Elucidating effects of cell architecture, electrode material, and solution composition on overpotentials in redox flow batteries

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Elucidating effects of cell architecture, electrode material, and solution composition on overpotentials in redox flow batteries

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Abstract

An improved method for quantitative measurement of the charge transfer, finite diffusion, and ohmic overpotentials in redox flow batteries using electrochemical impedance spectroscopy is presented. The use of a pulse dampener in the hydraulic circuit enables the collection of impedance spectra at low frequencies with a peristaltic pump, allowing the measurement of finite diffusion resistances at operationally relevant flow rates. This method is used to resolve the rate-limiting processes for the V^{2+}/V^{3+} redox couple on carbon felt and carbon paper electrodes in the vanadium redox flow battery. Carbon felt was limited by both charge transfer and ohmic resistance, while carbon paper was limited by charge transfer, finite diffusion, and ohmic resistances. The influences of vanadium concentration and flow field design also are quantified.

Keywords: electrochemical impedance spectroscopy; redox flow battery; rate constant; impedance-resolved polarization; finite diffusion resistance

1. Introduction

Redox flow batteries (RFBs) have been studied as a potential grid-scale energy storage solution [1–8]. A multitude of chemistries have been examined, with recent interest in organic and/or non-aqueous systems [5–8]. RFB architecture, however, has remained relatively unchanged; cell designs largely utilize an architecture where porous electrodes are pressed against a patterned graphite plate [8,9]. An ideal cell minimizes kinetic, ohmic, and mass transport voltage losses and parasitic pumping losses. For a given redox chemistry, cell optimization involves selection of electrodes that provide sufficient kinetic activity and membranes with acceptable conductivity and minimal crossover of the redox active materials. The electrode morphology and flow field pattern in concert with the flow rate define the hydrodynamics, controlling electroactive species transport and pressure drop [10]. A recent review summarizes optimization efforts of electrodes, flow fields, and membranes for the all-vanadium RFB [3]. The use of diagnostic techniques to quantify how the electrodes, membrane, and flow field contribute to battery overpotential provides an avenue for continued optimization of RFBs.

Electrochemical impedance spectroscopy (EIS) is a powerful tool that can be used to identify and resolve the sources of resistance within an electrochemical device, with deconvolution of porosity effects [11]. This permits the quantitative measurement of the effects of electrode and flow field properties on these limiting resistances. Stimming and coworkers developed a method based on a simple four-element equivalent circuit to quantify the kinetic rate constant of vanadium redox reactions, ultimately relating the electrode surface chemistry to the rate constant [12,13]. Sun et al. used EIS on an operating vanadium redox flow battery (VRFB) and identified the V^{2+}/V^{3+} couple as the limiting half-cell reaction [14]. They then resolved the

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4 ohmic, charge transfer, and finite diffusion resistances of the V^{2+}/V^{3+} couple. They showed that
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6 integrating the corresponding resistances with respect to current density yields the overpotential
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8 due to each process and that the sum of the ohmic, charge transfer/activation, and finite
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10 diffusion/concentration overpotentials is the total measured cell overpotential [15]. In that work,
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12 they also extended a model based on macrohomogeneous porous electrode theory to predict
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14 impedance spectra based on physical electrode parameters, allowing one to interpret EIS data
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16 without the use of simple equivalent circuits [16]. In order to measure the finite diffusion
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18 resistance, a gravity siphon with a low flow rate (1.5 mL min^{-1}) was required to avoid
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20 disturbances in the Nernstian boundary layer caused by the peristaltic pump [15]. Petek et al.
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22 also applied a macrohomogeneous porous electrode model to describe a flowing slurry electrode
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24 [17].
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32 In this work, we describe an experimental method to obtain finite diffusion resistances
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34 with operationally relevant flow rates (25 mL min^{-1}) through the use of a pulse dampener in
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36 conjunction with peristaltic pumps. The method was applied to a series of experiments in which
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38 the flow fields, vanadium concentration, and electrode materials were varied. The model
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40 presented by Sun et al. was used to interpret the complex impedance data [15]. Through
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42 resolution of the three sources of overpotential, the impact of cell design on electrochemical
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44 kinetics, mass transport, and ohmic processes within the cell was determined quantitatively.
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46 Using this approach, one can determine the limiting processes for any liquid-phase
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48 chemistry/material combination, allowing optimization efforts to focus on improving the rate-
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50 limiting steps in the RFB.
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57 **2. Methods**

58 *2.1 Experimental setup*

Cell testing was carried out on a single-cell 5 cm² geometric active area flow battery [9]. Two flow field patterns were tested: a square active area single-channel serpentine (2.23 x 2.23 cm) and a rectangular flow-through design (4 x 1.25 cm) shown in Fig. 1 [18]. Cells were built with one layer of carbon electrode on each side of the separator. The electrode materials were carbon paper (SGL 10AA, ~360 μm thickness, compressed to 240 μm) and carbon felt (SGL GFD3, ~3 mm thickness, compressed to 2 mm). Electrodes were soaked in nitric acid (70%, Alfa Aesar) for 10 minutes and then rinsed with deionized water five times. The separator was a Nafion 117 membrane (Ion Power), pretreated by immersion in 1 M sulfuric acid at 80 °C for 30 min followed by immersion in deionized water at 80 °C for 30 min. Two negative electrolyte solutions were prepared by electrolysis of VOSO₄ (Alfa Aesar, 99.9%) dissolved in a sulfuric acid supporting electrolyte (Alfa Aesar, ACS grade). Prior to electrolysis, the solutions were filtered to remove impurities [19,20]. The first solution consisted of 0.5 M total vanadium in 4 M sulfuric acid; the second was composed of 1.5 M total vanadium in 3.0 M sulfuric acid. A lower acid concentration was used with the higher vanadium concentration to preserve the total dissolved sulfate concentration. Both solutions were tuned to 50% state of charge (SoC), i.e. equal V²⁺ and V³⁺ concentrations, in a separate cell. The concentrations are described nominally as 0.5 and 1.5 M throughout the text for simplicity; the coulometrically-determined concentrations are listed in Appendix A. Nitrogen was purged over the solutions to prevent oxidation of the vanadium species.

The experimental setup is shown in Fig. 2. The symmetric cell configuration was used; i.e. the negative electrolyte was circulated through both sides of the cell in one continuous fluid circuit [21,22]. In this circuit, fluid flows from the electrolyte reservoir into the pump, enters a pulse dampener, is fed into the cell, and returns to the electrolyte reservoir. The dampener

consists of a sealed glass bottle with two ports. Pulsing from the pump is dampened by the gas headspace. Prior to startup, the bottle dampener was purged with nitrogen. During startup, pressure in the dampener builds until the bottle pressure reaches the cell pressure drop associated with the desired flow rate.

A Bio-Logic Instruments VSP potentiostat coupled to a 20 A booster was used for electrochemical measurement. The cell temperature was controlled at 30 °C. The cell was filled with the 0.5 M vanadium solution and then preconditioned using five potentiostatic cycles, with each cycle consisting of a +200 mV imposed cell overpotential for 30 minutes followed by a – 200 mV imposed cell overpotential for 30 minutes. After preconditioning, the polarization curve was recorded. The cell was then drained and the reservoirs were switched to the 1.5 M vanadium solution for another polarization measurement. Polarization curves were obtained by incrementing the cell overpotential from 0 to +200 mV in 25 mV increments. At each step, the cell potential difference was held constant for 30 seconds, followed by the acquisition of impedance data using 5 mV sinusoidal perturbations. Lead resistance and inductance were measured using a calibrated reactance-less resistor in place of the cell. The lead resistance was < 1 mΩ and the lead reactance was negligible at the highest frequencies used in this study. With large inductance, the high frequency intercept of the Nyquist plot is shifted. A two-electrode configuration was used because the impedance spectra measured relative to our reference electrode were distorted.

2.2 Symmetric cell considerations

The symmetric cell configuration has been demonstrated in the literature as a useful tool for certain flow battery diagnostics; the primary benefit is that the solution reservoir maintains the same SoC throughout the experiment [15,21–23]. Because the cell is operated at 50% SoC

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4 and the transfer coefficients of the V^{2+}/V^{2+} couple are 0.5, the cell overpotential should be
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7 equally distributed between both sides of the cell [15,21]. When the cell overpotential was 200
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9 mV, each individual electrode was polarized at 100 ± 10 mV relative to its open circuit potential.
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11 These individual overpotentials were measured using a Hg/HgSO₄ reference electrode in contact
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13 with the membrane at the perimeter of the cell, with the contact point wetted by 0.5 M H₂SO₄. At
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15 open circuit, the charge transfer resistance of each electrode is one half of the charge transfer
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17 resistance for the full cell. The measured cell open circuit voltage was < 1 mV.
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22 The maximum current with 0.5 M total vanadium concentration was 660 mA,
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24 corresponding to a 0.0175 M change in vanadium concentration with the 25 mL min⁻¹ flow rate.
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26 This is a 3.5% change in SoC from the cell inlet to outlet. Because the cell is operated at 50%
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28 SoC, this small change in vanadium concentration is not expected to appreciably affect the
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30 charge transfer resistance even at maximum current. Because the cell architecture is symmetric
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32 with respect to the electrodes, any ohmic losses not occurring through the separator can be
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34 equally divided between the two sides. The finite diffusion resistance should also split nearly
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36 equally between both sides at 50% SoC.
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42 At higher current and/or lower flow rates than those used in this work, the change in
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44 vanadium concentration between the inlet and outlet of the electrode may become significant.
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46 Under these conditions, the impedance of the positive and negative electrodes would not be
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48 equal. Our impedance model, which assumes a uniform electrolyte concentration across the
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50 electrode, would not be applicable.
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55 *2.3 Fitting data to impedance model*

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The single-electrode model developed by Sun and coworkers for the VRFB was adopted to fit the open circuit impedance data for each of the eight configurations tested [15]. The model was modified to account for the fact that the impedance data were collected for a whole cell:

$$AZ_{\text{cell,model}} = 2 \times AZ_p + R_{\text{series}} + j\omega L \quad [1]$$

AZ_p is the single-electrode impedance described in reference 15, L is the lead inductance, and R_{series} is the series resistance. The series resistance includes membrane ionic resistance and electronic bulk and contact resistances in the flow field blocks and current collectors. The electronic bulk and contact resistances are negligible. The values used for the model fixed parameters are shown in Appendix A. A non-linear least squares regression in MATLAB was performed allowing the fitted parameters to vary until the quantity $\sum F_k |AZ_{\text{cell,experimental}} - AZ_{\text{cell,model}}|$ over the entire frequency range (all F_k) was minimized. The values for these fitted parameters at open circuit are included in Appendix B. The fixed and fitted parameters are consistent with the notation used in reference 15 unless otherwise noted. The full form of the objective function used to perform the regression is included in Appendix C. The equations that determine the single-electrode impedance, AZ_p , are also included in Appendix C.

The resistances $R_{\text{distributed}}$ (distributed ohmic resistance due to the parallel combination of ionic and electronic resistances throughout the porous electrode, referred to as R_{hf} in reference 15), R_{ct} (charge transfer), and R_{fd} (general finite diffusion) are calculated for a single electrode according to Eqns. 2–4 below, which were derived in reference 15 from low frequency approximations for AZ_p . It is noted that the low frequency approximations are defined with respect to a particular process, e.g. the low frequency for charge transfer differs from the low frequency for finite diffusion.

$$R_{\text{distributed}} = b \frac{\rho_1 + \rho_2}{3} + b \frac{\rho_1 \rho_2}{3(\rho_1 + \rho_2)} \quad [2]$$

$$R_{\text{ct}} = \frac{A}{A_t} \frac{RT}{F i_0} \quad [3]$$

$$R_{\text{fd}} = \frac{A}{A_t} \frac{a}{f} \frac{RT}{F^2} \left(\frac{1}{C_R D_R} + \frac{1}{C_O D_O} \right) \quad [4]$$

These resistances can be integrated with respect to current density to obtain the overpotential associated with each process:

$$\eta_x = \int_0^i R_x(i) di \quad [5]$$

where x represents the series ohmic, distributed ohmic, charge transfer, and finite diffusion processes. To find the total cell overpotential due to each process, the model-calculated single-electrode overpotential η_x was doubled for each process except R_{series} .

2.4 Calculation of effective surface area and rate constant

In the impedance model, the double layer is described by a constant phase element (CPE) with impedance $Z_{\text{CPE}} = \frac{1}{(j\omega)^P Q}$. The quantity $A_t \times C_{\text{dl}}$ is interpreted as the CPE parameter Q . Brug et al. developed an equation to find the double-layer capacitance of a CPE; this method has been verified by others [24,25]:

$$CPE_{\text{dl}} = Q^{\frac{1}{P}} \left(\frac{1}{A} \frac{R_e R_{\text{ct}}}{R_e + R_{\text{ct}}} \right)^{\frac{1}{P} - 1} \quad [6]$$

where P is the CPE power factor, R_{ct} is the charge transfer resistance from Eqn. 3, and R_e is the half-cell total ohmic resistance calculated below:

$$R_e = \left(\frac{R_{\text{series}}}{2} + R_{\text{distributed}} \right) \quad [7]$$

The effective electrode surface area A_{eff} is then found:

$$A_{\text{eff}} = \frac{CPE_{\text{dl}}}{C_{\text{dl}}} \quad [8]$$

The rate constant k_0 for a one-electron Butler-Volmer kinetic model is related to the open circuit charge transfer resistance $R_{\text{ct},0}$ by [26]:

$$\frac{RT}{FR_{\text{ct},0}} = FA_{\text{eff}}k_0c_0^\alpha c_R^{1-\alpha} \quad [9]$$

3. Results and discussion

In the following sections, the complex impedance data and model fits are shown. Then, insights from impedance are used to discuss the effects of electrode material, flow field pattern, and vanadium concentration on charge transfer, finite diffusion, and ohmic processes. Afterward, the overpotentials from each process are summed to obtain the impedance-resolved polarization curves and finally, the limiting process for each cell is discussed.

3.1 Impedance spectra and model fit

The complex impedance spectra, shown in Figs. 3 and 4, exhibit clear resolution of the charge transfer and finite diffusion processes. The high frequency semicircle is the charge transfer process and the low frequency feature is the finite diffusion process. The linear feature at high frequency, particularly apparent in the spectra collected with GFD3 electrodes at 0.5 M total vanadium concentration, is a distributed ohmic resistance [11,17]. This distributed ohmic resistance is due to the parallel ionic and electronic resistances that occur in the liquid electrolyte and carbon fibers of the electrode material, respectively, throughout the thickness of the electrode. The distributed resistance feature may overlap with the charge transfer feature when the charge transfer kinetics are sufficiently facile; in this case, a linear distributed ohmic

resistance feature may not be visibly discerned. The open circuit fits in Figs. 5 and 6 show very good agreement between the model fit and experimental data. Commonly used three or four-element equivalent circuit models are unable to capture the distributed resistance.

An example of the calculated intercepts of the complex impedance data with the real axis according to Eqns. 2–4 is shown in Fig. 7 for the GFD3 electrode. The high frequency intercept of the Nyquist plot is a sum of R_{series} and the frequency-independent term of AZ_p , $b \frac{\rho_1 \rho_2}{(\rho_1 + \rho_2)}$, illustrated graphically in Fig. 7. In configurations where this frequency-independent term is small (such as with 10AA) and the series inductance is small ($< 10^{-6}$ H), the high frequency intercept is a good approximation of the series resistance; with the thicker GFD3, the frequency-independent term is not negligible and this approximation is no longer valid. With known electrode thickness and specific ionic and electronic resistivities, however, the series resistance can be calculated by subtracting the frequency-independent term from the high frequency intercept. The resistances obtained from the intercepts are plotted as a function of current density for the flow-through 0.5 M vanadium 10AA electrode case in Fig. 8. The subsequent integration to obtain the overpotentials due to each process is shown in Fig. 8 as well.

3.2 Charge transfer process

Rate constants for the V^{2+}/V^{3+} reaction under various conditions are summarized in Table 1. The rate constants for the GFD3 electrodes regardless of conditions were $2.6\text{--}3.2 \times 10^{-5} \text{ cm s}^{-1}$ and those of the 10AA electrodes were $7.6\text{--}15.0 \times 10^{-5} \text{ cm s}^{-1}$. This suggests that the activity of the graphitized paper is greater than the carbon felt. These values for rate constants are comparable to those in a list compiled by Fink and coworkers [12]. Shown in Fig. 9 are the charge transfer/activation overpotentials, η_{ct} for all conditions tested. GFD3 exhibited $3\times$ or

greater activation overpotential than 10AA, agreeing with the smaller rate constant. The GFD3 surface area is also lower than the 10AA surface area.

For 10AA, the flow field pattern had a large impact on η_{ct} : it was nearly $2\times$ higher for 10AA used in conjunction with the flow-through pattern in comparison with 10AA used with the serpentine pattern. The impedance data suggest a difference in surface area: the 10AA electrode in the serpentine cell was measured at 220 cm^2 of effective surface area in comparison with the 170 cm^2 in the flow-through cell. For GFD3, there was little difference in both η_{ct} and the surface area – 110 cm^2 (serpentine) vs. 98 cm^2 (flow-through). Electrodes removed from cells built with the serpentine pattern were imprinted with the flow channel pattern, which is an indication that the electrode material flexes into the channels; the flow-through pattern has little space for such flexing. The flexing into the channels may expose more fiber surface area. The extent of these geometric/mechanical effects on exposed surface area would be dependent on electrode material. Further study with additional flow field patterns is needed to shed light on this phenomenon.

3.2 Finite diffusion processes

The finite diffusion process is dependent on the bulk concentration of the electroactive species and the Nernstian diffusion layer thickness. The latter is a result of the electrode morphology, topology, and electrolyte velocity field. The flow field pattern can play a major role in determining the magnitude and distribution of the electrolyte velocity through the electrode [27]. Qualitatively, a high electrolyte velocity in the electrode decreases the boundary layer thickness around electrode fibers, reducing both the finite diffusion resistance and concentration polarization. Additionally, uniform electrolyte distribution (good mixing) through the electrode

decreases concentration polarization as a uniform concentration is maintained throughout the electrode.

The concentration polarizations, η_{fd} , of 10AA were greater than GFD3 for equivalent conditions (Fig. 10). At 0.5 M vanadium concentration and 50 mA cm^{-2} , η_{fd} was 12 mV for GFD3 (both flow fields) and for 10AA it was 25 and 40 mV (flow-through and serpentine, respectively). The flow field pattern strongly affected transport with 10AA electrodes, but had virtually no effect for GFD3. These observations are explained by considering the electrode materials and electrolyte transport mechanisms within the flow fields.

GFD3 is both more porous and thicker than 10AA (compressed porosity, 90% vs 80% [28] and $2000 \text{ }\mu\text{m}$ vs. $240 \text{ }\mu\text{m}$, respectively). The differences in porosity and thickness result in a significant difference in pressure drop. Measured with one layer of electrode material in the flow-through flow field at 25 mL min^{-1} , the pressure drop was 1 psi for GFD3 vs. 12 psi for 10AA. Generally speaking, high porosity and low tortuosity (such as in GFD3) promote uniform electrolyte distribution and lower η_{fd} .

Serpentine flow field designs rely on passive diffusion from the channels into the electrode and forced advection into the electrode over lands in the flow field (depicted by the arrows in Fig. 1a). The pressure drop *along the channel* versus *through the electrode* determines how much flow penetrates into the electrode and how much bypasses in the flow field channel. This leads to high-pressure drop materials having less flow forced through the electrode [27,28]. Therefore, with serpentine flow fields, one expects that η_{fd} increases with inherent pressure drop though a given material with electrode material. Thus, the lower pressure drop through GFD3 can explain the much lower η_{fd} than 10AA with the serpentine design.

The flow-through design forces all electrolyte through the electrode. Here the electrolyte velocity in the electrode is always greater than that in a serpentine flow field (all else equal) because there can be no bypass flow as occurs in the channels in the serpentine flow field. Therefore, one expects flow-through designs to possess lower η_{fd} than with serpentine designs; this result was confirmed as shown in Fig. 10 for 10AA. However, if the pressure drop through a material is sufficiently low, there will be little bypass flow in the serpentine channels, and little to no difference would be seen in η_{fd} by moving to a flow-through design. This is the case with the GFD3 electrode.

The expected effect of tripling concentration is to decrease the finite diffusion resistance and overpotential by 67%. In GFD3, the concentration overpotential decreased by 50%. In 10AA, the concentration overpotential decreased by only 25–30%.

3.3 Ohmic resistance

The ohmic resistance, resolved into the series and distributed resistances, is shown in Fig. 11. As described in Section 2.3, the series resistance is primarily due to the membrane. The distributed resistance is calculated in Eqn. 2 and is the parallel combination of the electronic resistance through the electrode and the ionic resistance through the liquid electrolyte located within the porous electrode.

The series resistances were ~ 0.28 and $\sim 0.41 \text{ } \Omega \cdot \text{cm}^2$ at 0.5 and 1.5 M vanadium concentration, respectively, and were independent of flow field and electrode configuration as shown in Fig. 11. Assuming series resistance was solely due to the 177 μm thick membrane, the implied membrane ionic conductivities are 0.063 and 0.043 S cm^{-1} at 0.5 and 1.5 M vanadium

concentration, respectively. These values are consistent with those calculated by Tang et al. [29], confirming that the membrane is the primary source of the series resistance.

The distributed resistances with 10AA were 0.042 and 0.062 $\Omega\cdot\text{cm}^2$ with 0.5 and 1.5 M vanadium concentration, respectively; with GFD3, the distributed resistances were 0.42 and 0.59 $\Omega\cdot\text{cm}^2$. The GFD3 compressed thickness was 8× the compressed thickness of 10AA and nearly entirely explains the 10× difference in distributed resistance. The remaining 20% difference is due to the difference in electrical conductivities, reported by the manufacturer as 0.012 and 0.30 $\Omega\cdot\text{cm}^2$ for 10AA and GFD3, respectively. The relatively small difference in distributed resistance in spite of the large difference in electrical resistivity is because the ionic resistance is approximately an order of magnitude larger than either of the electronic resistances.

These results show the significance of electrode thickness in determining the overall ohmic resistance: with thick carbon felts, 60% of the ohmic resistance is due to the distributed ohmic resistance of the electrode and electrolyte. With thin carbon papers, the membrane dominates the total ohmic resistance, accounting for 87% of the total. The ohmic resistance of a battery with GFD3 felt and no membrane would still exceed that of a cell built with 10AA and the relatively thick Nafion 117.

3.4 Overall cell behavior

Shown in Fig. 12 are the overall polarization curves. The 10AA electrodes always had a higher current density than GFD3 electrodes at any condition. Increasing the vanadium concentration increased the current density; however, the relative increase in current was less than the increase in concentration, suggesting that there are diminishing returns with increasing concentration to increase current and power density. The origin of this diminishing return is

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4 because increased vanadium concentration decreases ionic conductivity in the liquid electrolyte
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6 and membrane, countering the benefits of high concentration on kinetics and transport. The use
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8 of thinner membranes, such as Nafion 212, could partially mitigate the lower membrane
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10 conductivity. For 10AA, the effect of flow field was dependent on concentration: at 0.5 M
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12 vanadium, the flow-through design exhibited better performance; at 1.5 M vanadium, the
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14 serpentine was superior. These differences are attributed to the differences in activation and
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16 concentration polarization in sections 3.1.2 and 3.2. The flow field had no impact on the overall
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18 performance for GFD3.
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24 The impedance resolved polarization curves, shown in Fig. 13, allow for straightforward
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26 analysis of the relative contribution of each process to the total overpotential. The impedance-
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28 resolved overpotential matches the potentiostat-applied cell potential to within 4% for the GFD3
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30 1.5 M vanadium concentration cases and to within 1% for all other cases. This extremely good
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32 agreement means that all contributions to overpotential are accurately quantified.
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37 Figure 13 shows that for 10AA electrodes there is no clear limiting process. That is, the
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39 overpotentials of each process are of similar magnitude. However, the limiting process for GFD3
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41 electrodes is clearly charge transfer. That said, ohmic polarization with GFD3 electrodes is small
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43 at low concentration, but it is nearly half of the polarization at high concentration. The
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45 distributed resistance is the more significant of the two sources of ohmic resistance in cells with
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47 GFD3.
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52 This work highlights some of the tradeoffs of using a felt or paper-based carbon
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54 electrode. Ohmic losses with felt are much higher due to the electrode thickness, but finite
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56 diffusion overpotential is much lower. Using thinner paper electrodes can substantially decrease
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58 the ohmic resistance, but then a higher finite diffusion overpotential results. Off-the-shelf 10AA
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4 paper is kinetically more facile than GFD3 felt; however, it has been shown that a variety of
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6 pretreatments can be used to improve the kinetics [3]; thus, off-the-shelf kinetics need not be a
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8 determining factor in electrode material choice. An ideal electrode would be thinner than the
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10 commercially available felts today (GFD3 is among the thinnest) but would maintain their
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12 favorable transport properties. Thin electrodes based on gas diffusion layers such as the 10AA in
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14 this work must have improved transport properties to minimize concentration overpotential.
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20 The reader should take note of the fact that the results presented in this work are only
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22 relevant for the V^{2+}/V^{3+} couple. The limiting process for the positive side of the VRFB
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24 (VO_2^+/VO^{2+}) is likely different, given that the kinetics on the positive side are faster than that on
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26 the negative side [23,30,31]. Because commercial VRFBs operate at concentrations above 1.5 M
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28 vanadium concentration, where ohmic overpotential started to dominate the negative symmetric
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30 cell in this work, one might predict that the ohmic resistance would be the dominant source of
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32 overpotential in full cells under practical operating conditions. Given that increased vanadium
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34 concentration has competing effects on voltage efficiency – increase in ohmic overpotential and
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36 decrease in charge transfer and finite diffusion overpotentials – efforts to continually increase
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38 vanadium concentration will ultimately result in a tradeoff between increased energy density and
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40 decreased cell efficiency and power density.
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47 **4. Conclusions**

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50 The use of a pulse dampener with EIS is invaluable in obtaining quantitative information
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52 about the finite diffusion resistance at a practical flow rate and with short experimental times.
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54 This setup and methodology is a useful characterization tool for RFBs. This method was used to
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56 study the effects of electrode material, flow field design, and vanadium concentration on charge
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58 transfer, finite diffusion, and ohmic resistance and overpotential on the V^{2+}/V^{3+} redox couple.
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4 The use of impedance resolved polarization curves allow one to measure the influence of
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6 individual components and operating parameters on overall cell performance. With this
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8 approach, optimization efforts can be focused on relevant components and parameters that limit
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10 system performance, rather than spending research effort on a component that will have only
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12 marginal overall effects.
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17 We found that the charge transfer process was the dominant source of overpotential with
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19 GFD3 electrodes. Ohmic overpotential was also significant at high vanadium concentration, as
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21 the thick electrode results in a large distributed resistance. For 10AA-based cells, all three
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23 sources of overpotential contributed significant portions to the total cell overpotential. We
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25 quantitatively showed that flow field design had a significant impact on the finite diffusion
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27 overpotential with 10AA.
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Electrode	Flow Field	$c / \text{mol dm}^{-3}$	$k_0 / 10^{-5} \text{ cm s}^{-1}$	$A_{\text{eff}} / \text{cm}^2$
10AA	flow-through	0.5	7.6	170
		1.5	8.2	110
	serpentine	0.5	10.9	220
		1.5	15.0	110
GFD3	flow-through	0.5	2.8	98
		1.5	3.2	84
	serpentine	0.5	2.6	110
		1.5	3.0	97

Table 1. Rate constant and effective area of single 5 cm^2 electrode in the cell for the $\text{V}^{2+}/\text{V}^{3+}$ reaction.

Figure 1. Flow field patterns with outlined active area. In the serpentine design (a), electrolyte bypass flow in the channels is shown as dashed lines. Flow over the lands (through the porous electrode) is shown as curved arrows. In the flow-through design (b), all flow is forced through the electrode and primarily travels in the in-plane direction denoted by the solid arrows.

Figure 2. Schematic of the symmetric cell setup with pulse dampener.

Figure 3. Whole cell complex impedance spectra for 10AA electrodes with flow rate 25 mL min^{-1} and at 30°C . Spectra are labeled with the flow field and total vanadium concentration. Applied overpotential is for the whole cell.

Figure 4. Whole cell complex impedance spectra for GFD3 electrodes with flow rate 25 mL min^{-1} and at 30°C . Spectra are labeled with the flow field and total vanadium concentration. Applied overpotential is for the whole cell.

Figure 5. Model fit (○) to experimental data (×) for 10AA electrodes. Left: Nyquist plot. Right: Bode plot. The real impedances were normalized by first subtracting $\min(\text{Re}(Z))$ from all points and then dividing by the quantity $[\max(\text{Re}(Z)) - \min(\text{Re}(Z))]$. Imaginary impedances were normalized only by dividing by the quantity $[\max(\text{Re}(Z)) - \min(\text{Re}(Z))]$.

Figure 6. Model fit (○) to experimental data (×) for GFD3 electrodes. Left: Nyquist plot. Right: Bode plot. The real impedances were normalized by first subtracting $\min(\text{Re}(Z))$ from all points and then dividing by the quantity $[\max(\text{Re}(Z)) - \min(\text{Re}(Z))]$. Imaginary impedances were normalized only by dividing by the quantity $[\max(\text{Re}(Z)) - \min(\text{Re}(Z))]$.

Figure 7. Resolved resistances according to low frequency approximations in Eqns. 2–4 for the open circuit complex impedance spectrum of the GFD3 electrode with flow-through flow field and 0.5 M vanadium concentration. The ‘X’ marks the model-predicted high frequency intercept of the impedance spectrum. $X = R_{\text{series}} + b \frac{\rho_1 \rho_2}{(\rho_1 + \rho_2)}$.

Figure 8. Resistances and integrated overpotentials as a function of geometric current density. Resistances were extracted by fitting the data to the impedance model at each current density. Data shown are for 10AA electrodes with flow-through flow field at 0.5 M vanadium concentration.

Figure 9. Charge transfer overpotential. Left: 0.5 M total vanadium concentration. Right: 1.5 M total vanadium concentration.

Figure 10. Concentration overpotential. Left: 0.5 M vanadium concentration. Right: 1.5 M total vanadium concentration.

Figure 11. Ohmic overpotential separated into series and distributed contributions. Left: 0.5 M total vanadium concentration. Right: 1.5 M total vanadium concentration.

Figure 12. Overall polarization curves, all conditions.

Figure 13. Impedance-resolved polarization curves showing the contributions of ohmic, charge transfer, and finite diffusion overpotentials. Open circles represent the potentiostat-imposed overpotential.

Appendix A. Table of fixed parameters for model input.

Fixed parameter	Value	Units	Source
A	5	cm^2	direct measurement
b (10AA)	0.24	mm	direct measurement
b (GFD3)	2	mm	direct measurement
C_{dl}	20	$\mu\text{F cm}^{-2}$	typical value
c_{O} (low conc.)	0.28	mol dm^{-3}	coulometric measurement
c_{O} (high conc.)	0.76	mol dm^{-3}	coulometric measurement
c_{R} (low conc.)	0.28	mol dm^{-3}	coulometric measurement
c_{R} (high conc.)	0.76	mol dm^{-3}	coulometric measurement
D_{O}	0.57×10^{-6}	$\text{cm}^2 \text{s}^{-1}$	reference 32
D_{R}	1.1×10^{-6}	$\text{cm}^2 \text{s}^{-1}$	reference 32
ρ_1 (low conc.)	2.61	$\Omega \cdot \text{cm}$	calculated from reference 33
ρ_1 (high conc.)	3.88	$\Omega \cdot \text{cm}$	calculated from reference 33
ρ_2 (10AA)	0.012	$\Omega \cdot \text{cm}$	manufacturer specification
ρ_2 (GFD3)	0.3	$\Omega \cdot \text{cm}$	manufacturer specification
T	303.15	K	experimentally controlled

Appendix B. Table of model output fitted parameters at open circuit for each experimental case.

8	Electrode	Flow field	c / mol dm ⁻³	<i>A</i> _t	<i>i</i> ₀	<i>P</i>	<i>a</i>	<i>f</i>	<i>L</i>	<i>R</i> _{series}
9	10AA	flow-through	0.5	260	1.3×10 ⁻³	0.95	0.0009	0.18	1.9×10 ⁻⁷	0.28
10			1.5	370	1.8×10 ⁻³	0.87	0.0012	0.09	1.9×10 ⁻⁷	0.41
11		serpentine	0.5	230	2.8×10 ⁻³	0.99	0.0016	0.22	1.0×10 ⁻⁷	0.29
12			1.5	270	4.6×10 ⁻³	0.91	0.0018	0.15	1.2×10 ⁻⁷	0.39
13	GFD3	flow-through	0.5	140	5.5×10 ⁻³	0.96	0.0007	0.32	1.1×10 ⁻⁷	0.26
14			1.5	160	1.2×10 ⁻³	0.93	0.0008	0.46	0.7×10 ⁻⁷	0.41
15		serpentine	0.5	160	5.0×10 ⁻³	0.96	0.0008	0.38	1.0×10 ⁻⁷	0.29
16			1.5	190	1.1×10 ⁻³	0.92	0.0009	0.47	0.7×10 ⁻⁷	0.42
17				cm ²	A cm ⁻²	unitless	cm	unitless	H	Ω·cm ²

Appendix C. Objective function used to perform non-linear least squares regression.

$$\sum_k \left[(\text{Re}(AZ_{\text{cell,experimental}} - AZ_{\text{cell,model}}))^2 + (\text{Im}(AZ_{\text{cell,experimental}} - AZ_{\text{cell,model}}))^2 \right]$$

The subscript k indicates that the objective function is taken as the sum of above quantity over all k frequencies for a single impedance spectrum.

The quantity $Z_{\text{cell,experimental}}$ is a complex-valued number obtained directly from the experiment. The quantity $AZ_{\text{cell,model}}$ is a complex-valued number calculated in its entirety below:

$$AZ_{\text{cell,model}} = 2 \times AZ_p + R_{\text{series}} + j\omega L \quad [10]$$

$$AZ_p = b \frac{\rho_1^2 + \rho_2^2}{\rho_1 + \rho_2} \frac{\coth Q_2}{Q_2} + b \frac{2\rho_1\rho_2}{\rho_1 + \rho_2} \frac{1}{Q_2 \sinh Q_2} + b \frac{\rho_1\rho_2}{\rho_1 + \rho_2} \quad [11]$$

$$Q_2 = \sqrt{\frac{(\rho_1 + \rho_2) b A_t}{AZ_a}} \quad [12]$$

$$Z_a = \left[\left(\frac{RT}{Fi_0} + \frac{RTa}{fF^2 c_R D_R} \times \frac{\tanh\left(a \sqrt{\frac{j\omega_k}{D_R}}\right)}{a \sqrt{\frac{j\omega_k}{D_R}}} + \frac{RTa}{fF^2 c_O D_O} \times \frac{\tanh\left(a \sqrt{\frac{j\omega_k}{D_O}}\right)}{a \sqrt{\frac{j\omega_k}{D_O}}} \right)^{-1} + (j\omega_k)^P C_{dl} \right]^{-1} \quad [13]$$

The mathematical derivation of this expression is provided in reference 15.

List of symbols

A	cell geometric active area
A_{eff}	effective electrode surface area
A_t	electrode internal surface area (model parameter)
$AZ_{\text{cell,experimental}}$	total cell impedance obtained by experiment
$AZ_{\text{cell,model}}$	total model-predicted cell impedance
AZ_p	single electrode model-predicted impedance
a	effective boundary layer thickness
α	transfer coefficient
b	electrode thickness
C_{dl}	specific double-layer capacitance
c_{O}	V^{3+} concentration
c_{R}	V^{2+} concentration
CPE_{dl}	CPE double-layer capacitance
D_{O}	V^{3+} diffusion coefficient
D_{R}	V^{2+} diffusion coefficient
F_j	frequency
f	geometric scale factor
i	geometric current density
i_0	exchange current for a differential surface area element
k_0	kinetic rate constant
L	lead inductance
η_x	overpotential due to process x
P	CPE power factor
ρ_1	specific ionic resistivity of liquid electrolyte
ρ_2	specific electronic resistivity of electrode material
Q	CPE capacitance
R_{ct}	charge transfer resistance
$R_{\text{ct},0}$	open circuit charge transfer resistance
$R_{\text{distributed}}$	distributed ohmic resistance
R_{e}	half-cell total ohmic resistance
R_{fd}	finite diffusion resistance
R_{series}	cell series resistance
ω	radian frequency

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