Characterizing Slurry Electrodes Using Electrochemical Impedance Spectroscopy

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Techniques for interpreting electrochemical impedance spectroscopy of different flowing slurry electrodes configurations are presented based upon models developed for macrohomogeneous porous electrodes. These models are discussed with regards to three different slurry systems: particles in deionized water, in supporting electrolyte without redox active species (akin to electrochemical flow capacitors), and in electrolytes supporting aqueous redox couples (akin to redox flow batteries). Through investigating each of these systems, the individual properties of a slurry can be determined. It was found that traditional overpotential descriptions, (ohmic, activation, and mass transfer) were insufficient to fully describe the impedance and polarization of the slurry electrodes. An overpotential due to the distributed current distribution in the slurry electrode was considered in the frequency range of activation overpotentials that depend on the exchange current density and the ratio of the electronic and ionic conductivities. In slurry electrodes made with multi-wall carbon nanotube particles supporting the ferric/ferrous redox couple, the distributed overpotential was found to be about the same order of magnitude as the activation overpotential and the total voltaic efficiency was over 80% at 200 mA/cm².

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Manuscript submitted March 9, 2015; revised manuscript received May 19, 2015. Published June 11, 2015. This paper is part of the JES Focus Issue on Redox Flow Batteries—Reversible Fuel Cells.

Slurries, flowing suspensions of solid particles in liquid electrolyte, have been studied for their application as electrochemical electrodes for most of the last century. Heydecke and Beck1 cite fundamental work as early as 1928. Originally, electrochemical slurry electrodes were investigated almost exclusively for waste water treatment.2–7 In the late 1970’s, slurry electrodes were used in the zinc-air battery system for energy storage.8–10 In the last few years, particular interest has been given to other energy storage applications,8–25 particularly non-aqueous lithium-ion batteries11–15 and electrochemical systems studied to date. Most of the recent investigations studied slurry electrodes made with suspensions of high surface area carbon black particles.

Slurry electrodes are inherently dynamic. Particles are constantly moving and are constantly making and breaking contact with each other. Percolation theory describes a critical loading, fc, above which there are enough particles in the slurry that, at any point in time, a continuous network of particles is formed that spans the distance from one boundary to another.26–27 It is due to these networks that slurries are able to conduct electrons out into the electrode and away from the current collector to utilize the high surface area of the particles for electrochemical processes. At a single instant in time, slurry electrodes resemble porous electrodes such as stationary carbon felt,28–31 or packed beds,32–36 bicontinuous electrodes with both electronic and ionic conductivity.

There are many advantages to using slurry electrodes over conventional stationary electrodes. The use of a slurry allows the electrode (1) surface area to be scaled independently of the separator area, (2) to be easily manufactured and replaced without disassembling the cell, (3) and to be easily recycled with filtration.

Electrochemical impedance spectroscopy (EIS) is a versatile technique employed to investigate electrochemical systems. With an understanding of the system, equivalent circuit models can be developed that describe the EIS response and can be used to determine individual properties. These equivalent circuit models have been developed for a variety of macrohomogeneous porous electrodes.28–31 This paper will study how these EIS equivalent circuit models can be applied to slurry electrodes in order to better characterize their electrochemical properties leading to better engineered electrodes.

Experimental

Materials.— Three different carbon particles were investigated and their physical properties are described in Table II. Asbury Carbons (Asbury, NJ, USA) graciously provided 230 U, a natural flake carbon with an average diameter of 20 μm, thickness of 100 nm, a reported surface area of 6.5 m²/g, and a carbon purity of 99.4%. Asbury Carbons also provided Nano27; carbon platelets with an average diameter of 100 nm, thickness of 2.5–10 nm, a reported surface area of 250 m²/g, and a carbon purity of > 99%. MWCNTs were purchased from Nanostructured and Amorphous Materials, Inc. (Houston, TX, USA). These MWCNTs have an OD of 50–80 nm, length of 10 μm, reported surface area of 40 m²/g, and a carbon purity of > 95%. For these studies, all carbon particles were used as received. Before tests were performed, particles were mixed by hand in electrolyte and then pumped through the system for at least 30 min.

All salts used in the subsequent experiments were reagent grade and were obtained from Fisher Scientific (USA). All solutions were made with DI water (> 18 MΩ-cm). When using ferrous salts, solutions were made under a continuous nitrogen blanket and experiments were performed with the electrolyte under a continuous nitrogen purge to mitigate the air oxidation of ferrous to ferric iron.29,30 All tests were conducted at room temperature (20–25 °C).

It was observed that when the volume fraction of the solid particles was above some critical concentration, there was no longer enough liquid in the slurry to fully wet all of the particles. When the volume fraction of solids rose above this critical volume fraction, the slurry transitioned quite quickly to a semi-solid gel. At this point, the slurry is no longer able to flow readily. This viscosity critical volume fraction, fc*, is given in Table II and described in detail by Youssry et al.12

Electrochemical studies.— Electrochemical impedance spectroscopy (EIS) was performed using a Solartron 1280B potentiostat (Ametek, UK). Each test was performed at the open circuit potential (OCP) with a sinusoidal perturbation of 10 mV amplitude over the frequency range 20 kHz-0.2 Hz. The EIS experiments were controlled using ZPlot (Scribner, USA). Cell polarization and an oscilloscope (Tektronix, USA) were used in concert to ensure that the response of the system under perturbation remained linear.
Aluminum rods were cleaned and degreased with methanol and then every time a new particle was investigated using this technique, the particles present. These steps were repeated until the resistance between the two rods was less than $5 \times 10^{-4} \Omega$ and was subsequently considered negligible.

$$
\sigma = \frac{1}{\delta / \Lambda} [2]
$$

The electrical conductivity of the slurry electrodes was characterized while flowing in a tubular cell, designated the “flowing conductivity cell”, for suspensions in DI water with no added salts. This cell was constructed from a polycarbonate tube with 1.3 cm inner diameter and a length of 13 cm. Four pieces of platinum wire, each with a diameter of 1 mm, were situated in the tube so that EIS could be performed on the flowing slurry. The two platinum wires that served as the reference electrodes were 1 cm apart and the two platinum wires that served as the working and the counter electrodes were 8 cm apart. All four wires protruded into the flow $< 1 \text{ mm}$ and were situated on the same side of the tubular cell as shown in Figure 2. The electrical conductivity of the slurry was determined using Equation 2 and the measured real high frequency resistance of each slurry electrode. To determine the cell constant of the flowing conductivity cell, $\delta / \Lambda$ in Equation 2, EIS was performed on solutions with known ionic conductivities (1–100 mS/cm) made with varying concentrations of HCl.

### Table I. A brief summary of the electrochemical systems investigated with slurry electrodes.

| System                  | Particles                        | Size [μm] | vol. % | Electrolyte | $\sigma$ [mS/cm] | $\kappa$ [mS/cm] | Ref. |
|-------------------------|----------------------------------|-----------|--------|-------------|------------------|------------------|------|
| Water Treatment         | Organic & Inorganic Hg           | Carbon Black MWCNTs | $10^{-2} - 10^{-1}$ | 0.2–20 | Aqueous n/r | n/r | 2–5 |
| Electrochem. Energy     | Cap. Dl | Activated Carbon Zinc metal Li-Oxide & Carbon Black | $10^{-1} - 10^{3}$ | 2–3 < 1 | 10–25 | n/r | 1–3 |
| Storage                 | Zn-Air Battery                   | Carbon Black | $3 \cdot 10^{-3}$ | 1–2 | Non-aqueous | 2–20 | 1.5 |
| Metal-Oxide Battery     | Poly-aniline or Poly-pyrrole     | $3–30$ | n/r | Aqueous n/r | n/r | 17,18 |
| ZnAg Battery            | Ag doped Poly-aniline & Graphite | n/r | 5–10 | Aqueous n/r | n/r | 19 |
| Capacitor               | Graphite or Activated Carbon & Carbon Black | $10^{-2}$ | 5–15 | Aqueous | $< 20$ | 60–300 | 20–25 |

### Table II. Slurry carbon particle physical properties.

| Particle | Diameter | Length | Aspect Ratio | $f_{cv}$ |
|----------|----------|--------|--------------|----------|
| 230U     | 20 μm    | 200 nm | 0.01         | 0.17     |
| Nano27   | 100 nm   | 10 nm  | 0.1          | 0.08     |
| MWCNTs   | 50–80 nm | 10 μm  | 100–200      | 0.06     |

The ionic conductivity of the electrolytes used has been characterized using a glass conductivity cell with platinized platinum electrodes. This apparatus has a cell constant of 200 cm$^{-1}$ and a length of 13 cm. The real limit of the impedance at high frequency, $R_{HF}$, of the ionic liquid can be used to find the ionic conductivity, $\kappa$, characterized using a glass conductivity cell, designated the “flowing conductivity cell”, for suspensions in DI water with no added salts. This cell was constructed from a polycarbonate tube with 1.3 cm inner diameter and a length of 13 cm. Four pieces of platinum wire, each with a diameter of 1 mm, were situated in the tube so that EIS could be performed on the flowing slurry. The two platinum wires that served as the reference electrodes were 1 cm apart and the two platinum wires that served as the working and the counter electrodes were 8 cm apart. All four wires protruded into the flow $< 1 \text{ mm}$ and were situated on the same side of the tubular cell as shown in Figure 2. The electrical conductivity of the slurry was determined using Equation 2 and the measured real high frequency resistance of each slurry electrode. To determine the cell constant of the flowing conductivity cell, $\delta / \Lambda$ in Equation 2, EIS was performed on solutions with known ionic conductivities (1–100 mS/cm) made with varying concentrations of HCl.

![Figure 1](https://ecsd.org/site/terms_use) unless CC License in place (see abstract).
The cell constant was found to be 0.76 cm$^{-1}$ over this conductivity range.

All other electrochemical experiments were conducted in an in-house channel cell through which the slurry electrodes flow. This “channel cell” was defined by two CPVC flow fields containing straight rectangular channels with a width of 1 cm and length of 12 cm (in the direction of flow) and is described by Figure 3. The current collectors were 1 cm wide and 6.725 cm long ($A = 6.725$ cm$^2$) graphite plates that were centered in the middle of the CPVC channel. The gap between the current collect of each channel and the separator was either 0.1 cm or 0.2 cm. A peristaltic pump (Cole-Parmer, USA) was used for pumping the slurries. In all experiments, the slurry was pumped vertically up through the electrochemical channel cell. The inlet and exit ports of the channel cell were at roughly 30° angles (with respect to the current collector face) to minimize any clogging. Current was collected from this cell through two brass plates that were centered in the middle of the current collectors. The cell assembly was compressed with 8 bolts that were tightened to 90 in-lbs of torque. The reservoirs used to hold the slurry that was pumped through the channel cell were Nalgene bottles modified to be bottom drawn. Unless otherwise noted, all materials were purchased from McMaster-Carr (Cleveland, OH, USA).

The cell constant of the channel cell was determined by performing EIS on solutions with known conductivities (1–100 mS/cm) made with varying concentrations of HCl without a separator between the two cell halves. The cell constant was found to be 0.029 cm$^{-1}$ and 0.058 cm$^{-1}$ for cells with 0.2 cm and 0.4 cm total channel depths, respectively. This is in good agreement with the theoretical values of 0.030 cm$^{-1}$ and 0.059 cm$^{-1}$ determined from the cell geometry.

For the experiments in which a membrane was used to separate the two channels of the channel cell, Nafion 1035 (Ion Power, DE, USA) was used. The Nafion was pretreated by boiling in 5% H$_2$O$_2$ and then in DI water. The membranes were equilibrated in electrolyte prior to use. Each step was for at least one hour. The swelled thickness of Nafion 1035 was measured to be about 100 μm.

### Analytical EIS Models

**EIS of a bicontinuous electrode.**—An equivalent circuit model of a slurry electrode, ignoring any dynamic nature, is shown in Figure 4 for an electrode between a current collector (left) and an ionically conductive separator (right). Because the dynamic nature is ignored, this equivalent circuit is akin to those of typical porous electrodes.28–31 In this figure; $R_e$ is the resistance of a finite length of the electronic phase (including any particle-to-particle contact resistance); $R_{ion}$ is the resistance of a finite length of the ionically conductive liquid phase; $\zeta$ is the impedance of the interface between the slurry electronic and ionic phases; $R_{c-e}$ is the contact resistance (if any) between the current collector and particles in solution; and $\zeta_{c-i}$ is the impedance of the interface between the ionic phase and the current collector. $\zeta$, and $\zeta$ will always be of the same form (e.g. a capacitor or a capacitor and resistor in parallel) for the systems studied here but the former applies to the real active area of the current collector while the latter corresponds to the active area of the slurry solid phase. From the carbon particle loading in the slurry and the reported active area, the predicted area of the slurry electrode should be on the order of $10^2$–$10^3$ cm$^2$; at least 2–5 orders of magnitude greater than that of the current collector. For the studies presented in this paper, the impedance associated with the current collector interface will be ignored.

Equation 3a and Equation 3b describe the impedance, $Z$ [Ω], of a bicontinuous electrode, ignoring the current collector interface, as developed for macrohomogeneous porous electrodes.28–31 Assuming the system is macrohomogeneous allows the electronic and ionic phases to be described by length average resistances, $r_e$ and $r_{ion}$, respectively, described by Equation 4. Any particle-to-particle contact resistance is included in $r_c$.

$$Z = \frac{r_e r_{ion}}{r_e + r_{ion}} \delta + \frac{r_e r_{ion}}{r_e + r_{ion}} \frac{2\lambda}{\sinh \left( \frac{\lambda}{2} \right)} + \frac{r^2_c + r^2_{ion}}{r_e + r_{ion}} \coth \left( \frac{\delta}{\lambda} \right) \tag{3a}$$

$$\lambda = \left( \frac{\zeta_{c-i}}{r_e + r_{ion}} \right)^{1/2} \tag{3b}$$

Figure 3. A schematic of the electrochemical channel cell (not to scale) used to characterize the slurry performance. The channel is defined by the flow frame and the electric field is defined by the inset current collectors. The slurry flows up vertically through the cell and the inlet/exit are at approximately 30 degrees to vertical to help mitigate clogging. Not shown are the materials to compress the cell and the brass plates from which current is drawn.

Figure 4. General equivalent circuit model of a porous electrode that is terminated electrically at a current collector (left) and ionically at an ionically conductive separator (right).
averaged capacitance of the solid phase double layer, is shown in Figure 5. Figure 6 shows the typical Nyquist plot of the system being studied. (In this paper, the area impedance, $Z \cdot A[\Omega \cdot cm^2]$, is reported.)

$$r = \frac{1}{\delta} \sum R = [\sigma \cdot A]^{-1} \text{ or } [x \cdot A]^{-1}$$  \[4\]

EIS of slurry electrodes with ionically conducting electrolyte in the absence of a redox couple.— Salt containing electrolytes with suspended particles have both ionic and electronic conductivity. Slurries such as these, in the absence of Faradaic current, are akin to the electrochemical flow capacitor. Without a double layer present, current may only pass from the electronic to the ionic phase through the charging of the double layer capacitance of the solid particles. The impedance of this interaction is described by Equation 5 and is a function of the frequency of the perturbation, $\omega [s^{-1}]$, and the length averaged capacitance of the solid phase double layer, $c_{dl} [F/cm]$.

$$\tilde{Z}_e = (j \omega c_{dl})^{-1} = (j \omega c_{dl} A f)^{-1}$$  \[5\]

In the absence of flow, the equivalent circuit model for an electrochemical slurry capacitor electrode with an ionically conducting separator (the right side) terminated by a current collector (left side) is shown in Figure 5. Figure 6 shows the typical Nyquist plot of the full impedance model of the static electrochemical slurry capacitor, Equations 3–5, in the electrochemical channel cell with and without separators (single channel with thickness of $2\delta$, or a channel with thickness $\delta$ on either side of a separator). A real resistance equal to the separator impedance, $0.5 \Omega \cdot cm^2$, was added to the system without a separator to make the high frequency impedance between the two models congruent. In both cases, the real impedance increases as the frequency of the potential perturbation decreases. At the high frequency limit, Equation 5 approaches zero and, therefore, Equation 3a reduces to Equation 6; the parallel combination of the ionic and electronic paths. As the frequency decreases, the Nyquist plot of the system with an ionically conductive separator tends to negative infinity in the imaginary axis while the Nyquist plot of the system without a separator has a finite low frequency limit. This low frequency behavior exists because without a separator the electronic phase conduction can complete the circuit between the working and counter electrode. The depression of this semi-circle, and the region in the system with a separator, are due to the distributed nature of the electrode, discussed below.

$$R_{HF} = R_i = \frac{r_e r_{ion}}{r_e + r_{ion}}$$  \[6\]

The EIS model presented in Figure 5 and Figure 6 describes a stationary two-phase electrode in the absence of Faradaic currents. Under non-stationary conditions, there exists additional current that results from the flow of the particles. The current arises because particles with charged double-layers leave the cell at the outlet thereby permitting uncharged particles (that are hence receptive to accepting current) to enter at the inlet. This current could potentially be modeled in the context of Figure 5 with the inclusion of a volume flow rate dependent source/sink. However, this advective capacitive current (also called "hydraulic current") has multi-dimensional characteristics (e.g. boundary layers of overpotential that grow as the slurry flow proceeds downstream along the electrode) that make analysis with 1-D equivalent circuit models problematic. Thus, impedance analysis of these situations is difficult.

However, it is possible to estimate the impedance response at the high and low frequency limits. At high frequencies (relative to the residence time of the slurry in the cell), the slurry behaves as a quasi-static solid matrix, and therefore has the same EIS behavior as in the static case (although perhaps with an altered electronic conductivity due to shear-rate effects). At low frequency, the current response tends toward the steady-state, DC charging value that can be predicted using available models. Thus, even in the situation with a separator present, the Nyquist plot still returns to the real axis at low frequency (instead of having its imaginary component diverge to negative infinity as in the stationary case). The evolution of the Nyquist plot at intermediate frequencies is difficult to ascertain though as the advection-diffusion of surface charge combined with sinusoidal perturbations requires time-dependent, two-dimensional numerical simulations of the governing slurry electrode equations. This approach is beyond the scope of this work.

EIS of slurry electrodes supporting Faradaic current.— Slurry electrodes containing electroactive redox species have been of significant interest for electrochemical device applications including energy storage and water treatment. An equivalent circuit representing a slurry electrode, ionically terminated, that supports a redox reaction is shown in Figure 7. The impedance of the liquid-solid interface in the presence of a redox couple is described by Equation 7. In this equation, $r_{ct} [\Omega \cdot cm]$ is the length specific charge transfer resistance.

$$\tilde{Z}_c = \frac{r_{ct}}{1 + j \omega r_{ct} c_{dl}}$$  \[7\]

The advected currents from the previous section also simultaneously exist along with the Faradic reaction currents for slurry electrodes in the presence of redox active species. However, if the kinetics are fast enough and the flow rates are slow enough, the advected...
capacitive current is generally small and can be ignored. Therefore, the subsequent studies do not include any advective effects.

The impedance of slurry electrodes supporting redox couples are the same whether ionically or electronically terminated due to the presence of the charge transfer resistance. At high frequencies, Equation 7 approaches zero and the total impedance, Equation 3a, reduces to that of the parallel combination of the ionic and electronic resistance, Equation 6. At low frequencies, Equation 7 approaches the impedance of the charge transfer resistance. Because the charge transfer resistance is real and finite, it can bridge the solid phase and the ionic phase at low frequencies.

The first term of Equation 3a represents the parallel combination of the conductive paths and is real, finite, and independent of the voltage perturbation. The second and third terms of Equation 3a, however, are a combination of the electronic, ionic, and charge transfer resistances that encompass the distributed nature of the electrode. At all finite frequencies, the second and third term of Equation 3a, combined with Equation 7, have both real and imaginary components. Figure 8 shows an example Nyquist representation of the impedance of a slurry electrode. In this figure, the specific contributions of the second and third term of Equation 3a are shown. The constant real impedance of the first term is added to the second term while the separator impedance is added to the third term. Doing this only shifts the second and third term in the x-axis of Figure 8. As Figure 8 shows, both the second and third term have unique contributions to the "distributed shape" of the overall impedance response. While the general shape of the total impedance of the redox active slurry electrode (the solid line in Figure 8) is similar to that of the electronically terminated electrochemical flow capacitor (the dashed line in Figure 6), the loop trending back to the real axis at low frequencies is in fact due to the redox couple active at the electrolyte-solid interface, highlighting the importance of applying the correct model to the system being investigated.

Figure 9 investigates the effect of the charge transfer resistance on Equation 3a for a slurry electrode supporting a redox reaction. At high frequencies, a near 45° feature is present in the Nyquist plot for all values of the charge transfer resistance. As the frequency decreases, the real impedance increases and the Nyquist plot begins to roll toward the real axis forming a feature similar to the charge transfer loop of traditional Randles circuits. However, as the charge transfer resistance increases (the reaction kinetics become slower), the low frequency feature begins to separate from the high frequency feature.

As Equation 3a and Figure 9 indicate, the total impedance of a slurry electrode approaching low frequencies is more than the sum of the high frequency resistance and the charge transfer resistance typical of Randles circuits. The additional impedance will be described as a distributed resistance, \( R_{\text{dist}} \). The total impedance of a slurry electrode at the low frequency, or DC, limit can be described by Equation 8. Using the model parameter for the length specific charge transfer resistance, the total charge transfer resistance of a single electrode can be described by Equation 9.

\[
Z_{\text{LF}} = R_{\text{DC}} = R_{\text{HF}} + R_{\text{ct}} + R_{\text{dist}}
\]

\[
R_{\text{ct}} = \tilde{r}_{\text{ct}} / b
\]

The distributed resistance is a result of the specific current distribution that arises when current can flow through both electronic and ionic phases of the slurry electrode. When charge transfer resistance exists, the current distribution is not that which minimizes ohmic losses, but rather is the distribution that minimizes the total overpotential losses. The additional losses associated with this current distribution are termed the distributed resistance.

Combining the low frequency approximations of Equation 3 with Equations 7–9 allows for the distributed resistance of the slurry electrode to be determined. Figure 10 shows how the distributed resistance depends upon the charge transfer resistance. As the charge transfer resistance decreases, the distributed resistance also decreases. This occurs because, as \( \tilde{r}_{\text{ct}} \) approaches zero, it shorts out the solid-liquid interface and the impedance of the slurry electrode approaches Equation 6 at all frequencies. Conversely, as the charge transfer resistance increases, the slurry electrode behaves more and more like an electrochemical flow capacitor. At this limit, the distributed resistance approaches a constant value. This maximum distributed impedance (\( R_{\text{dist}} \) for the capacitor) is a function of the ratio of electronic resistance to ionic resistance and is described in Figure 11. The distributed resistance, normalized by the high frequency resistance, is at a minimum value of 1/3 when the electronic resistance equals the ionic resistance. As the electronic and ionic resistances move further apart, the normalized distributed resistance continues to grow. It should be noted that the high frequency "foot" in Figure 9 does not encompass the distributed impedance. As shown in Figure 8, both the second and third terms of Equation 3a contribute to the distributed resistance.
Figure 10. The distributed resistance of a slurry electrode supporting a redox reaction as a function of the length averaged charge transfer resistance. In this model, all other parameters are the same as those described in Figure 6.

**Results and Discussion**

Maximum slurry electronic conductivity.— All slurry electrodes investigated in this study are made of electrically conductive particles suspended in an ionically conductive electrolyte. Before attempting to separate the electronic conductivity from the ionic conductivity in a dynamic flowing slurry, the electronic conductivity was first investigated in a system without electrolyte.

The maximum electronic conductivity occurs when the volume fraction of the liquid phase is zero. However, a “slurry” without electrolyte is not flowable. Therefore, the electrical conductivity of the slurry particles, in the absence of any electrolyte, was measured in the pellet press. The results are shown in Table IV and were found to be weak functions of applied compression over the range tested. Each particle type exhibited conductivity 10³ times lower than that of pure graphite. This decrease in conductivity can be attributed to particle-to-particle contact resistances and packing efficiencies. In the flowing slurry electrodes, the particles are under no significant force to pack. Even at the lowest pressures, the dry pressed pellet conductivity will over-estimate the electrical conductivity of the flowing slurry electrode. However, it is interesting to note that the conductivity of the packed particles is similar for the three particles considered, despite their different size and shapes.

Slurries in DI water.— Evaluating slurries where the liquid contains no supporting ions (DI water) is a useful diagnostic system to isolate the electronic conductivity. This slurry has negligible ionic conductivity and the EIS response, without an ionic separator, is a single point on the real axis of the Nyquist plot and can be modeled as a pure resistor. The electronic conductivity, $\sigma$, can be found using the measured resistance, $R$, and the cell geometry, $\delta/A$, as in Equation 2.

Figure 12 shows the electronic conductivity of slurry electrodes with each particle at varying volume fractions in DI water as determined in the flowing conductivity cell. The conductivity quickly rises with increasing loading of particles above some critical percolation concentration, $f_c$, where the volume fraction of particles is high enough to create fully percolating conductive networks. The critical percolation concentration and the rate at which the conductivity rises as a function of increased loading is a factor of particle shape and particle-to-particle interactions. As a flowing slurry, the particles exhibit electrical conductivity $10^2$–$10^3$ times smaller than the dry packed pellets. This again can be attributed to particle-to-particle contact resistances and a further decrease in packing efficiencies.

EIS of slurry electrodes supporting Fe$^{2+/3+}$.— The ferric/ferrous couple, a common positive couple in redox flow batteries, was used to investigate the performance of the slurry electrodes supporting an aqueous redox couple. The electrolyte used in these studies was 1.0 M FeCl$_2$, 1.0 M FeCl$_3$, and 1.0 M NH$_4$Cl. This electrolyte simulates the composition of iron electrolytes at 50% state-of-charge.

For the following electrochemical experiments, a single reservoir containing the slurry/electrolyte was used to feed both sides of the electrochemical channel cell (divided by a separator; Nafion 1035). The draw from the reservoir was split and fed into two separate heads on the peristaltic pump before entering the cell so that the volumetric flow rate on either side of the cell was directly controlled. After leaving

![Table IV. The electronic conductivity of the slurry particles in the pellet press. No liquid electrolyte present.](image)

| Particle       | Conductivity (S/cm) |
|----------------|---------------------|
| 230U           | 5.5 ± 0.2           |
| Nano27         | 6.1 ± 0.2           |
| MWCNTs         | 6.9 ± 0.3           |

![Figure 11. The ratio of the distributed resistance to the high frequency resistance as a function of the ratio of the electronic resistance to the ionic resistance. In this figure, $R_{ct} = 10^{10}$, e.g. $R_{dist}$ is at the maximum value for each $R_e/R_{ion}$.](image)

![Figure 12. Conductivity of slurries in DI water as a function of the solid phase volume fraction. Conductivity determined from the high frequency real intercept of the impedance for each particle in the flowing conductivity cell.](image)
the electrochemical cell, the slurry from both sides of the cell were combined into one stream before reentering the reservoir. The volume of the reservoir used was typically 700 mL.

This experimental design, deemed a symmetric cell configuration, greatly simplifies the analysis of slurry or porous electrodes in the presence of a redox couple.\(^\text{45}\) Using a symmetric cell configuration ensures that the composition of the electrolyte will remain constant throughout all electrochemical tests. Ferric ions are reduced to ferrous ions at the cathode at the same rate that ferrous ions are oxidized at the anode. Since both streams are remixed, the reservoir composition does not change. The other advantage to the symmetric cell configuration is the simplified EIS analysis. The positive and negative slurry entering the cell should be identical. Also, because the ferrous/ferric couple is facile and symmetric (similar polarization whether reducing or oxidizing), the total overpotential of each electrode should be identical. This allows both slurry electrodes in the cell to be modeled by one circuit, Figure 7, instead of two on either side of a membrane and therefore reduces the number of fit parameters significantly. To model the entire symmetric electrochemical cell, Figure 7 is modeled in series with the separator resistance and hardware inductance. It is necessary to include the hardware inductance because, at \(\approx 10^{-7}\) H, the curves have a finite positive slope when the imaginary impedance is zero.

The ferric/ferrrous couple was investigated on slurry electrodes made with MWCNTs in the symmetric channel cell. Focus was put on these particles due to their higher electronic conductivity while suspended in a flowing slurry as shown in Figure 12 and due to their smaller primary particle size. For application in continuously circulating slurry electrodes, as opposed to pulse flow,\(^\text{11}\) the stability of the slurry is primarily related to the settling of particles. With the MWCNTs in stagnant slurries, no appreciable settling was observed for at least two hours. However, with the larger particles, settling was visibly observed in shorter time frames (\(<30\) minutes). Also, with the MWCNTs, the pumping action has been observed to be enough to keep the slurry well mixed for well over a week without any noticeable settling in the reservoir.

Figure 13 shows the EIS response for slurry electrodes of MWCNTs in 1.0 M FeCl\(_2\), 1.0 M FeCl\(_3\), and 1.0 M NH\(_4\)Cl. There are three frequency regions to the impedance response dominated by different processes. At high frequencies, above \(10^3\) Hz, the impedance is dominated by the hardware inductance and the parallel ohmic resistance, Equation 6. At intermediate frequencies, 10–10\(^{3}\) Hz, the characteristics of the charge transfer reaction are present (akin to Figure 8). The third region in the impedance plots of Figure 13 are effects due to mass transfer and the advective current at frequencies below \(10^2\) Hz. Of these three regions, only the effects due to mass transfer and advective current should depend on the flow rate of the slurry electrode; impedance due to both decreases with increasing flow rate. Comparing the EIS results as a function of flow rate (curves b-d in Figure 13) to the analytical model shows that there is non-negligible low frequency effects at all flow rates investigated. Since the impedance models developed earlier do not account for mass transfer or hydraulic current, the model, Figure 7 in series with hardware inductance and membrane resistance, was only applied to the data range above \(10^2\) Hz. Over this range, the impedance of curves b-d are near identical; confirming that mass transfer and the advective current are only significant at lower frequencies. When the impedance model was fit to the data, the ionic phase resistance, estimated using Equation 1 and Table III, and the separator resistance, \(0.5\ \Omega \cdot \text{cm}^2\) corresponding to Nafion 1035 in the iron electrolyte, were fixed. The change in ionic conductivity due to the volume of electrolyte displaced by slurry particles should be negligible (<5%)\(^\text{47}\) at 5 vol% MWCNTs.

Table V shows the fitting results of the impedance model to the data presented in Figure 13. The electronic conductivities of the slurry electrodes estimated in Table V match very well with the results shown in Figure 12. While the difference in electrolyte between Figure 12 and Figure 13 can change the particle-to-particle interactions\(^\text{26,27,40}\) the fact that the electronic conductivity was similar in both electrolyte is thought to be due to the high aspect ratio of the MWCNTs which force long range percolation. In this case, the aspect ratio of the MWCNTs is more important to the conductivity than the interactions between particles. Also, the good agreement between the electronic conductivities in Table V and Figure 12 implies that the contact resistance between the particles and the current collector is negligible.

Table V shows the charge transfer resistance and the double layer capacitance of each fit in Figure 13. The symmetric configuration allows the entire cell to be modeled by one equivalent circuit (Figure 7) in series with a membrane; each electrode should have the same overlapping EIS response. The total capacitance predicted by this analysis is only half that of each electrode, \(C_{dl} = 2C_{dl,\text{total}}\), because they are two identical capacitances in series. Conversely, the total charge transfer resistance is twice the charge transfer resistance of each electrode, \(2R_{ct} = R_{ct,\text{total}}\). Two identical resistances in series. It should be noted that the double layer capacitance values in Table V are estimates that are included simply for complete disclosure of the model fits applied in Figure 13. Determining these values is inherently difficult when a fast redox couple is present due to the fact that the capacitive effects never truly dominate the impedance response (the magnitude of the phase angle is never above four degrees) and the limited frequency range to which the model is applied.

### Table V. Results from the impedance model as shown in Figure 7 in series with hardware inductance and membrane resistance, applied to the data shown in Figure 13. For these fits, the membrane (Nafion 1035) resistance is fixed at 0.5 \(\Omega \cdot \text{cm}^2\) and the ionic phase conductivity is fixed at 130 mS/cm corresponding to the electrolyte as indicated in Table III. Values in the table are for each slurry on either side of the separator.

| Channel | vol% | \(r_e\) (\(\Omega\) cm\(^2\)) | \(\sigma\) (S/cm) | \(r_{ct}\) (\(\Omega\) cm) | \(c_d\) (F/cm) |
|---------|------|-----------------|----------------|-----------------|-----------|
| 1 mm    | 4.8  | 2.22            | 0.067          | 0.6 \times 10^{-3}| 16.7      |
| 2 mm    | 5.8  | 1.75            | 0.085          | 1.0 \times 10^{-3}| 1.46      |

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**Figure 13.** Nyquist (upper) and Bode phase angle (lower) representations of EIS results on MWCNT slurry electrodes supporting the ferrous/ferric redox reaction. The data points represent experimental data while the solid lines are analytical fits without mass transfer or advective effects; Figure 7 in series with hardware inductance and membrane resistance. (The model was fit to the data above \(10^2\) Hz, fit results in Table V.) Triangles (a) represent data for a cell with 1 mm channels at 200 mL/min with 4.8 vol% MWCNTs. Data sets b-d are with 2 mm channels at 25 mL/min (squares), 200 mL/min (diamonds), and 550 mL/min (circles), respectively, with 5.8 vol% MWCNTs. All data is with a Nafion 1035 separator.
Figure 14. Polarization curve and overpotential breakdown of the symmetric Fe$^{2+/3+}$ slurry electrode consisting of 5.8 vol% MWCNTs in 1.0 M FeCl$_3$, 1.0 M FeCl$_2$, and 1.0 M NH$_4$Cl flowing at 550 ml/min through a 1 mm gap with a Nafion 1035 separator at 200 mA/cm$^2$. The lines are overvoltages as determined from the EIS analysis for an individual electrode and the solid black line (a) is the total overpotential of the symmetric cell as determined by summing the individual overvoltages. The open squares represent average data points taken from cyclic voltammetry at 25 mV/sec.

Conclusions

Techniques for interpreting electrochemical impedance spectroscopy results to characterize different flowing slurry electrodes configurations were presented based upon models developed for porous electrodes. These models were discussed with regards to three different slurry systems; particles in deionized water, in supporting electrolyte without redox active species (electrochemical flow capacitor), and in electrolytes with redox couples (redox flow batteries). Through investigating each of these systems, the individual properties of slurry electrodes were determined. It was found that traditional overpotential descriptions, (ohmic, activation, and mass transfer) were insufficient to fully describe the impedance and polarization of the slurry electrodes.

In addition to the traditional overpotentials associated with electrochemical electrodes, there exists an overpotential due to the distributed nature of the current between the electronic and ionic phases of the slurry. This overpotential is a significant contribution to the cell polarization on the order of both the charge transfer and mass transfer overpotentials. It was found that this distributed overpotential is a function of the slurry electrode charge transfer resistance as well as the ratio of the electronic and ionic phase conductivities. Reducing the charge transfer resistance of the slurry electrodes to $10^{-4}$ Ω · cm$^2$ will lower the distributed overpotential significantly (over a factor of three for the MWCNT slurries).

With the ferric/ferrous redox couple, MWCNT slurry electrodes were found to operate at over 80% voltaic efficiency at 200 mA/cm$^2$. The electrode polarization was dominated by the ohmic losses in the slurry electrode. By increasing the slurry electronic conductivity, the performance of these electrodes can be significantly improved.

Table VI. Overpotential breakdown and voltaic efficiency of different 5.8 vol% MWCNT slurry electrodes in 1.0 M FeCl$_2$, 1.0 M FeCl$_3$, and 1.0 M NH$_4$Cl. All overpotentials are for 200 mA/cm$^2$ operating current density.

| Channel | Flow [mL/min] | $\eta$slurry-IR [mV] | $\eta$CT [mV] | $\eta$LF [mV] | $\eta$Dist [mV] | $\eta$tot [mV] | $\eta_{Voltaic}$ |
|---------|---------------|----------------------|---------------|--------------|----------------|--------------|----------------|
| 1 mm    | 200           | 93                   | 8.1           | 17           | 21             | 139          | 82%            |
| 2 mm    | 200           | 186                  | 6.7           | 51           | 52             | 296          | 62%            |
| 2 mm    | 550           | 186                  | 6.7           | 51           | 52             | 296          | 62%            |

The authors thank Nicholas Sinclair, Jason Pickering, and Mirko Antloga for assistance in conducting experimental trials and maintaining laboratory equipment. The funding for this project is through ARPA-E, contract number DE-AR0000352.

List of Symbols

A Geometric area, cm$^2$

a True active area, cm$^2$

$\hat{a}$ Active area per volume, cm$^2$/cm$^3$
$C_{dl}$ Capacitance, $F$

$\bar{C}_{dl}$ Length average capacitance, $F/cm$

$\tilde{C}_{dl}$ Specific capacitance, $F/cm^2$

$E^\circ$ Standard potential, $V$

$F$ Faraday constant, 96,485 C/mole e$^-$

$f$ Solid volume fraction

$i_0$ Exchange current density, $A/cm^2$

$R$ Resistance, $\Omega$

$R_{G}$ Gas constant, 8.314 $\frac{V}{mol \cdot K}$

$r$ Length average resistance, $\Omega/cm$

$\bar{r}$ Length specific resistance, $\Omega \cdot cm$

$T$ Temperature, $K$

$Z$ Impedance, $\Omega$

$Z_i$ Impedance of interface, $\Omega \cdot cm$

$z$ Electron per redox species, $mole e^- / mole j$

$\delta$ Length parallel to current, $cm$

$\eta$ Overpotential, $V$

$\kappa$ Ionic conductivity, $S/cm$

$\sigma$ Electronic conductivity, $S/cm$

$\omega$ Frequency, $1/s$

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