Vanadium crossover through the ion exchange membrane in vanadium-based redox flow battery systems results in self discharge and variations in electrolyte concentration. VO\(^+\)\(_2\) and VO\(^2+\) crossover rate, or permeability, through various Nafion membranes was measured directly with a hydrogen-vanadium reversible fuel cell. Measuring crossover of electrolyte species directly with a fuel cell, as compared to an idealized dual-chamber system, allows for determining permeability under actual fuel cell testing conditions. This new in-situ technique for measuring VO\(^+\)\(_2\) and VO\(^2+\) crossover with a fuel cell is shown to be reliable and easy to use. The crossover measurement method shows increased crossover rates with thinner ion exchange membranes. Electrospun blended nanofiber membranes were also fabricated and tested in the hydrogen-vanadium reversible fuel cell leading to lower crossover rates and high fuel cell performance, as compared to commercial Nafion films.

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As the use for intermittent energy sources, such as wind and solar, continues to increase globally, the need for efficient and cost-effective energy storage solutions will grow. These energy storage solutions will enable the existing energy infrastructure to take full advantage of load levelling during peak and non-peak demand periods.\(^1\)\(^–\)\(^5\) The hydrogen-vanadium reversible fuel cell is one of the energy storage technologies being considered to meet future energy demands. The charge and discharge reactions for the hydrogen-vanadium reversible fuel cell are as follows:

\[
\text{Vanadium (+) Electrode: } 2\text{VO}^2+ + 2\text{H}_2\text{O} \rightleftharpoons 2\text{VO}^+ + 4\text{H}^+ + 2e^- \quad \text{E}^{\circ}_{\text{red}} = +0.99 \text{ V} \quad [1] \\
H_2 (-) \text{ Electrode: } 2\text{H}_2 + 4e^- \rightleftharpoons 4\text{H}^+ \quad \text{E}^{\circ}_{\text{red}} = +0.00 \text{ V} \quad [2] \\
\text{Overall Reaction: } 2\text{VO}^2+ + 2\text{H}_2\text{O} \rightleftharpoons 2\text{VO}^+ + 2\text{H}_2 + 4\text{H}^+ \quad \text{E}^{\circ}_{\text{cell}} = +0.99 \text{ V} \quad [3]
\]

During charge, vanadium (IV), VO\(^2+\), is converted to vanadium (V), VO\(^+\)\(_2\) at the vanadium electrode, and hydrogen gas is produced at the hydrogen electrode. During discharge, the reactions are reversed to consume hydrogen gas at the hydrogen electrode and vanadium (V) at the vanadium electrode. A polymer electrolyte membrane separates the hydrogen/vanadium electrodes and provides an ionic medium for transporting hydronium ions.

One of the advantages of the hydrogen-vanadium fuel cell over the all-vanadium flow battery is the reduced volume of vanadium electrolyte. Due to the high cost of vanadium, reducing the quantity of vanadium electrolyte directly impacts the overall system cost.\(^6\) Additionally, any crossover of electrolyte in the hydrogen-vanadium fuel cell is more easily separated due to the gas-liquid electrolyte pairing, as compared to flowing liquid electrolytes through both the positive and negative electrodes. Crossover in vanadium-based redox flow batteries leads to self-discharge and electrolyte composition variations over time. Yufit et al. first demonstrated the feasibility of the hydrogen-vanadium reversible fuel cell by attaining a peak discharge performance of 114 mW/cm\(^2\).\(^2\) Most recently, our group demonstrated improved fuel cell performance (540 mW/cm\(^2\)) by using a carbon nanotube (CNT) vanadium electrode, thinner membranes, and interdigitated flow fields.\(^8\) The previous work on the hydrogen-vanadium reversible fuel cell sparked our group’s interest in examining the effect of vanadium crossover through the polymer electrolyte membrane. Xie et al. studied Nafion processing and pretreatment effects on vanadium transport through Nafion films.\(^7\) His group measured the vanadium permeability of various membranes by using a dual-chamber, direct-permeation cell. The permeation test consisted of clamping a membrane between two chambers. Then, each chamber was filled with equal volumes of two solutions. Chamber one was filled with vanadyl sulfate (VOSO\(_4\)) and sulfuric acid (H\(_2\)SO\(_4\)), while chamber two was filled with magnesium sulfate and sulfuric acid. Finally, a UV-vis-NIR spectrometer was used to measure the increase of vanadyl sulfate concentration in chamber two over regular time intervals. Other studies have used a similar dual chamber technique to measure diffusion rates of various species through different types of membranes.\(^10\)–\(^15\) These past studies required the use of a stand-alone two chamber apparatus for calculating diffusion rates, instead of being able to determine the diffusion rate in-situ using a fully assembled fuel cell. Our group expects the membrane permeation rate within a fuel cell to be different than that in the ideal two chamber setup. The crossover rate in an actual fuel cell is expected to be different due to the migrational (electric field) effect across the membrane, the reduction in the membrane area due to the solid phase of the electrodes, the compressive forces exerted on the membrane during fuel cell assembly, the effect of the membrane electrode assembly (MEA) hot pressing technique on membrane thickness and surface chemistry, and the fuel cell operating conditions (i.e. electrolyte flow and pressure on each side of the membrane). In this work, we explore a new technique for determining in-situ the crossover rates of vanadium ions (VO\(^2+\) and VO\(^+\)\(_2\)) for a fully assembled fuel cell. The technique was applied to MEAs made with different Nafion membranes. Additionally, MEAs were made with electrospun blended nanofiber (EBN) membranes. The EBN membranes were developed to reduce vanadium crossover rates while maintaining high fuel cell performance.

**Experimental**

While exploring the performance characteristics of the hydrogen-vanadium fuel cell, our group observed a self-discharging phenomenon. We first charged the vanadium electrolyte solution to convert vanadium (IV) to vanadium (V). During the charging
operation, the color of the vanadium electrolyte changed from clear bright blue (denoting the presence of vanadium (IV)) to dark violet (denoting the presence of vanadium (V)). Next, the open circuit voltage (OCV) for the fuel cell was monitored for 24 hours while recirculating vanadium solution and hydrogen gas through the positive and negative electrodes, respectively. We found that the vanadium electrolyte solution reverted to the clear bright blue color, indicating that the vanadium (V) species had converted back to vanadium (IV). In order to study this observed self-discharge phenomenon and confirm that the self-discharge reaction occurs at the hydrogen (negative) electrode, we recharged the vanadium electrolyte solution to make vanadium (V) and then transferred the charged vanadium electrolyte into two new storage bottles (labelled bottle A and B). Hydrogen was then purged through both bottles. A single piece (2 cm × 2 cm) of plain gas diffusion layer (GDL) (SGL35BC without catalyst) was placed in bottle A and a Pt-coated GDL (0.48 mg/cm² Pt loading, 0.16 mg/cm² Nafion ionomer, SGL35BC from TVN Systems, Inc.) was placed in bottle B. As shown in Figure 1, the vanadium electrolyte color in bottle B reverted back to clear bright blue within an hour, indicating that vanadium (V) converts to vanadium (IV) in the presence of hydrogen gas and a Pt catalyst. No changes were observed with the control bottle (bottle A). Furthermore, after sufficient time was allowed to elapse, the generated vanadium (IV) in bottle B converted to vanadium (III) because the reduction potential of vanadium (IV) to vanadium (III) is more positive than the potential of the hydrogen reactions:

\[ VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O, \quad E_{\text{red}}^O = +0.34 \text{ V} \]  

The long duration observed for conversion of vanadium (V) to vanadium (IV) is due to the slow vanadium (V)/vanadium (IV) reaction rate and the large amount of vanadium (V) in the original solution. These preliminary results indicate that the hydrogen-vanadium fuel cell can self-discharge if vanadium (V) crosses through the membrane to reach the hydrogen electrode. Additionally, the crossover of hydrogen gas to the vanadium electrode does not lead to noticeable self-discharge, which is expected since carbon is a very poor catalyst for hydrogen oxidation.

Another in-situ self-discharge experiment was also conducted. In the next setup, we added a small carbon electrode and a SCE reference electrode to bottle B as shown in Figure 2. The small carbon electrode was used as a sensing electrode to measure the composition of the electrolyte by measuring its open-circuit potential relative to the SCE reference electrode. Using the measured open-circuit potential, two Nernst equations for the vanadium V/IV and vanadium IV/III reactions and mole balances on the individual vanadium ions we could correlate the measured potential at the sensing electrode to the individual vanadium ions in the solution as it undergoes self-discharge by the hydrogen reaction. The approach is shown in the Appendix. The results from this study are shown in Figure 3. Note that while it

Figure 1. Vanadium solution self-discharge in the presence of hydrogen gas and Pt-coated GDL.

Figure 2. Experimental setup used to study the effect of self-discharge of vanadium (V) to vanadium (IV) and vanadium (IV) to vanadium (III) to the solution’s vanadium composition.

Figure 3. Open-circuit voltage and composition of vanadium during self-discharge.
took about 3 hr to convert all vanadium (V) to vanadium (IV) with the platinum electrodes placed in the solution, it took only about 12 min to convert most of vanadium (IV) to vanadium (III) on the same platinum electrodes once the reduction potential of vanadium (IV) was reached.

Our proposed mechanism of the self-discharge phenomenon is provided in Figure 4. In the first step, vanadium (V) crosses through the membrane from the vanadium electrode to the hydrogen electrode. Next, vanadium (V) is reduced to vanadium (IV) at the platinum containing negative electrode, on both carbon and platinum surfaces, where the source of electrons comes from the oxidation of hydrogen to hydronium ions at the platinum catalyst of the negative electrode. This overall self-discharge reaction is identical to the overall discharge reaction given in Equation 3. The consumption of vanadium (V) sets up a concentration gradient across the membrane which leads to permeation of additional vanadium (V) from the vanadium electrode to the hydrogen electrode. First, this self-discharge will create a mixed potential at the negative electrode that is higher than the hydrogen reaction potential. The value of this mixed potential occurs at the point where the hydrogen oxidation rate is equal to the vanadium (V) reduction rate and is expected to depend on the transport rate of vanadium (V) ions from the position electrode, through the membrane to the negative electrode. Since the mixed potential is more negative than the vanadium V/IV reaction potential, the vanadium (V) reduction rate is expected to be at mass transport limited current as shown in Figure 5. The hydrogen oxidation rate is not expected to be mass transport limited since hydrogen gas is abundant at the hydrogen electrode and gas transport is much faster than ion transport in an aqueous solution. While it is not illustrated, it is expected that as soon as vanadium (IV) is generated it will be quickly be reduced to vanadium (III). The production of vanadium (III) at the hydrogen electrode sets up a concentration gradient across the membrane leading to the permeation of vanadium (III) from the hydrogen electrode back to the vanadium electrode. More discussion on this phenomenon will be given in the Results and discussion section.

The positive shift in the hydrogen negative electrode potential, as discussed above, results in a decrease in the fuel cell open circuit voltage. If this self-discharge is allowed to occur continuously at open-circuit, it will lead to the depletion of vanadium (V) in the electrolyte that is circulated through the positive electrode and the reduction of hydrogen pressure at the negative electrode leading to a
further drop in the cell open-circuit voltage. Note that if the hydrogen pressure at the negative electrode is held constant, then the drop in the cell open-circuit potential is caused primarily by the depletion of vanadium (V) and production of vanadium (IV) and (III). This unsteady state (crossover rate changes with concentration of vanadium (V)) and continuous drop in the cell open-circuit voltage can be used to determine the permeation rate of vanadium (V) across the membrane as shown in Figure 4a.

Now, if a potentiostat is used to hold the fuel cell at a constant voltage, as shown in Figure 4b, then a steady-state, (charge) current will be supplied by the potentiostat to support the self-discharge rate of vanadium (V) to vanadium (IV) and then vanadium (III). In this mode, electrons flow from the potentiostat to the negative hydrogen electrode to feed the vanadium (V) and vanadium (IV) reduction reactions so that no net hydrogen oxidation occurs and the hydrogen pressure remains constant. An equal number of electrons is withdrawn by the potentiostat from the vanadium electrode resulting in the oxidation of vanadium (III) to vanadium (V). At steady-state, these two currents are equal to the crossover rate of vanadium (V) across the membrane toward the negative hydrogen electrode. This phenomenon is known to many secondary battery researchers and users. Consequently, this steady-state charging current can be used to measure the crossover rate of vanadium (V) across the membrane to the negative electrode. While it is possible that this charging current could be controlled by the transport rate of vanadium (III) across the membrane from the hydrogen electrode to the vanadium electrode, results in the literature have shown that the diffusion rate of vanadium (III) is four times higher than that of vanadium (V) making it very reasonable to assume that the steady-state charging current is controlled by the crossover rate of vanadium (V).

Finally, if both vanadium (V) and vanadium (IV) are present at the positive electrode, the measured crossover current would be equal to the combined crossover rates of both ions. As described above, the observed self-discharge phenomenon for the hydrogen-vanadium reversible fuel cell enables us to directly measure the crossover rate of vanadium ions through the polymer electrolyte membrane. Two different crossover studies were completed on the hydrogen-vanadium reversible fuel cell. Both crossover studies investigated the effect of membrane type and thickness on the rate of vanadium crossover. In the first study (steady-state method), the fuel cell voltage was held constant at 1.05 V while measuring the current. The current was measured for more than 5 hours so that a steady-state charging current was reached. Once the current reached steady-state, we transitioned directly into the second study. For the second study (unsteady-state method), open circuit voltage (OCV) was monitored for greater than 5 hours in order measure the OCV drop over time.

Vanadium electrolyte solution (100 mL) was prepared by dissolving an appropriate amount of vanadyl sulfate (Sigma Aldrich) in 2.5 M sulfuric acid (H2SO4) and then charging to 50% state of charge (SOC) in order to produce a 1 M vanadium (V), 1 M vanadium (IV), and 3 M sulfuric acid electrolyte solution. The membrane electrode assembly (MEA) was prepared by hot pressing a polymer electrolyte membrane between a Pt-coated GDL (0.48 mg/cm2 Pt loading, 0.16 mg/cm2 Nafion ionomer, SGL35BC from TVN Systems, Inc.) and a nitric-acid-treated GDL (SGL10AA) at 135 °C and 0.552 MPa (80 psi) for 5 min. One side of the nitric-acid-treated GDL (side facing the membrane) was coated with a Nafion solution (Ion Power Inc.) and dried prior to MEA hot pressing in order to ensure proper adherence of the nitric acid treated GDL onto the membrane. MEAs were constructed using various Nafion membranes, including NR211 (~25 μm thick), NR212 (~51 μm thick), N115 (~127 μm thick), N117 (~183 μm thick) and two EBN membranes (~30 and 40 μm thick).

EBN membranes were made from Nafion/PVDF blended fiber mats, which were created by electrospinning the blend from a mixed solvent of N,N-dimethylacetamide (DMAc) and tetrahydrofuran (THF). Nafion (1100 EW) was dissolved into DMAc to make a 40 wt% solution. A 12.5 wt% solution of PVDF (Kynar HS900) was prepared by dissolving the powder into a 7:3 (wt:wt) DMAc:THF mixed solvent. The proper amounts of the two solutions were mixed so that the final Nafion:PVDF (wt:wt) ratio in solution was 80:20. The total solids content in the electrospinning solution was 30 wt%. The Nafion/PVDF blended fibers were fabricated using a custom-built electrospinning apparatus with humidity control, where the relative humidity was maintained at 25% at a temperature of 22–24 °C. The electrospinning solution was loaded into a syringe fitted with a 22-g needle. The needle tip-to-collector distance was 8 cm. While the solution was pumped at a constant flow rate of 0.25 mL/hr, a 10 kV voltage was applied between the needle and a rotating and oscillating grounded drum collector. A blended polymer fiber jet emitted from the needle deposited onto the drum forming a highly porous mat. After electrospinning, the fiber mat was dried at 60 °C overnight to remove residual solvent and then pressed at 177 °C for 5 minutes at 4000 psi.

The resultant transparent, nonporous membrane was annealed for 90 min at 150 °C under vacuum. Finally, the membrane was soaked in 1.0 M H2SO4 at room-temperature for 16 hr, followed by soaking in room-temperature water for 16 hr. Two EBN membranes were fabricated, with a dry thickness of 30 and 40 μm, and the same composition (80 wt% Nafion and 20 wt% PVDF).

The fuel cell was assembled at 1.103 MPa (160 psi) using expanded polytetrafluoroethylene (PTFE) gaskets and interdigitated tantalum flow fields (9 cm2). When assembling the fuel cell, two additional layers of nitric-acid-treated GDL (for a total of 3 layers) were used as the vanadium electrode. The nitric-acid-treated GDL for the vanadium electrode was prepared using a 3-step process. First, the GDL was submerged in deionized water while using a vacuum pump at ~0.03 MPa for 5 min to create a vacuum above the solution. This step ensured the pores of the carbon paper were filled with deionized water and fully wetted. Next, the GDL was soaked in 2M nitric acid for 24 hr. This was done to improve the carbon surface wettability. Finally, the GDL was thoroughly rinsed in deionized water and dried at room temperature.

All fuel cell testing was completed at room temperature (±23 °C). Hydrogen was recirculated at a pressure of 0.136 MPa (5 psi) and vanadium electrolyte was recirculated with a peristaltic pump at 12 mL/min. A fuel cell startup procedure was carried out to ensure the membrane was properly hydrated prior to testing. The startup procedure consisted of cycling the fuel cell between discharge (0.6 V) and charge modes (1.3 V) every 10 min for more than 12 h. Polarization curves were obtained for the EBN membranes in order to compare their performance to our previously published results for NR211, NR212, N115 and N117. Charge and discharge polarization curves were obtained using a constant voltage staircase mode with 50 mV increments every 2 min.

Results and Discussion

In the first study (steady-state method), current was monitored while holding the fuel cell voltage at 1.05 V. The ratio of vanadium (V) to vanadium (IV) at this voltage is about 1:1 (1.2 M vanadium (V) and 0.8M vanadium (IV)). Figure 6 shows the steady-state current density for multiple membrane types when holding the cell voltage constant at 1.05 V. Note that a different cell voltage could be used. Since each cell voltage corresponds to a different vanadium (V) and vanadium (IV) ratio (assuming the hydrogen gas pressure in the negative electrode is held constant), the permeation rate of vanadium (V) and vanadium (IV) can be measured at different concentrations to determine the concentration dependence of their crossover rates. The crossover rate of a hydrogen vanadium fuel cell at 100% state of charge (SOC), which consists of only vanadium (V), would be the crossover rate of vanadium (V), and, similarly, the crossover rate of the same fuel cell at 0% SOC would be that of vanadium (IV). As expected, the steady-state current density required to maintain the voltage at 1.05 V was higher for thinner membranes. The increased crossover rate associated with thinner membranes requires a higher steady-state current density to maintain 1.05 V. The steady-state current density dropped quickly as membrane thickness was increased from ~25 um (NR211) to ~51 um (NR212). As membrane thickness was increased above ~127 um (N115) to ~183 um (N117), a less pronounced drop in steady-state current density was observed. The observed trend is in agreement.
with other research groups who reported increased crossover rates for thinner membranes using a dual-chamber, direct-permeation cell.9,19

Table I lists the steady-state crossover current density measured for each membrane in a hydrogen-vanadium fuel cell. The crossover rates of vanadium (V) and vanadium (IV) for fuel cells with the conventional Nafion membranes ranged from 2 mA/cm² for thermally-extruded Nafion N117 (the thickest membrane) to 27 mA/cm² for solution-cast Nafion NR211 (the thinnest membrane). The steady state crossover rates of the electrospun membranes were 3 mA/cm² and 7 mA/cm² for the 40 μm and 30 μm membranes, respectively. The 30-μm electrospun membrane (EBN30) was designed to match the sheet resistance of Nafion NR212 while providing high permselectivity (lower crossover rates of vanadium ions). The 40-μm electrospun membrane (EBN40) was designed to match the permselectivity of Nafion N115 while providing a lower sheet resistance. Also shown in Table I are the thickness-normalized crossover rate data of these membranes. The thickness-normalized data shows very interestingly that both solution-cast Nafion membranes (NR211 and NR212) have similar permselectivity. Additionally, both thermally-extruded Nafion membranes (N115 and N117) show similar permselectivity. Even though all the Nafion membranes are made from the same polymer, their transport properties are affected by the synthesis process. This phenomenon could be related to their ionic surface properties identified in our recent study that showed how the membrane fabrication method (cast versus extruded) determines the membrane’s surface structure (hydrophilic versus hydrophobic) and surface ionic activity.20–23 This surface phenomenon seems to affect the diffusion of other ions (i.e., vanadium (V) and vanadium (IV)) similarly to hydronium ions. In other words, the increased surface hydrophilicity of cast membranes as compared to extruded membranes seems to contribute to higher vanadium (V) and vanadium (IV) diffusivity. Finally, the thickness-normalized crossover data for the two electrospun membranes shows no correlation, which could be due to the potentially non-random distribution of the two polymer phases in these composite membranes.

In the second crossover study (unsteady-state method), the OCV drop was measured for more than 5 hr. Figure 7 shows the change in OCV over time for the various membranes. The thinnest membrane (NR211) experienced a rapid OCV drop throughout the test. The drop rate increases sharply at approximately 4 hr due to depletion of the vanadium (V) ion. The OCV drop for the other five membranes (NR212, N115, N117, EBN30, and EBN40) is very gradual for more than 10 hr. The difference in OCV drop between NR212, N115 and N117 could not be discerned in Figure 7 because the vanadium ion permeabilities are small relative to the concentration of salt in the positive electrolyte reservoir. After narrowing the voltage axis to an appropriate range, Figure 8 reveals a trend in voltage drop as the membrane thickness increases. The thickest membrane (N117) exhibits the slowest voltage drop. The lower permeability expected when using a thicker membrane is in agreement with the trends shown in Figures 7 and 8. The behavior shown in Figures 7 and 8 is expected since lower permeability for a thicker membrane would lead to a lower conversion rate of vanadium (V) to vanadium (III) at the hydrogen electrode.

As you may recall, immediately prior to the second study, the cell voltage was held at 1.05 V until steady-state current was reached. This was done to ensure that all tests had the same starting point.

Table I. Steady-state V⁵⁺ and V⁴⁺ crossover current density in a hydrogen-vanadium fuel cell when the holding cell voltage at 1.05 V.

| Membrane Type     | Steady State Crossover Rate | Normalized by Thickness |
|-------------------|-----------------------------|-------------------------|
|                   | (Thickness in μm)            | mA/cm²                  | (mA-μm/cm²)               |
| NR211 (~25 μm)    | 27                          | 687                     |
| NR212 (~51 μm)    | 12                          | 608                     |
| N115 (~127 μm)    | 3                           | 382                     |
| N117 (~178 μm)    | 2                           | 356                     |
| EBN 30 (30 μm)    | 7                           | 210                     |
| EBN 40 (40 μm)    | 3                           | 120                     |
In the final study, EBN membranes were tested in the hydrogen-vanadium reversible fuel cell. The resulting polarization and discharge power density curves were compared to previously published data by our group with NR211, NR212, N115, and N117 films. EBN membranes were designed to reduce crossover while maintaining high fuel cell performance. The performance of the two EBN membranes (30 μm and 40 μm thick) are shown in Figure 10 by overlaying the discharge and charge performance curves with those using conventional Nafion membranes (NR211, NR212, N115, and N117). The 30-μm thick EBN membrane had similar fuel cell performance as NR212, as indicated by a steady-state crossover current density of 7 mA/cm² versus 12 mA/cm² when holding the voltage at 1.05 V. Additionally, the 40-μm thick EBN membrane outperformed N115, while maintaining a similar crossover rate as N115 (3 mA/cm²). The lower crossover rate for the EBN membranes as compared to conventional Nafion membranes of similar thickness is a result of the inert polymer phase (i.e., PVDF) of the EBN membrane which physically restricts ionic channel swelling of the Nafion phase by electrolyte during cell operation.

**Summary**

In summary, we measured the permeability of vanadium (V) and vanadium (IV) ions directly in a hydrogen-vanadium reversible fuel cell using various membrane types (extruded, solution-cast, nanofiber-based) and thicknesses. For the first time, vanadium ion permeability was measured directly with a fully assembled fuel cell. Two different methods (steady-state and unsteady-state) were explored for measuring the crossover rate. The steady-state method proved to be a more accurate method for measuring the crossover rates of vanadium (V) and (IV) ions. Additionally, EBN membranes, made from a hot-pressed mat of blended electrospun Nafion/PVDF nanofibers, performed very well in a hydrogen-vanadium reversible fuel cell with reduced crossover rates. EBN membrane optimization will continue in an effort to lower crossover rates while increasing fuel cell performance.

Further investigations will be done using a solution of only one vanadium ion (i.e., with only vanadium (V), at 100% SOC, or vanadium(IV), at 0% SOC) in the solution to determine permeability rates for these membranes. We will also explore if the new crossover measurement technique can be applied to other two-phase hybrid fuel cell systems, such as the hydrogen-iodine and hydrogen-bromine fuel cells. For this new measurement technique to work, the electrolyte at the positive electrode must be able to react on the Pt catalyst at the hydrogen electrode when crossover occurs while not poisoning the catalyst.

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**Appendix**

**Equations Correlating OCV with Mole Balance of Vanadium Ions**

For,

\[ \text{VO}_2^+ + 2H^+ + e^- \leftrightarrow V^2+ + H_2O \]

\[ E_{ocv} = 0.99 + \frac{RT}{FP} \ln \left( \frac{[\text{VO}_2^+]}{[H^+]} \right) \]

and

\[ \text{VO}_2^+ + 2H^+ + e^- \leftrightarrow V^3+ + H_2O \]

\[ E_{ocv} = 0.34 + \frac{RT}{FP} \ln \left( \frac{[\text{VO}_2^+]}{[H^+]} \right) \]

From the acid concentration, value of \([H^+]\) will be known. Hence, by measuring \(E_{ocv}\), the following ratios can be calculated:

\[ \frac{[\text{VO}_2^+]}{[\text{V}^3+]} = \delta_1 \]
\[
\frac{[V O^{2+}]}{[V^{3+}]} = k_2
\]

From the above two equations, we can also write:
\[
\frac{[V O^{2+}]}{[V^{3+}]} = k_1 \times k_2
\]

From the mole balance we know,
\[
[VO^{2+}] + [V O^{2+}] + [V^{3+}] = m
\]

where m is the concentration of all vanadium ions in the starting solution. By substituting the ratios into the mole balance, we obtain:
\[
[VO^{2+}] \left( 1 + \frac{1}{k_1} + \frac{1}{k_1 \times k_2} \right) = m
\]

\[
[VO^{2+}] = \frac{m}{\left( 1 + \frac{1}{k_1} + \frac{1}{k_1 \times k_2} \right)}
\]

Similarly,
\[
[VO^{2+}] = \frac{m}{(k_1 + 1 + \frac{1}{k_2})}
\]

\[
[V^{3+}] = \frac{m}{(k_1 \times k_2 + k_2 + 1)}
\]

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