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An Analysis of the Contributions of Current Density and Voltage Efficiency to the Capital Costs of an All Vanadium Redox-Flow Battery

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Abstract

This paper utilizes new data on voltage efficiency for all-vanadium redox flow batteries to show improved system costs for grid-level applications. As more and more renewable power production is added to the grid the need increases for large scale storage alternatives.

Keywords: Current density; Analysis

Introduction

The potential of the redox flow battery (RFB) for use in grid scale energy storage is well documented [1-5]. Revenue streams for RFBs are somewhat complex, including peak shaving, load leveling, energy reserve and grid stabilization capabilities to improve the performance of the utility grid and deferral of investments for additional generation capacity [2]. In a series of papers Banham-Hall and others establish the technical viability of these potential revenue streams for VRBs integrated into a system of renewable power generation [6-8]. Using grid-based prices and other relevant information, Fare and others showed the value of VRBs for frequency regulation to be about $1500/kW [9]. The combination of renewable energy production and energy storage enables the system to behave more like a conventional power generation systems [7-9]. The all-vanadium redox flow battery (VRB) is currently the leading battery alternative. The VRB has been developed for several applications and is a continuing subject of research and development [3-5]. A schematic of a vanadium redox battery system is shown in Figure 1. The battery cells consist of carbon felt electrodes and a cation exchange membrane which divides the cell into two compartments. One compartment is filled with a solution of V(II) and V(III) ions while the other compartment is filled with a solution of V (IV) and V (V) ions. The vanadium ions are dissolved in sulfuric acid, usually 1 to 2 mol/liter. The electrochemical reactions occurring at each electrode while the battery is being charged are given in equations 1 and 2. The reactions occurring while the battery is being discharged proceed in the opposite direction [10].

$$\text{Negative Half-Cell: } V^{3+} + e^- \leftrightarrow V^{2+} \quad (1)$$

$$\text{Positive Half-Cell: } VO^{2+} + H_2O \leftrightarrow VO_2^{+} + 2H^+ + e^- \quad (2)$$

In the paper of Zhang et al., the installed fixed capital cost (FCI) of the VRB operating at a current density of 40 mA/cm^2 was shown to be a strong function of the cost of the electrolyte (vanadium) and the cost of the ion exchange membrane [1]. The cost of the ion exchange membrane, such as Nafion, is expected to come down in coming years as the production rate increases due to increased use, largely in fuel cells. In this paper the effect of the VRB current density on their estimated FCI, costs of ion exchange membranes and vanadium is examined as a function of the current density. The cost of the ion exchange membrane in this paper is expected to decline in the future at high production rates. The estimation model used in the current paper is taken from that presented by Moore et al. [10]. The effect of current density on the VRB performance is from experimental data. Engineering economic estimation is based on the expected cost of materials and equipment at a certain time. Over the period 2007 to 2011 the cost of vanadium has been as high as $50.78/kg of V ($/12.92/lb of V_2O_5); in the last reported period (2011) the average costs were $26.72/kg of V ($6.80/lb of V_2O_5) [11]. These vanadium costs are for a technical grade; the cost of highly refined vanadium is much higher. Jossen and Sauer's presentation at the First International Renewable Energy Storage Conference includes an estimate of the VRB fixed capital investment (FCI) of $200/kWkh for a 2 kW/30 kWh VRB [12]. Their costs for the membrane were about $35 per m^2, and their costs of V as V_2O_5 were about $11.20/kg ($5.08/lb) ($20.00/kg of V). Both the costs of ion exchange membranes and vanadium appear to be reasonable estimates (especially if the membrane thickness is assumed to be 1 or 2 mills). The purchase cost of V is not indicated in economic papers of Schoenung and Eyer, Schoenung or Oudalov et al. [13-15]. The purchase cost of vanadium in the EPRI (2007) work as V_2O_5 is about $12.49/kg (7.00/lb) ($27.51/kg of V) in 2007; the future purchase cost as V_2O_5 is estimated at about $8.03/kg ($4.50/lb) ($17.69/kg of V) [2]. Moore et al. and Zhang estimated the purchase cost of V as V_2O_5 is about $6.39/kg ($11.41/lb) ($21.13/kg of V) [1,10]. The purchase cost of a 1 mill thick Nafion membrane at large future production rates is projected by James et al. to be $20.73/m^2 ($16.24 – materials, $4.48 – labor) in 2010 and $22.29/m^2 ($17.20 – materials and $5.08 –labor) in 2015 [16]. A 1-mill thick Nafion membrane is N211. A high production rate purchase cost for a thicker membrane such as N117 (7 mill thickness) may be extrapolated from the numbers of James et al. at $118.23 to $145.11/m^2 (2010) or $125.48 to $155.96/m^2 the high and low values being related to how the labor costs are scaled [16]. The purchase cost of membranes is not indicated in papers of Schoenung and Eyer, Schoenung or Oudalov et al. [13-15]. The purchase cost of membranes in the EPRI work is based on 1 to 2 mill thick Nafion is $125 to $350/m^2 for small quantity purchases and $25 to $65 for large quantity purchases in 2007 [2]. Moore et al. and Zhang estimated a purchase cost of $500/m^2 for Nafion N 117 (7 mill thick) for large-scale purchases in 2012 [1,10]. There are three different

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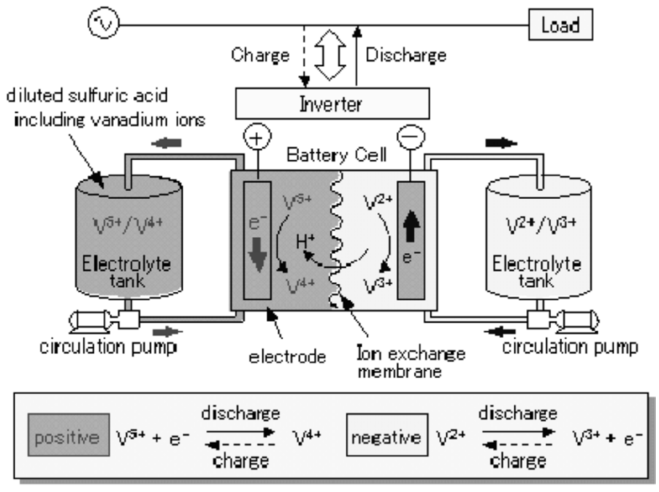

Figure 1: Schematic of a vanadium redox-flow battery [1].

categories of FCI in energy storage – cost that scale proportional to power capacity, costs that scale proportional to energy capacity and fixed costs [10]. Expressed in equation form,

FCI=(Power Capacity × Scaled Capacity Costs)+(Energy Capacity × Scaled Energy Capacity Costs+Fixed Costs) 3

or

FCI=x × ($/kW)+y × ($/kWh) + z 4

Where x, y and z corresponded to the analogous equation above. For example the membrane stacks relate to power capacity (kW) and the quantity of electrolyte relates to energy capacity (kWh). The above FCI is approximately that of a fully installed and operable facility and does not include costs for working capital, contingencies, fees or auxiliary equipment. Several publications have presented FCI associated with a VRB, many of which give the total costs of a VRB per kilowatt and kilowatt-hour and are listed in Table 1 [2,13,14,16]. EPRI's thorough analysis gives both the purchase costs of the components used in manufacturing a VRB, overall costs per kilowatt and kilowatt-hour, as well as important cost considerations. An alternative to the above FCI estimation, based on the purchase costs of the major equipment items, was used by Moore et al. [10] this method is used in this paper to examine the relationship between current density, voltage efficiency, and various costs related to VRBs. This approach is believed to provide a more systematic view of the relation between overall costs and the cost of different components under a range of operating condition. The current density is a measure of the current capacity of the VRB per area of the cell electrode and for the analysis here, the approximate cell membrane area. Increasing the current density has the effect of providing equivalent current, and therefore power, with a smaller cell stack. Unfortunately, increasing the current density lowers the voltage efficiency. The voltage efficiency has a strong affect on the cost associated with the VRB. As the voltage efficiency decreases, the number of cells of the (constant power) stack must increase in order to compensate for the lost power, increasing the costs of the cell stacks. With the increase in the size of the cell stacks comes a greater demand for vanadium electrolyte, increasing the total electrolyte capacity of the battery. This balance between the voltage efficiency and the current density is crucial to determining the size, and therefore the FCI, of the VRB. Understanding the relationship between the voltage efficiency, current density, and FCI provides design parameters for a rudimentary design before the more exhaustive process begins.

Methodology

The methodology used to calculate the manufacturing costs for a VRB, taken from Moore et al. [10], has a number of assumptions, including:

- The costs of the cell stacks are based on the approximate membrane area (more exactly the electrode area) [10]
- The purchase costs of vanadium are based on prices for industrial grade vanadium set by the USGS [11]
- The power rating of the battery is based on the electrical potential at 50% state of charge (SOC) [2]
- The current efficiency is approaching 1 at the open circuit voltage.

In this costing method, the total electrode area needed to meet the VRB's power capacity is calculated from equations 5, 6, and 7: [10]

$$I_S = CD \times A_{Cell}\ s \qquad 5$$

$$N_C = \frac{P}{I_S \times E_0 \times N_S \times \xi_V} \qquad 6$$

$$A_{Total} = N_C \times N_S \times A_{Cell} \qquad 7$$

Where I_S is the current per cell, CD is the current density, A_{Cell} is the electrode area of one cell, N_C is the number of cells in one stack, P is the power rating of the battery, E_0 is the open circuit voltage of the cell, N_S is the number of stacks in the battery, and ξ_V is the voltage efficiency for charging or discharging. Combining the equations and canceling terms gives equation 8:

After cancelling like terms in the numerator and denominator (as indicated), the equation is simplified to

$$A_{Total} = \frac{P}{CD \times E_0 \times \xi_V} \qquad 8$$

The purchase cost of the cell stacks is determined by the total electrode area, so the cost of the cell stacks are proportional the to the total electrode area, giving equation 9.

$$Purchase\ Cost\ of\ Cell\ Stacks \propto \frac{P}{CD \times E_0 \times \xi_V} \qquad 9$$

The important factors for changes in the cost of cell stacks are power, current density, open circuit voltage and voltage efficiency. The open circuit voltage at a state of charge of 50% and the power are specified for any battery application. If the current density is increased while the power of the battery and the open circuit voltage are specified (unchanged), then equation 9 can be written as:

$$Purchase\ Cost\ of\ Cell\ Stacks \propto \frac{1}{CD \times \xi_V} \qquad 10$$

Source	Energy Related Cost	Power Related Cost	Balance of Plant Cost
Schoenung and Eyer [15]	$350 per kWh	$175 per kW	$30 per kW
Schoenung [14]	$600 per kWh	$400 per kW	
Oudalov [13]	$258-$2,322 per kWh		
EPRI (2007 dollars)	$300 per kWh	$2,300 per kW	$250,000
EPRI (2013 dollars)	$210 per kWh	$1250 per kW	$280,00

Table 1: Parameters for Fixed Capital Investment Estimates.

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Equation 10 shows that for a VRB of a constant power capacity, the cost of the cell stacks is inversely proportional to the product of the current density and the efficiency. The mass of the vanadium electrolyte needed for a VRB, and thus the estimated purchase cost of the electrolyte, can be found by calculating the number of electrons oxidized by the VRB during the entire charge or discharge process. Since the oxidation or reduction of vanadium ions involves one electron, the moles of electrons oxidized will equal the moles of vanadium electrolyte that are oxidized. The calculation of moles of vanadium oxidized is shown with equation 11.

$$M_V = \frac{I_S}{F} \times t \times N_C \times N_S \qquad 11$$

Where M_V is the minimum number of moles of vanadium needed for the anolyte or catholyte, F is Faraday's constant, and t is the total time for a charge or discharge cycle. (It has been assumed that the charge and discharge times are equal). Combining equation 11 with equation 6 and canceling like terms gives equation 12.

$$\frac{t \times P}{F \times E \ \times} \qquad 12$$

Since the mass of the vanadium electrolyte needed determines the purchase cost of the electrolyte, equation 12 can be written as:

$$\textit{Purchase Cost of Vanadium Electrolyte} \propto \frac{t \times P}{F \times E_0 \times \xi_V} \qquad 13$$

The time of the charge or discharge and the power are design parameters (set by the application), and Faraday's number is a universal constant, leaving only the efficiency to change as the current density increases. If the current density is changed while the design parameters of the battery are held constant, the cost of the vanadium electrolyte is inversely proportional to the product of the open circuit voltage and the efficiency. The efficiency in this case is defined as:

$$\xi_V \equiv \frac{E_{CD}}{E_0}$$

Where E_{CD} is the electrical potential at a defined current density. Equation 13 for a specific application (specifying the power required and the energy produced per cycle) can then be written as:

$$\textit{Purchase Cost of Vanadium Electrolyte} \propto \frac{E_0}{E_{CD}} \qquad 14$$

Results

The laboratory data shown in Figure 2 was used for the voltage efficiencies at current densities between 0 and 2600 mA/cm^2 [17]. Electrical potential at a current density of 0 mA/cm^2 represents the open circuit voltage, which in this case is 1.64 volts. To get the voltage efficiency for charging or discharging at any current density the potential at that current density is divided by the open circuit voltage. With the voltage efficiencies associated with current density, the capital costs for VRB's at a range of current densities from 50 mA/cm^2, to 2500 mA/cm^2 were calculated using the method described by Moore et al. and the design variables listed in Table 2 [10]. Figure 3 shows the capital costs per kWh associated with the current density of the electrodes. After an initial drop off at very low current densities the rate of the increase in FCI is approximately steady until reaching about 2000 mA/cm^2, where it begins to escalate dramatically. Figure 3 shows the ideal range of current densities to design the battery in order to minimize the capital costs. The design variables for the estimate of the FCI are in Table 2. If the FCI of the VRB's are approximated as the costs of the stacks and the costs of the vanadium electrolyte (where the majority of the capital costs are), equations 10 and 14 can also be used to approximate the ideal range of current densities for the VRB design. Figure 4 shows the purchase costs per kWh of the cell stacks associated with the current density of the cell membranes (electrodes), which can be compared with a plot of Equation 10 in Figure 5. Membrane costs of \$25, \$75, and \$127 per square meter were used to illustrate that the shape of the curve is not affected by the cost of the membrane. In all other FCI calculations the membrane cost used was \$25 per square meter. Since the majority of the purchase costs for the cells stacks are associated with the membrane, [10] the trend is illustrated again in Figure 6 which shows the total membrane area required for the VRB vs the current density. By comparing the minimal FCI in Figure 4 to the total capital cost (FCI) of Figure 3, it may be noted that the cost

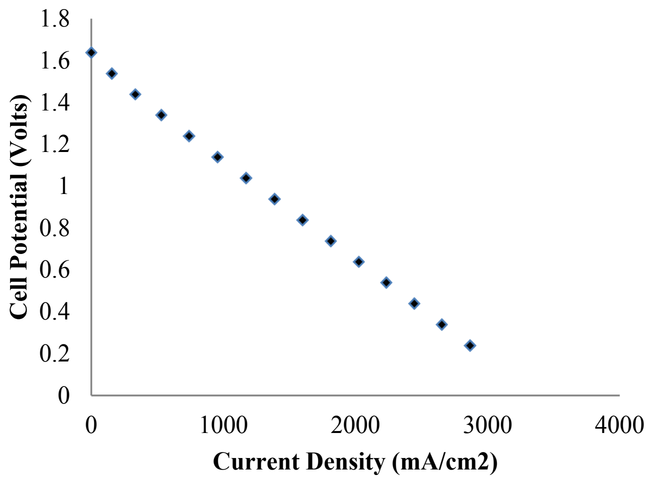

Figure 2: Cell Potential vs Current Density for a Laboratory VRB (ion exchange membrane=Nafion N 211; temperature=30°C; and V and H_2SO_4 concentration are 1.7 and 3.3 mol/L).

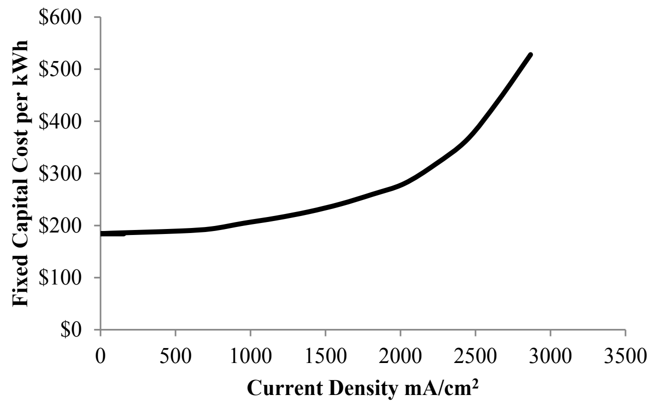

Figure 3: Fixed Capital Investment per kWh vs Current Density.

Power Capacity	1000 kW
Charge Time	12 hr
Electrical Potential of 1 Cell	1.639 Volts
Number of Cell Stacks in Batter	20
Cost of Vanadium	25.13 \$/kg
Cost of Ion Exchange Membrane	25 \$/m^2
Cost of Current Collectors	51 \$/m^2
Cost of Carbon Felt	20 \$/m^2

Table 2: Design Variables for Estimate of VRB Fixed Capital Investment.

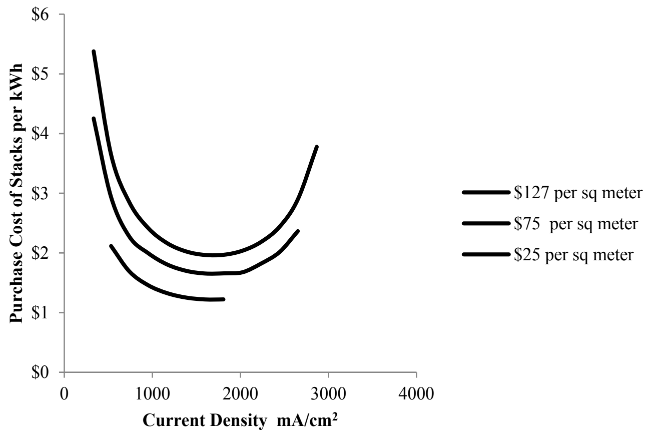

Figure 4: Purchase Cost of Stacks per kW/hr vs Current Density.

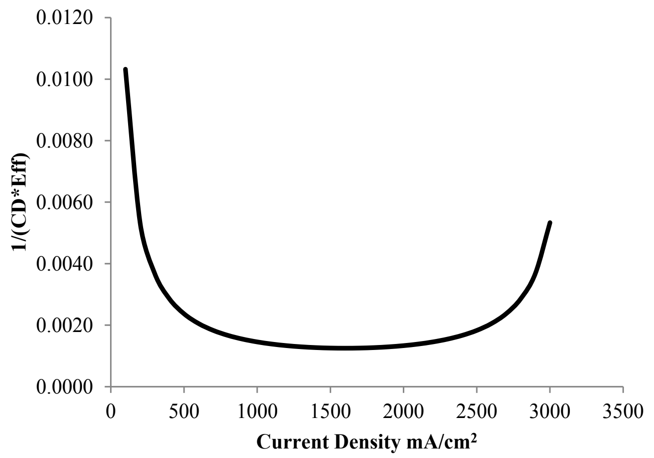

Figure 5: 1/(CD*ξ_v) vs Current Density.

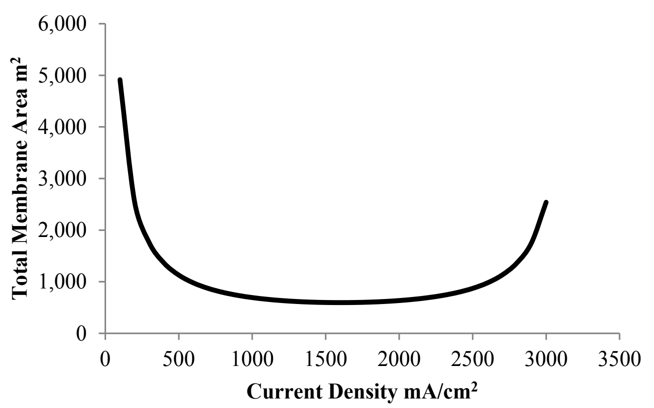

Figure 6: Total Membrane Area vs Current Density.

of stacks (including membranes) has become only a small fraction of the FCI. Figure 7 shows the purchase costs per kWh of the vanadium electrolyte associated with the current density of the electrodes, and Figure 8 shows the amount of vanadium electrolyte required vs current density. Since the vanadium costs are on a per mass basis, these curves show a similar shape and trend, a slow increase in vanadium required/cost, until the current density approaches 2000 mA/cm^2 where the rise in vanadium required/cost becomes much more pronounced. The shape and trend of these curves appears to be well represented in Figure 9, a plot based on equation 14 at varying current density. The similarities between Figures 7-9 suggest that the ideal range of current density for minimizing the costs of the vanadium can be easily predicted with equation 14.

Conclusion

The range of current densities used for battery operations continues to expand due to developments in research [17]. Considering that the majority of the FCI of the VRB are in the purchase costs of the cell stacks and vanadium, [10] it is useful to find the optimum range of the current density to minimize these costs. The purchase costs of the stacks and the vanadium, and how they are affected by changes in current density can be examined quickly and easily. Using new current density information from a different system (membrane, electrodes, and solution, [17] the simple method presented here can predict the trends in the FCI of the cell stacks and vanadium over a range of current densities and show the optimal range of current densities. This simplified perspective provides a quick and sound preliminary basis for the selection of specific operating conditions (current density) for any intended application. In addition, this simplified perspective is valid regardless of the scale of the battery unless the scale should become large enough to affect the cost of vanadium or cell membranes.

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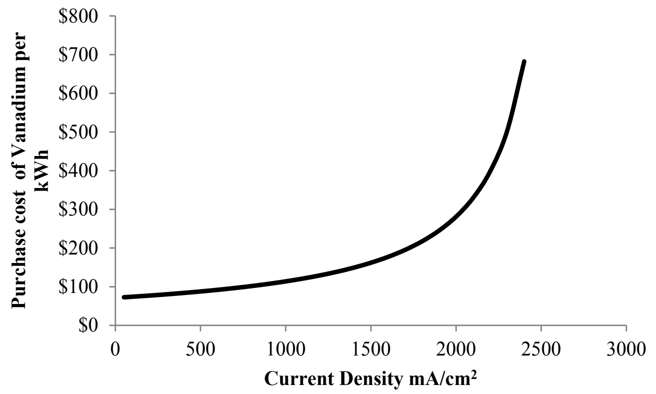

Figure 7: Purchase Cost of Vanadium per kWh vs Current Density.

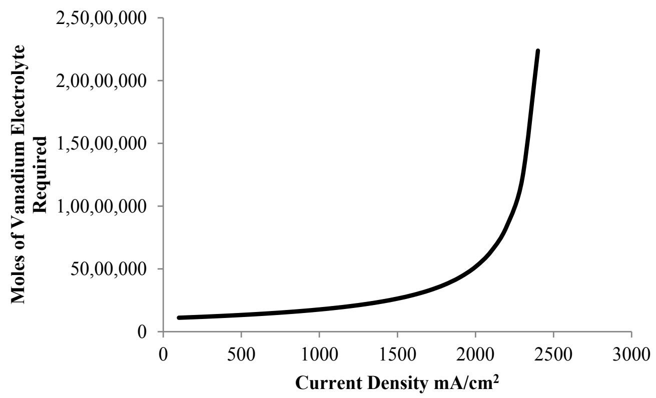

Figure 8: Moles of Vanadium Required vs Current Density.

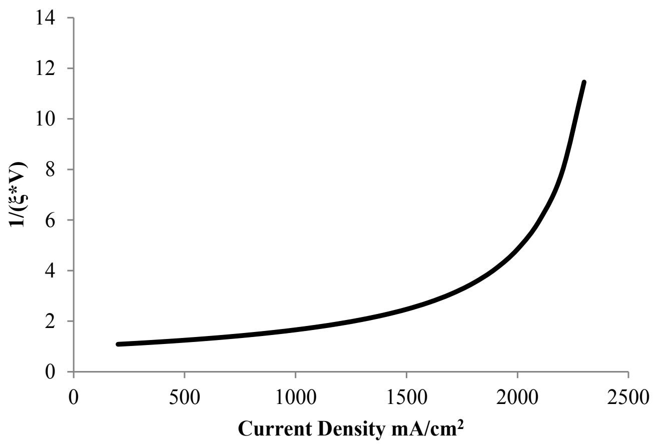

Figure 9: 1/(ξ*V) vs Current Density.

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