

# **The Optimization of a Quinone Battery for Large-Scale Energy Storage**

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**Abstract:**

With the rise in the use of intermittent renewable energy sources, such as solar and wind power, it is important to create an electrical system that can optimize their potential. This system requires an external means to store unused energy and release it on demand, such as a battery. Current batteries are not optimal because of their high operating costs, toxic materials and/or explosive components. Researchers at the University of Southern California are developing a liquid redox flow battery that relies on organic molecules for energy storage and transfer. These molecules are initially bonded to sodium ions in the stock solution. In earlier tests the amount of sodium seemed to pose a problem to the efficiency of the liquid battery and subsequently was removed and replaced with hydrogen ions. Removal of sodium ions was believed to reduce resistance across the cell. In this study these claims were tested in a liquid redox flow battery using sulfuric acid electrolyte with a Nafion® 117 membrane with sodium sulfate as the source for sodium ions. The evaluated performance resulted in a non-linear trend with a decrease in resistance for up to 5000 part per million of sodium followed by an increase in resistance for sodium concentrations over 5000 parts per million. The results from this study indicated that the resistance effects of the addition of sodium ions inside of a liquid redox flow battery justify the addition of hydrogen ions in place of sodium ions.

<b><u>Section</u></b>	<b>Table of Contents</b>	<b><u>Page</u></b>
Introduction	...	4
Materials and Methods	...	8
Results	...	10
Conclusion and Discussion	...	11
References	...	12
Collection of Graphs	...	14

### **List of Figures and Tables**

Figure 1	...	6
Figure 2	...	8
Figure 3	...	10
List of Supplementary Graphs	...	14

**Introduction:**

The increasing use of alternative energy sources has created a demand for long term energy storage due to their intermittent nature. These sources include solar and wind energy which do not produce energy during times without sunlight or wind. This problem could be solved by using large-scale batteries for the storage of electrical energy during the production hours of renewable energy sources and the release of this energy when needed.

A battery functions through the oxidation and reduction reactions that occur at the opposite ends of the cell. The negative end, called the anode, reacts with an electrolyte in a process called oxidation. During this process, electrons are released onto the anode, and positive ions are deposited into an electrolyte solution. At the cathode, the positive ions are reduced or and are deposited on the cathode surface. A connection from the anode to the cathode can convert this stored chemical energy into electric energy. In a galvanic state battery, two electrolytic solutions are connected by a salt bridge that releases ions towards each solution with negative ions traveling to the anode, and positive ions traveling to the cathode. This reaction is called the galvanic state of a battery and is thermodynamically favorable due to the difference in reduction potential of the anode and cathode. A rechargeable battery will experience an electrolytic reaction which is simply the opposite of a galvanic reaction and is not thermodynamically favored which is why electricity is required for recharging.

Today's common batteries include lithium ion, vanadium, and lead-acid (Yang, 2014). These types of batteries all contain metal, which can be toxic. These metal-based batteries can suffer many flaws that cause the battery to short-circuit, explode or overheat (Yang, 2014). Lithium-ion batteries, for example, can experience the growth of dendrites on the electrodes which can short-circuit the battery. Most metal batteries function at high temperatures which can

lead to thermal runaway if not under temperature control, which can be costly (Poullikkas, 2013). An effective solution to the problems associated with current batteries lies within an organic battery. Not only would this eliminate the need for harmful elements, but the common components inside such a battery would allow it to be cost effective, unlike the expensive metals used for lithium-ion and vanadium batteries. Organic batteries would also eliminate the need for expensive cooling systems that are needed for metal batteries as they do not generate higher temperatures for it to function (Szondy, 2014). The lower performance temperatures would also reduce the risk of thermal runaway, effectively making batteries safer and more reliable for grid-scale applications. Organic materials are also generally non-toxic and easily procured and synthesized, unlike many of the metals mentioned

The type of organic battery that is being developed at the University of Southern California (USC) use a molecule known as a quinone as the basis for their redox active material. Quinones are defined as a molecule with one or more benzene rings with two carbonyl groups, as shown in Figure 1. Quinones are a model molecule for the production of organic batteries as they experience fast, two-proton, two-electron oxidation and reduction at relatively low temperatures (Morton, 1965). Quinones are relatively easy to obtain, being that they are the by-product of the hydrogen peroxide industry. Additionally they are found readily in nature. Almost every living organism contains some form of a quinone, as they are also known as the essential nutrient of vitamin K (Morton, 1965). Quinones could be extremely beneficial to the world of batteries as their easy production mode from hydrogen peroxide and their relatively easy extraction method from plants and organic matter makes these molecules much more economically efficient than current metal batteries.

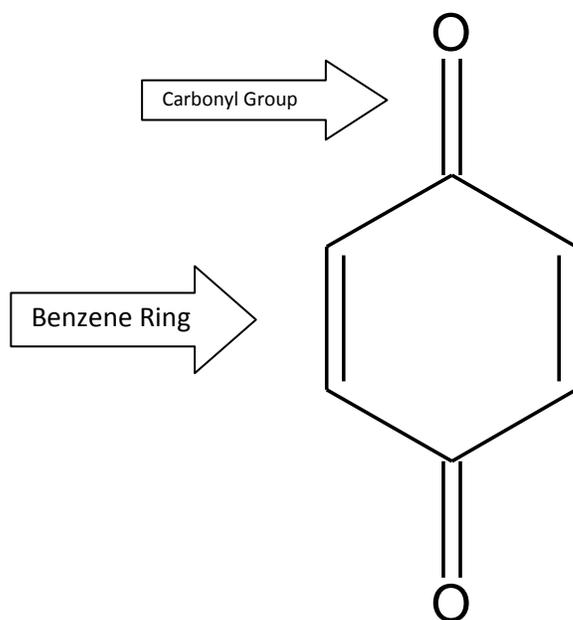


Figure 1: Molecular structure of a quinone with carbonyl group substituents

In this battery hydrogen atoms are transferred across a membrane from the two electrolytes to allow the transfer of electrons to generate electricity (Yang, 2014). This transaction of hydrogen ions does not generate enough heat energy to cause damaging variations in temperature; this is because the electrolyte remains in the liquid state with water as the main

solvent. Each quinone is in an aqueous environment and performs at relatively low temperatures (Nawar, 2013). There are an estimated 1710 different types of quinones based on benzoquinone, naphthoquinone, and anthraquinone with added substituents (Er, 2014). Currently, anthraquinone is the main quinone for use as the anode while benzoquinone is the quinone most used for the cathode (Er, 2014; Nawar, 2013; Yang, 2014). The battery itself is comprised of two end-plates, two holding chambers for the electrolyte compounds, two carbon electrodes, and a polymer proton exchange membrane (Nawar, 2013; Yang, 2014).

This study follows the research conducted at the University of Southern California by Yang et al. in 2014. Yang established the protocol for the fabrication of a reaction cell and subsequent materials such as storage tanks, peristaltic pumps, potentiostats, and chemicals. During initial testing Yang speculated that an increase in resistance may be caused by the high concentration of sodium ions within the battery as the quinone form that was being utilized in the battery was the sodium salt form. The high resistance in turn, reduces the efficiency of the battery. In these tests, we observed the resistance as a function of sodium concentration in a flow style battery. The frequency in the cell is defined as the voltage applied to the battery, with high voltages measuring overall cell, internal cell resistance and lower voltages measuring transfer resistance. Resistance at high frequencies was focused on for their representation of overall resistance. This study focused on the effect of sodium ions on mass transport resistance and membrane resistance inside the battery. The objective was to determine the relationship between sodium levels and resistance, so as to optimize conditions within the battery for maximum efficiency.

## Materials and Methods:

Materials included in this study were based on the organic-aqueous redox flow battery from the Naravan Group at the University of Southern California illustrated in Figure 2 (Yang, 2014). The battery included two storage tanks filled with one molar sulfuric acid on each side along with a power cell center that contains two chambers for the electrolyte to flow through. The power cell also contained two carbon felt electrodes that were separated by a Nafion® 117 polymer membrane for proton transfer.

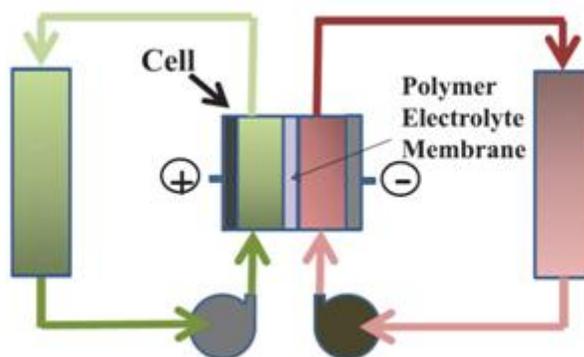


Figure 2. Flow battery diagram (Yang, 2014)

Experiments progressed by three levels. The first level began with the addition of sodium sulfate to a single tank at 100ppm sodium sulfate with a five minute delay in impedance tests until 5000ppm was achieved. The second level was the addition of 200ppm of sodium sulfate to the same tank until 10,000ppm was achieved with a 10 minutes delay in impedance tests. The third level was the addition of 1000ppm of sodium sulfate to the same tank until 20,000ppm was achieved with 10 minute delay in impedance tests. The control for these experiments was the data collected from the impedance test of one molar sulfuric acid alone. Each measurement was taken by a Princeton Applied Sciences potentiostat device which calculated and displayed the

impedance measurements. These devices were similar to those used in the initial quinone battery experiments done by Yang et al. in 2014. For each test, the frequency was in a range of 10,000 hertz to 0.1 hertz.

The variables included the dependant variable of resistance measured in ohms ( $Z_{re}$ ) and the independent variables of sodium ion concentration, measured in parts per million, and frequency, measured in hertz. The data extracted from the measurements were then put into an excel spreadsheet and converted into graphical data with corresponding least squares regression lines along with a coefficient of determination. All data for frequencies of base 10 were graphed four ways; the first was a standard graph, the second was the log of only the dependant variable, the third was the log of only the independent variable, and the fourth was the log of both variables.

**Results:**

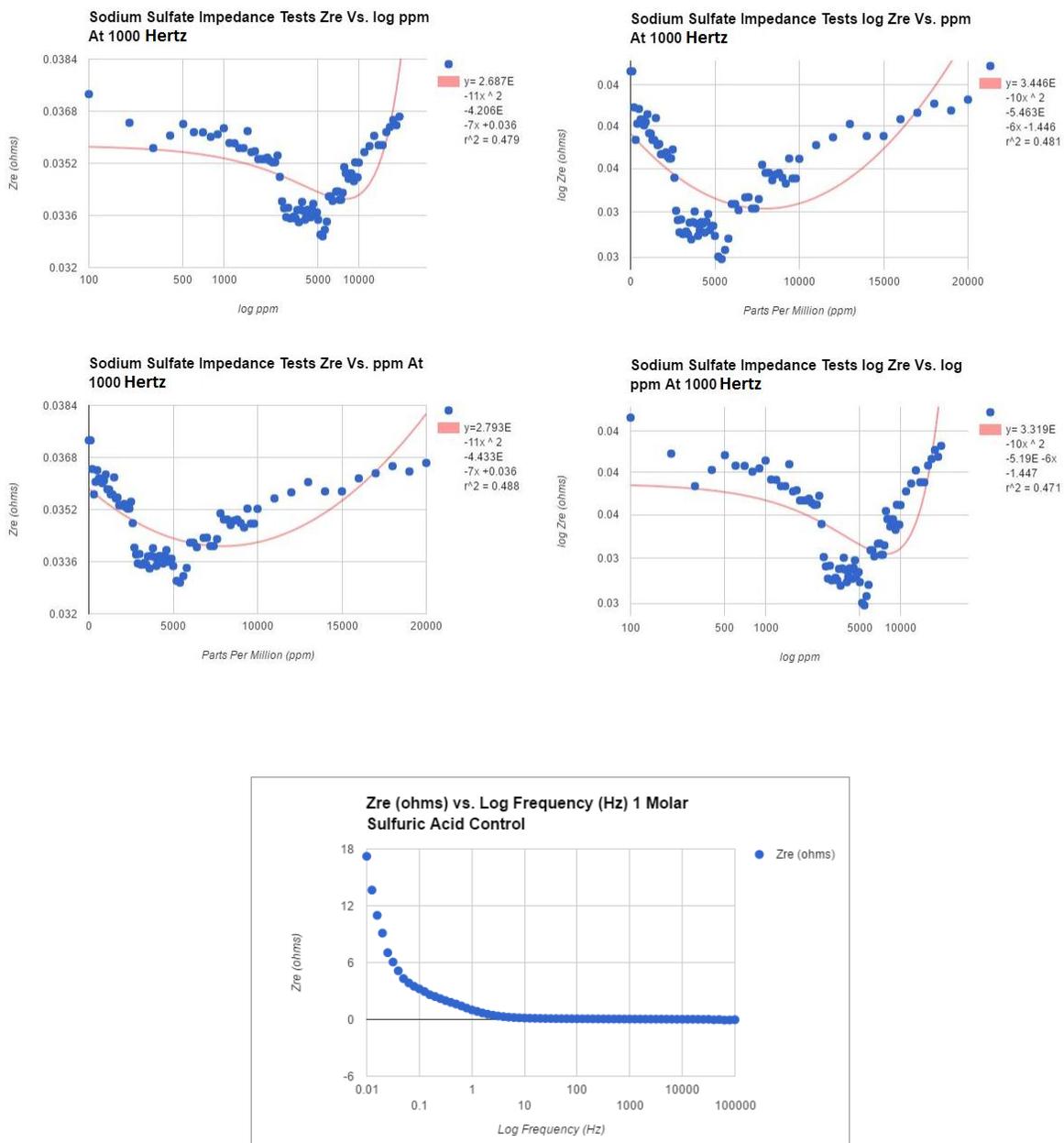


Figure 3: Battery Resistance as a Function of Sodium Sulfate Concentration shown with correlation coefficient (all graphs are located after references)

In Figure 3, each data graph showed differing values of resistance, with a decrease in resistance over a span of up to 5000ppm of sodium ions. Past 5000ppm the resistance of the battery increased with the addition of sodium in each test until the final addition of a total of 20,000ppm of sodium ions. Each graph displays the data collected from all tests when measured at a frequency of 1000 Hertz. These graphs have normal variables with logs of the dependant, independent, the log of both variables, and a graph of the control in the respective graphs to better visualize the correlations between each aspect. The correlation coefficient showed us how each set of data correlated to a least squares regression line and how well the line fit the data.

### **Conclusion and Discussion:**

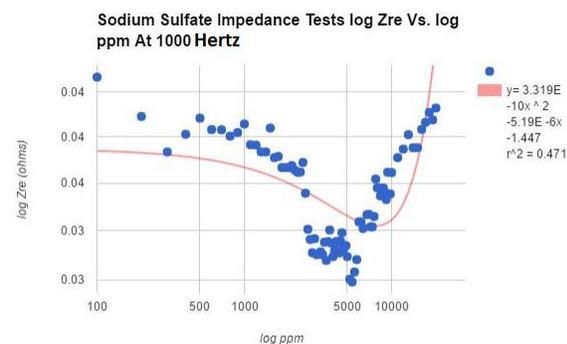
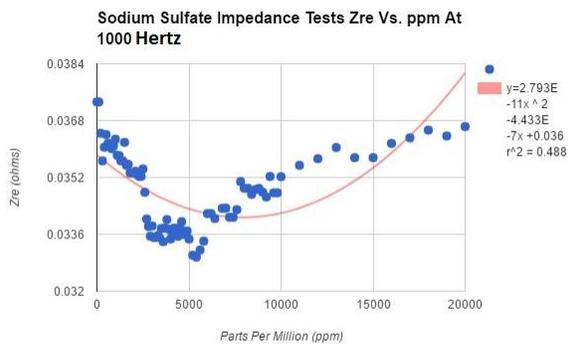
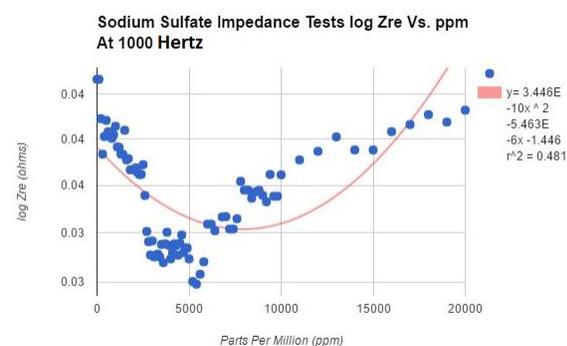
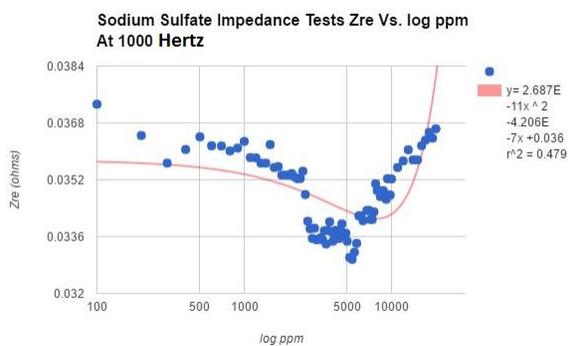
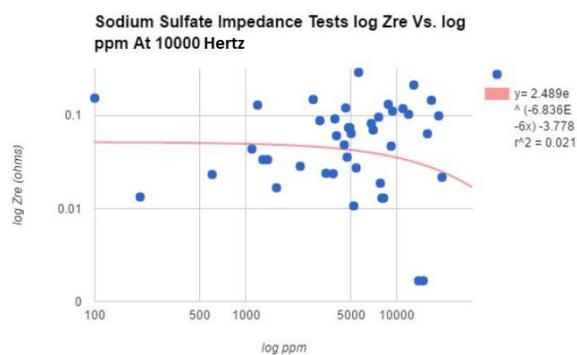
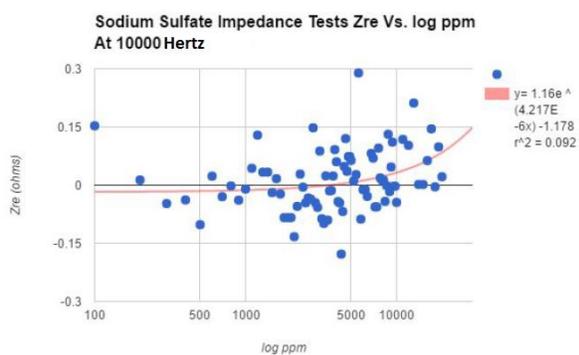
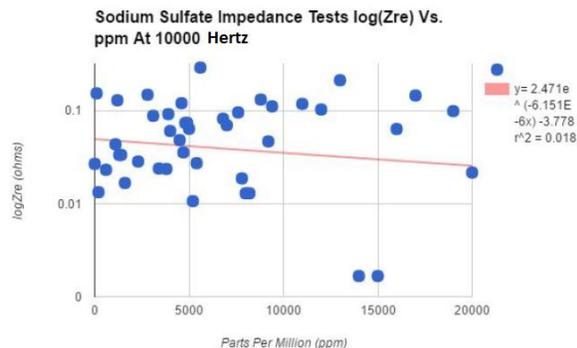
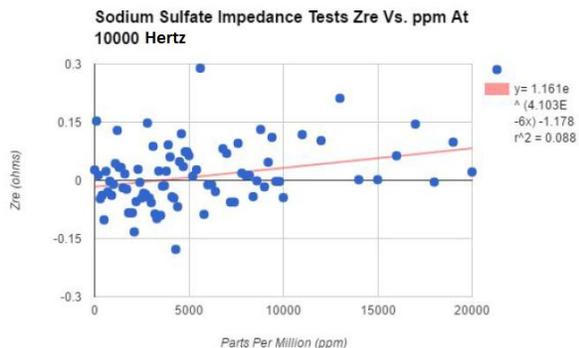
This study showed that the addition of sodium ions to the redox flow battery inhibited the performance of the cell, as it was determined that the addition of sodium ions increased the resistance in the cell. This confirms that the actions taken to remove sodium ions from electrolytes and to replace them with hydrogen ions were valid and essential. In order to promote further research, more studies must be conducted on each of the variables that may affect the battery performance including the temperature, flow rate, and pH of the solvent to further the understanding and reparations of a quinone based battery.

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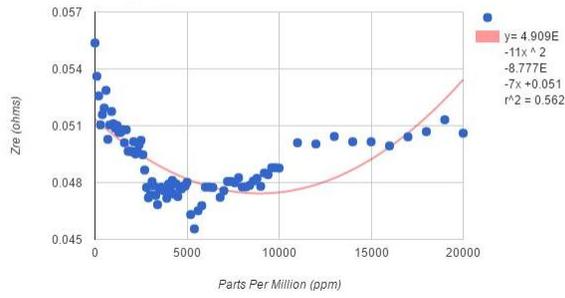
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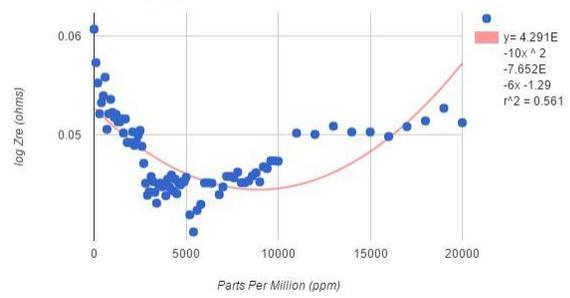
## All Sodium Test Graphs At Varying Frequencies



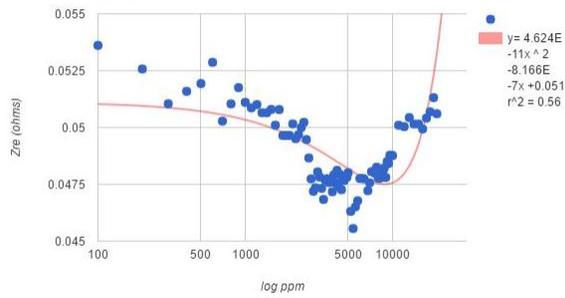
Sodium Sulfate Impedance Tests Zre Vs. ppm At 100 Hertz



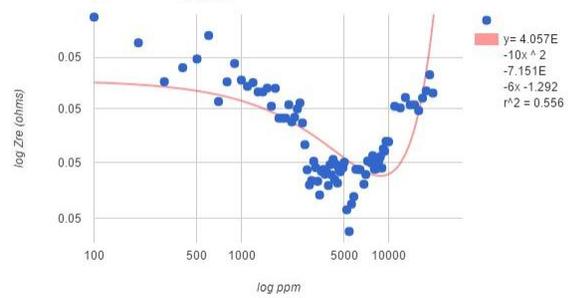
Sodium Sulfate Impedance Tests log Zre Vs. ppm At 100 Hertz



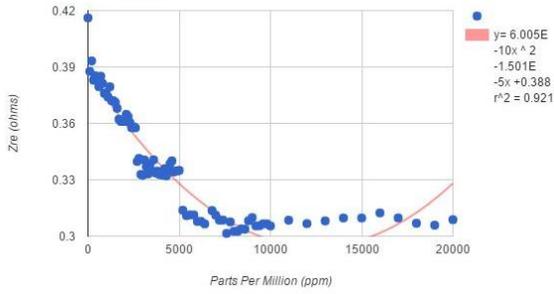
Sodium Sulfate Impedance Tests Zre Vs. log ppm At 100 Hertz



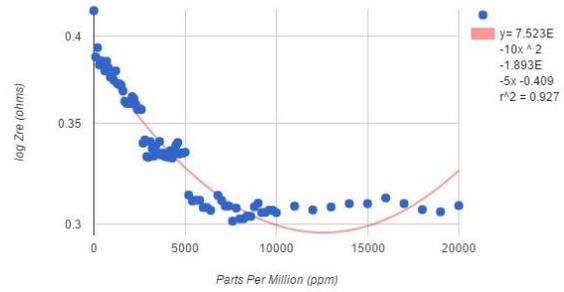
Sodium Sulfate Impedance Tests log Zre Vs. log ppm At 100 Hertz



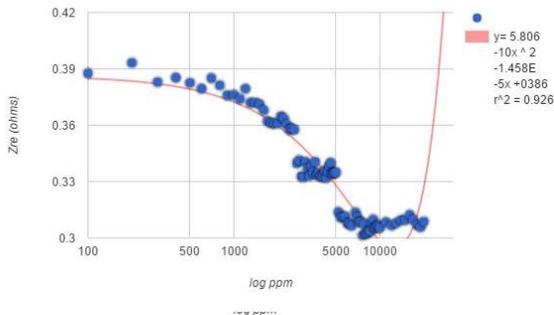
Sodium Sulfate Impedance Tests Zre Vs. ppm At 1 Hertz



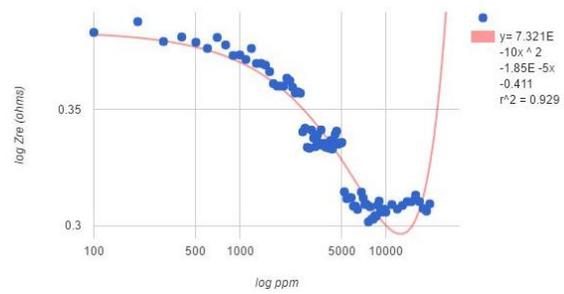
Sodium Sulfate Impedance Tests log Zre Vs. ppm At 1 Hertz



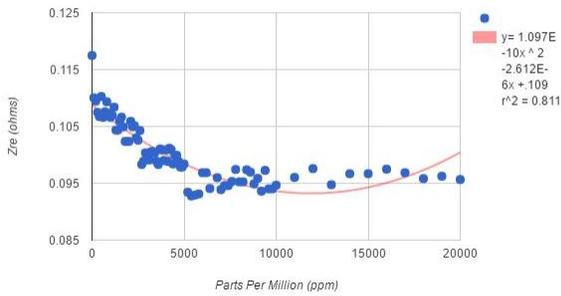
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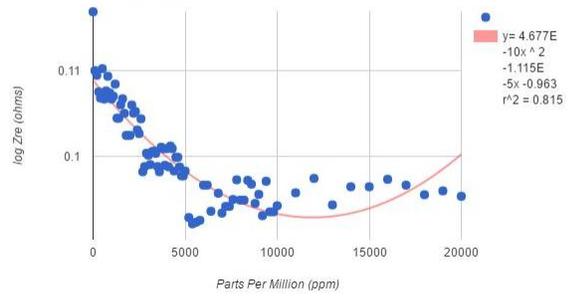
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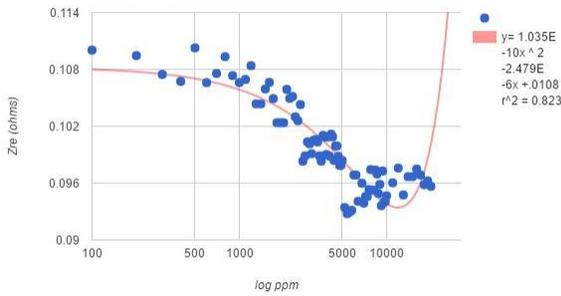
Sodium Sulfate Impedance Tests Zre Vs. ppm At 10 Hertz



Sodium Sulfate Impedance Tests log Zre Vs. ppm At 10 Hertz



Sodium Sulfate Impedance Tests Zre Vs. log ppm At 10 Hertz



Sodium Sulfate Impedance Tests log Zre Vs. log ppm At 10 Hertz

