying conductivity values for the membrane along the flow direction. An improved design can eliminate this by providing more uniform distribution of the protons and bisulfate ions within the electrodes.

Acknowledgments

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