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# Controlled release of corrosion inhibitors: Zinc and Magnesium containing Sodium Chromate

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# **Controlled release of corrosion inhibitors: Zinc and Magnesium containing Sodium Chromate**

4250: 497-003 Honors Project

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## Executive Summary

Corrosion can be combated by multiple methods, where the primary purpose is to minimize degradation of metal surfaces. Corrosion inhibitors are one of the most effective methods of corrosion protection. Inhibitors are substances that minimize corrosion in aggressive environments, with only a low concentration required. The inhibitors are chemically adsorbed on the surface of the metal and a protective thin film is formed <sup>[5]</sup>. The mechanism of the inhibitors could be described as anodic, cathodic, or a mix of the two. Anodic inhibitors, also known as passivation inhibitors, alter an anode reaction. Corrosion potential of the metal is shifted to more positive values. Cathodic corrosion inhibitors prevent the cathodic reactions of a metal. The film reduces the diffusion restriction of reducible species.

Inhibitors can dissolve quickly in intense environments and there are certain situations where the inhibitor addition is not practical. It would be ideal to release the inhibitor to the material when needed. Inhibitor would be released according to the environment and the corrosion behavior of the metal. Releasing the inhibitor as needed results in corrosion mitigation as well as self-curing <sup>[11]</sup>. An epoxy coating with the inhibitor could allow the inhibitor to release at a specific pH. One of the important parts to consider is that the correct amount of the inhibitor needs to be released. An insufficient amount of the inhibitor could affect the film protection. If the metal is not completely covered, this could cause localized corrosion <sup>[5]</sup>. The overall goal is to have continuous corrosion protection.

The corrosion inhibitors would open at a specific pH, initiated by a polymer. Sodium chromate is a strong inhibitor and is to be used for testing. This project is built upon previous research on inhibitor release. Previous studies were performed on the effect of aluminum powder on sodium chromate. Aluminum is synthesized with sodium chromate. Varying amounts of the powder was mixed with sodium chromate. Corrosion tests were performed on the aluminum with sodium chromate. The same studies are performed with zinc and magnesium.

Sodium chromate will be mixed with both magnesium and zinc at varying percentages using ball milling. A mixture of sodium chromate and zinc is to be tested. One sample of 1 wt. % of zinc with sodium chromate is prepared, as well as a sample of 5 wt. % of zinc. Both samples containing sodium chromate are compared to pure zinc. Samples of the same weight percent with magnesium are made and are compared to pure magnesium. Corrosion behavior is observed from different tests. The hypothesis is epoxy allows for the inhibitors to be released in controlled doses.

Four tests were run in sequence on each sample using EC-Lab software. The first test run is Evs. Time (EVT), which measures the corrosion potential versus time. Potential Electrochemical Impedance

Spectroscopy (PEIS) performs impedance measurements in potentiostatic mode. A second EVT test is run following the PEIS technique. The fourth and final test run is upward Potentiodynamic polarization (PDP) scan using Cyclic Potentiodynamic Polarization (CPP). Three-electrode electrochemical cell was used to perform corrosion tests. Platinum was used as a counter electrode and saturated calomel electrodes were used as reference electrodes. Graphs of the same test were compared with varying amounts of sodium chromate. The purpose of these tests are to run a preliminary analysis on the corrosion behavior with the added sodium chromate. After conducting trials, a clear increase in performance against corrosion is shown with higher concentrations of sodium chromate.

## Background

Corrosion is the deterioration and destruction of a material because of its reaction with the environment. All environments are corrosive. Environments with higher temperatures and higher pressures have more severe corrosion conditions [Fontana 4]. The primary cause for all corrosion is the lowering of Gibbs energy of a system. The main purpose of corrosion study is to protect materials from corrosion <sup>[12]</sup>. Environmental considerations and protection of product quality are the main objects for research in corrosion <sup>[12]</sup>. The surface of every metal is covered with anodic and cathodic sites. The sites comes from compositional differences, microstructural heterogeneities, surface irregularities, and stress/strain conditions. Corrosion is a result of a difference in electrical potential, which allows current to pass through, resulting in a reaction at the anodic and cathodic sites.

An inhibitor is a substance that decreases the corrosion rate when added in small concentrations to the environment <sup>[10]</sup>. Inhibitors are classified according to their mechanism and composition. Adsorption-type inhibitors are organic compounds which adsorb on the metal surface. The inhibitors affect both the anodic and cathodic processes. The selection of an inhibitor is done based on its solubility and its disposability for the specific environment <sup>[12]</sup>. There are criteria which must be satisfied for an inhibitor to be used in a system <sup>[12]</sup>.

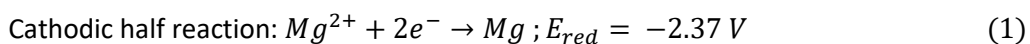
- 1) Good corrosion protection at low concentration of the inhibitor.
- 2) Protection of all exposed materials.
- 3) Efficient in extreme operating conditions.
- 4) No significant change in corrosion rate at an over or under dosage of the inhibitor.

Most corrosion inhibitors diminish contact with aggressive environments by forming a protective film on the metal surface <sup>[12]</sup>. There are multiple factors for the performance of a corrosion inhibitor. A few of these factors can be studied through preliminary analysis. The electrostatic force of attraction of the

inhibitor and the electric charge on the metal can affect the adsorption of the inhibitor<sup>[12]</sup>. The inhibitor's functional group and structure can have an effect on the bonding to metal surfaces. The inhibitor's interaction with water molecules can result in a displacement reaction. Adsorption of the inhibitor molecules involve the removal of adsorbed water molecules from the metal's surface<sup>[12]</sup>. Another factor considered is the reaction of inhibitors. The corrosion inhibitor may react resulting in secondary inhibition<sup>[12]</sup>.

There are limitations to using inhibitors as corrosion prevention. One of the issues is that inhibitors may not be applied to specific corrosive systems because they contaminate the environment<sup>[10]</sup>. Certain inhibitors are toxic and cannot be used in products that come in contact with humans. It is important that inhibitors maintain the performance of the system while also protecting metal components from corrosive action<sup>[12]</sup>.

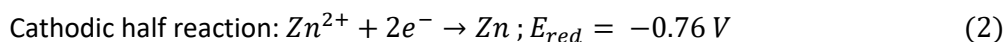
Magnesium is one of the lightest commercial metals, due to its low density and capability of forming mechanically resistant alloys<sup>[12]</sup>. Magnesium has a density of 1.74g/cm<sup>3</sup>, only two-thirds of aluminum<sup>[16]</sup>. It has many applications where its light weight is important. Magnesium components are widely used in agriculture and industry. Magnesium joins together with most non-metals and almost every acid. Magnesium is used as a catalyst and promotes organic reactions of condensation, reduction, and addition<sup>[16]</sup>. The cathodic half reaction of magnesium has a negative standard electrode potential of -2.37 V, relative to the Standard Hydrogen Electrode (SHE)<sup>[13]</sup>.



Magnesium has a low corrosion resistance, especially in aqueous solutions. Magnesium weakens and loses its functionality as it gets corroded. Magnesium is not a passive metal and corrosion occurs at its free corrosion potential. Research has shown that intergranular corrosion can occur in magnesium alloys<sup>[22]</sup>. Previous studies were conducted with observing the corrosion rate with an increase in sodium chloride concentration. It was observed that the corrosion rate of magnesium steadily increases with increasing NaCl concentration<sup>[1]</sup>. The corrosion rate decreases as pH increases. Studies have also shown that anodic branches are more affected from polarization in comparison to cathodic branches.

Zinc is a reactive metal that will combine with oxygen and other non-metals. Zinc will react with dilute acids to release hydrogen. The density of zinc is 7.11 g/cm<sup>3</sup> at room temperature. Its main use is for galvanizing iron, as more than 50% of metallic zinc goes into galvanizing steel<sup>[16]</sup>. Zinc occurs naturally and

can be added during industrial activities, such as mining or coal processing. The cathodic half reaction of magnesium has a negative standard electrode potential of -0.76 V, relative to the SHE <sup>[7]</sup>.



Zinc is susceptible to atmospheric corrosion, resulting in self-corrosion while serving as a coating for steel <sup>[21]</sup>. Zinc has a higher corrosion resistance than steel in most natural atmospheres. Zinc forms insoluble carbonate films, resulting in a higher degree of resistance [16]. Polarization curves of zinc show that its corrosion is significant under cathodic control. At higher pH, a slight passive behavior is observed. Surface oxides formed over zinc do not serve as an effective corrosion protection barrier. At pH between 1 and 3, there is well-defined passivity. Zinc corrosion proceeds through cathodic control. It was observed that the chemical kinetics of a hydrogen evolution reaction controls the overall corrosion rate of zinc <sup>[21]</sup>. Coatings of metallic zinc are one of the most economically efficient means of corrosion protection <sup>[4]</sup>.

Sodium chromate is an inorganic compound as well as a passivating inhibitor. It is able to cause a large anodic shift of corrosion potential. The anodic shift forces a metallic surface in the passivating range. Sodium chromate is an oxidizing anion which passivates steel in the absence of oxygen <sup>[20]</sup>. Previous studies have shown that sodium chromate significantly lowers corrosion rates at concentrations of 1.0 and 1.5 M, while there is no significant change in rates at 0.5 M. Further investigation was completed with examining the inhibition efficiency of sodium chromate, based on concentration over time. The data further demonstrated that sodium chromate only becomes significantly efficient at 1.0 M concentration and beyond <sup>[20]</sup>. It is expected for 5% sodium chromate to have a greater increase in corrosion performance in comparison to 1% sodium chromate.

## Introduction

Corrosion is an electrochemical process where a difference in electrical potential develops between two metals <sup>[12]</sup>. A difference in potential may also occur between different parts of a single metal. The voltage can be measured when a metal is electrically connected to a standard electrode. The voltage can be expressed as either positive or negative, as the electrical potential of the metal may be more or less compared to the standard electrode. The potential difference allows current to pass through the metal, causing a reaction at both the anodic and cathodic sites.

The first test in the process is the EVT, which plots  $E_{WE}$  versus time.  $E_{WE}$  is the stationary potential measurement for corrosion potential, measured in voltage. Current (I) is measured in mA <sup>[15]</sup>. The reference electrode, saturated calomel electrode (SCE) is based on the reaction between elemental mercury and mercury (I) chloride <sup>[19]</sup>. The potential of the electrode remains constant as the HCl solution used in the experiment partially evaporates. The disadvantage of using SCE is that the solubility of the solution is sensitive to changes in temperature. Any disturbances to the system can result in changes to the potential.

Electrochemical Impedance Spectroscopy (EIS) is used to evaluate electrochemical properties of materials and their interfaces with electrodes. EIS can be used to estimate physical parameters such as surface roughness and porosity of an electrode <sup>[18]</sup>. The PEIS experiment performs impedance measurements into potentiostatic mode. PEIS is a technique where the total coulombic charges of electricity required to complete an electrochemical reaction is determined, while the potential of the working electrode is held at a constant value <sup>[20]</sup>. Ohm's law is used to determine resistance. The relationship between voltage and current is a differential equation. R is used to denote resistance in the simpler form. Complex impedances which may contain capacitance or inductance are denoted by Z. Z is a complex term which has both a real and imaginary part. The relationship between PEIS graphs the real impedance versus the imaginary impedance, measured in Ohms.

The second EVT test runs the exact same method as the initial EVT test. The purpose of the second test is to observe the potential after the PEIS technique runs an electrochemical reaction. The potential of the second EVT may also be compared to the initial to further analyze the PEIS technique.

The fourth and final test is the Cyclic Potentiodynamic Polarization (CPP). CPP test applies a forward voltage with a current limit (ip) on the measured current. When the measured current reaches the current limit, the forward voltage is stopped, and a reverse voltage sweep is applied. The plot of I versus  $E_{WE}$  can determine values such as corrosion potential, corrosion current, and pitting potential. Localized corrosion ( $E_{pit}$ ) causes the increase in anodic current density. The pitting potential coincides with corrosion potential, where there is an oxide film on the material surface before polarization <sup>[9]</sup>. Corrosion inhibitors are expected to increase the pitting potential. The difference between pitting potential and corrosion potential is the important parameter when evaluating a material's corrosion resistance <sup>[9]</sup>.

The underlining purpose of this study is to be able to control the release of inhibitors. Encapsulating corrosion inhibitors inside ceramic particle will provide a sustained release of inhibitors <sup>[3]</sup>. The corrosion inhibitor is released whenever water penetrates the coating due to condensation, immersion, or chemical damage. The controlled release is used for quick action on exposed surfaces or



for extension of coating life <sup>[3]</sup>. The material also would be able to withstand an extrusion step with premature release of the inhibitor <sup>[3]</sup>. The goal is to provide a quick release when corrosion occurs, or a slow release to extend the life of the coating by giving corrosion prevention over a longer lifetime <sup>[3]</sup>.

## Materials and methods

Six samples of zinc and magnesium powder were prepared with varying amounts of sodium chromate. The pure samples remained unmilled while the mixed samples were run through a high- energy ball mill for 100 hours.

- 1) Pure Zn unmilled.
- 2) Zn- 1 wt% Na<sub>2</sub>CrO<sub>4</sub>. 100h milled.
- 3) Zn- 5 wt% Na<sub>2</sub>CrO<sub>4</sub>. 100h milled.
- 4) Pure Mg unmilled.
- 5) Mg- 1 wt% Na<sub>2</sub>CrO<sub>4</sub>. 100h milled.
- 6) Mg- 5 wt% Na<sub>2</sub>CrO<sub>4</sub>. 100h milled.

A small volume of the powder, between 0.1 and 0.3 cm<sup>3</sup>, was compressed into a circular sample. The effect of compression on a powder can vary based on the properties of the powder. Surface characteristics, frictional properties, and particle size all influence the compression of the powder. <sup>[14]</sup>. There is a great number of particle contacts per unit volume for smaller particles. For smaller particles, there is also a greater likelihood of fragile arching systems being developed <sup>[14]</sup>. This would result in either loosely compacted powder or particle deformation. The powders were analyzed under a microscope to predict particle rearrangement in their packing state.

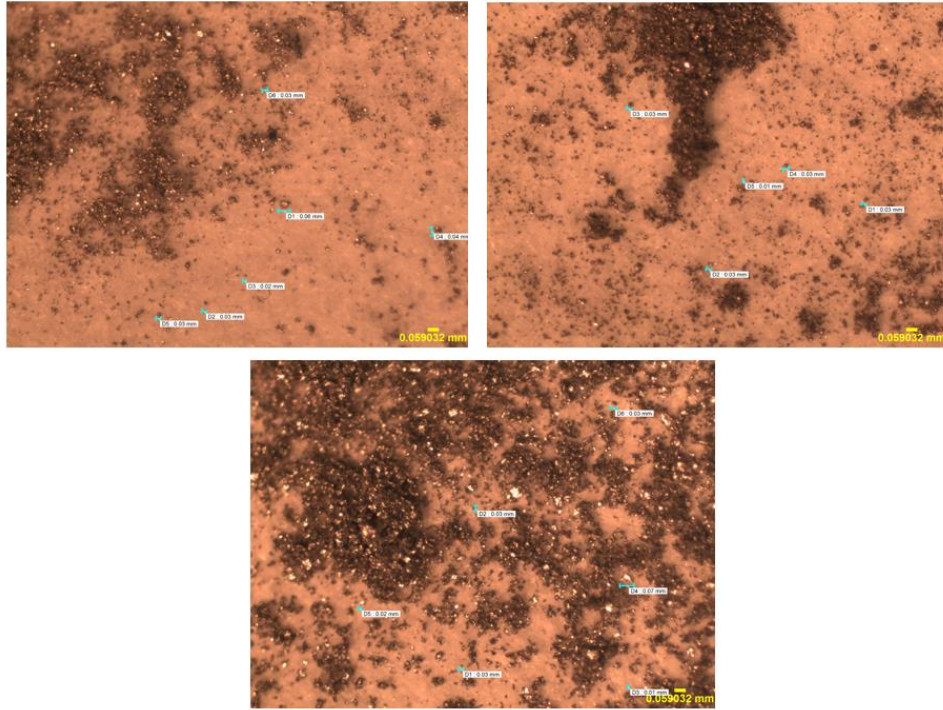


Figure 1: Microscopic images of magnesium with varying amounts of sodium chromate. Top left: Mg- 1 wt% sodium chromate. Top right: Mg- 5 wt% sodium chromate. Bottom: Pure Mg.

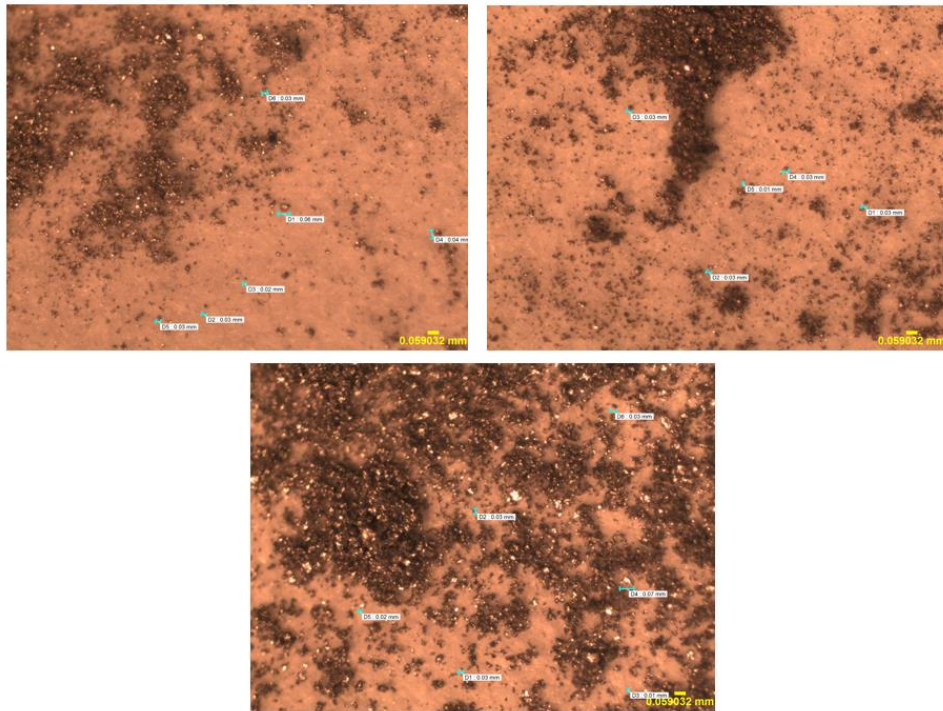


Figure 2: Microscopic images for zinc with varying weight percentages of sodium chromate. Top left: Zn- 1 wt% sodium chromate. Top right: Zn- 5 wt% sodium chromate. Bottom: Pure Zn.

Figure 1 and Figure 2 show the microscopic images for the six sample groups that were prepared. Figure 1 shows a finer powder as the amount of sodium chromate increases in each sample. The average particle size decreases at higher weight percentages of sodium chromate for magnesium. Zinc has the opposite trend as the particles tend to conglomerate when milled with sodium chromate. Zinc with 5 weight percent sodium chromate is significantly coarser when compared to the unmilled zinc. The analysis was used to determine the amount of powder necessary to compress into a utilizable sample. Too little powder would result in a thin sample which would not provide enough material to test. Too much sample would result in a loose compacted powder that could result in faulty data.

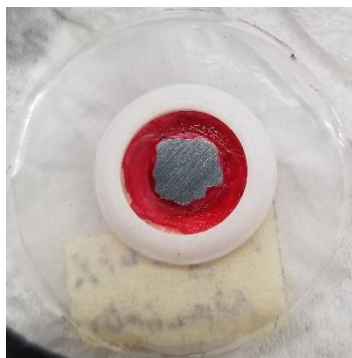
*Table 1: Two methods to compress powdered sample.*

	Method 1	Method 2
Time (s)	Force (lbf)	
30	1000	1000
30	5000	3000
30	10000	5000
30	15000	8000
30	20000	11000
30	26200	14000
30		17000
30		20000
30		23000
30		26200
30		
30		
30		
30		
30		

The powdered sample was loaded in between two steel plates, with enough powder to compress into a useable sample. Compression of a powdered material is an irreversible dynamic process <sup>[14]</sup>. The stress applied results in a change in density, as a result of a decreasing volume. It is important to be consistent with the stress application in order to minimize variability. Two methods were used to compress the powdered samples. The force was set and ran for a certain interval of time. The force would then be increased and applied for the same amount of time. For the first method, a force of 1000 pounds was applied to the sample for 30 seconds. The force was increased to 5000 lbs, followed by 10000, 15000, and 20000 lbs. The final force is 26200 lbs and is applied for 6 minutes. The second method had the same initial force of 1000 lbs. The increase in force was initially 2000 lbs, followed by an increase of 3000 lbs

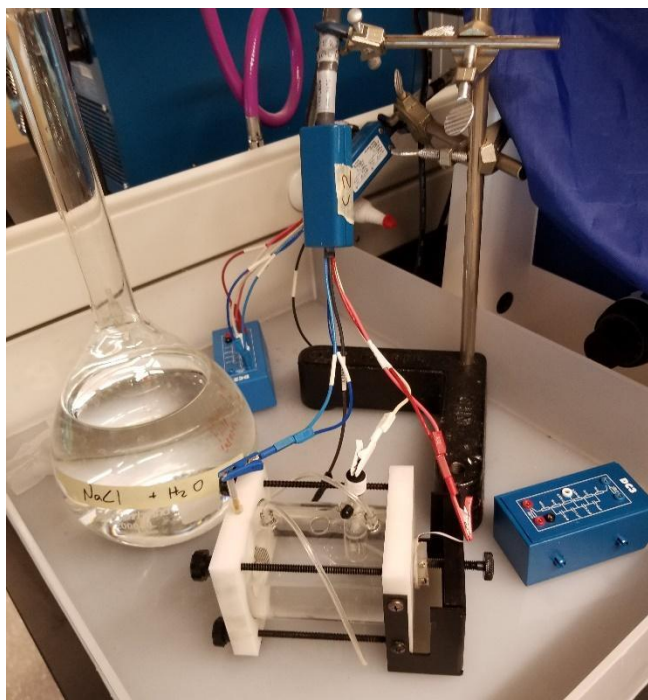
every 30 seconds. The final force of 26200 lbs is also applied for 30 seconds. A few factors were considered when comparing the two methods. When subject to high stress, the sample could crack or result in a particle fracture. Another factor that was considered was the number of voids created as a result of a lack of compactness. It was determined that method 2 provided the most consistent and viable samples for testing. Method 1's larger intervals of force applied would occasionally result in cracking of the sample. Another issue with method 1 was that the sample would be compressed into a thickness that would be too small to use for an experiment. Method 2's steady increase of force would result in minimal voids of the sample. After a sample was prepared, a mixture of an epoxy and epoxy hardener was applied around the edge of the sample. Both sides of the sample remained untouched by the epoxy. The mold was left curing overnight.

In order to perform accurate tests on the samples, it is important for the sample to be smooth. Any scratches and surface elevation changes can result in inaccurate measurements. The samples are to be grounded before undergoing any sort of corrosion testing. The sample were ground on grit silicon carbide paper. At the initial grit size of 120, samples are polished using a Sample Grinding & Polishing Machine. As the grit size increases, polishing can be done by hand. The final grit size used for the sample is 1200.



*Figure 3: Magnesium 1 wt. % sodium chromate sample.*

Once samples were polished, the area of the sample was measured. Lacquer was applied around the edge of the sample to cover any holes between the sample and the lube. The polish was also used to determine what area of the sample the program would take measurements from. Figure 3 shows a sample of magnesium 1 wt. % sodium chromate. The area of the sample is measured using ImageJ. The white ring is used to calibrate with an area of  $1 \text{ cm}^2$ . The area inside the red is traced and an area is calculated. The area is used for testing and is entered as a cell characteristic. Afterwards, lacquer is left to dry overnight.



*Figure 4: Experimental setup for EVT, PEIS, and CPP testing.*

Once the sample is dry, a copper wire is attached to top side of the sample. The sample is then fitted into the apparatus, with the bottom side of the sample exposed to the solution. Figure 4 shows the experimental setup. A solution 0.1 M NaCl solution is used for reference and immerses the sample. The red, blue, and white wires show the electrodes connection. The red wire is for the working electrode potential and is connected to the copper wire, which is attached to the sample. The white wire is for the electrode potential and is attached to the reference node, which is immersed in the sodium chloride solution. The blue wire is for the counter electrode potential and is attached to a rod at the bottom of the apparatus. The experiment is then ready to be run. The experiment runs a sequence of EVT, PEIS, second EVT, and CPP. The sequence takes a total amount of time between 45 minutes to 1 hour and 30 minutes. Once the sequence is completed, the solution is disposed, and the sample is no longer used. A single sample may be used twice if the sample is polished for a second time. An average of four trials were run for each type of sample. The plots which showed the least amount of disturbance and pseudo-values were chosen for comparison.

## Results and discussion

$E_{WE}$  is the working electrode potential versus the reference potential. Figure 5 shows the curve of  $I$  vs.  $E_{WE}$ . The graph shows a non-linear circuit, which depends on the working electrode potential and

amplitude. Multiple impedance measurements are necessary to characterize the behavior of non-linear systems.

During the EVT method, no potential or current is applied to the cell. The technique corresponds to the corrosion potential when the circuit is open versus time.



Figure 5: EVT test for three trials of Zinc 5% Sodium Chromate.

Figure 5 shows the EVT testing for three different samples of Zinc 5% Sodium Chromate. The y-axis shows the stationary potential for the impedance measurement in reference to the saturated calomel electrode. The potential is measured in voltage over time. The initial potential values can be explained by the sample stabilizing in the sodium chloride solution. Trial 3, shown by the green line, is the most stable with a value of approximately 0.98 V. Trial 1 and 2 both show larger variances in the potential values. Trial 1's potential settles in the range of 0.6 and 0.8 V. Trial 2 averages the same values as Trial 2. An average potential of the three trials could be approximated to be 0.8 V. When comparing Zn- 5%  $\text{Na}_2\text{CrO}_4$  to Pure Zn and Zn- 1%  $\text{Na}_2\text{CrO}_4$ , Trial 3 would be the most appropriate to use, as it has the no disturbance as well as a stable potential.



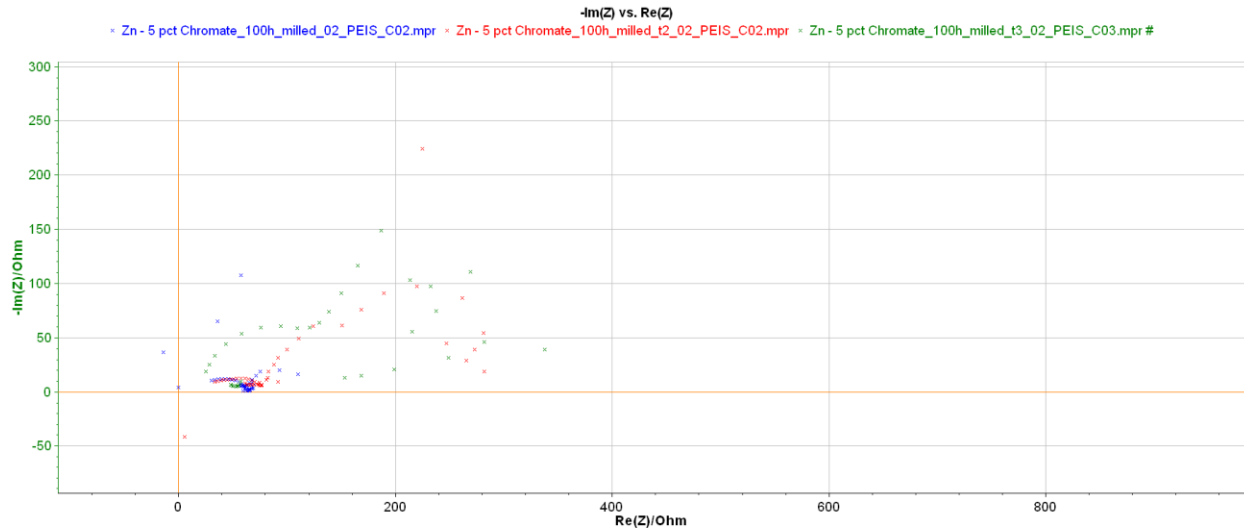


Figure 6: PEIS test for three trials of Zinc 5% Sodium Chromate.

The PEIS method performs impedance measurements into potentiostatic mode.  $Z$  denotes impedance, which is the complex generalization of resistance. The x-axis measures the real impedance while the y-axis measures the imaginary impedance, both measured in Ohms. The plot shows the points centered at  $60 \Omega$  for the real impedance and  $10 \Omega$  for the imaginary impedance. The diagram is expected to show a semi-circle where the diameter is dependent on the electrode potential. The impedance of a non-linear system, a system where impedance is not proportional, is dependent of the potential.

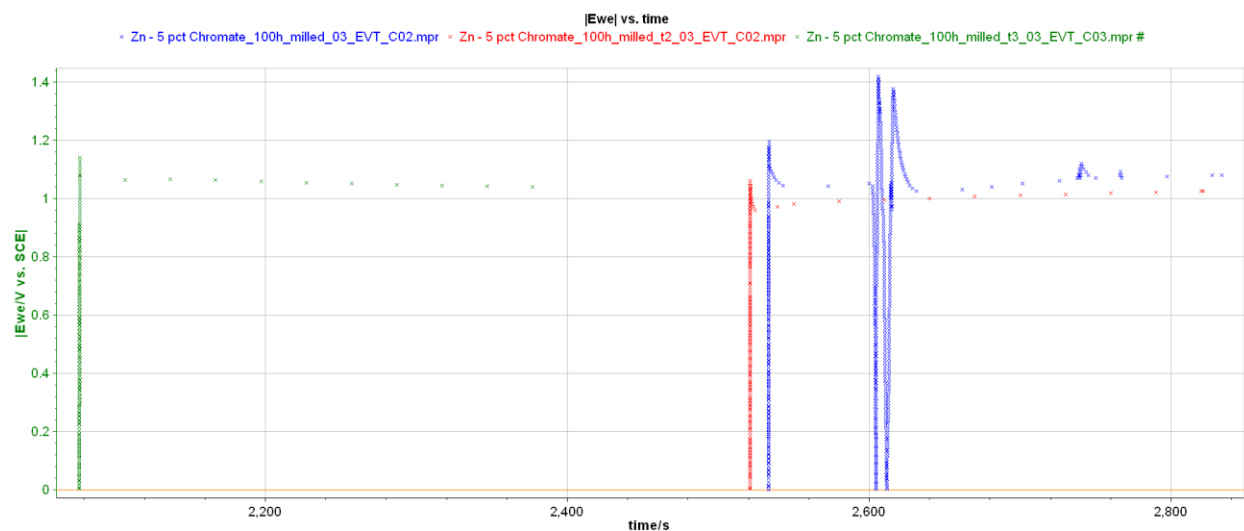


Figure 7: Second EVT test for three trials of Zn- 5% Sodium Chromate.

Following the PEIS technique, a second EVT test is run. The test measures the follow up of the corrosion potential when the circuit is open. The electrode potential is measured with no additional potential supplied. Figure 7 shows the EVT testing for three different samples of Zinc 5% Sodium Chromate. The y-axis shows the stationary potential for the impedance measurement in reference to the

saturated calomel electrode. The two readings that can be noted for the second EVT test is the time in which the first reading is taken as well as the stabilized stationary potential. Trial 3, shown by the green line, is first read at 2000 s. The stationary potential is measured at approximately 1.05 V. Trial 2's potential is read at 2520 s with a value of 1 V. Trial 1 is initial read at 2530 seconds and shows interference at 2600 seconds. The potential of Trial 1 can be approximated to be 1.05 V. The average stationary potential can be estimated to be between 1 and 1.1 volts.

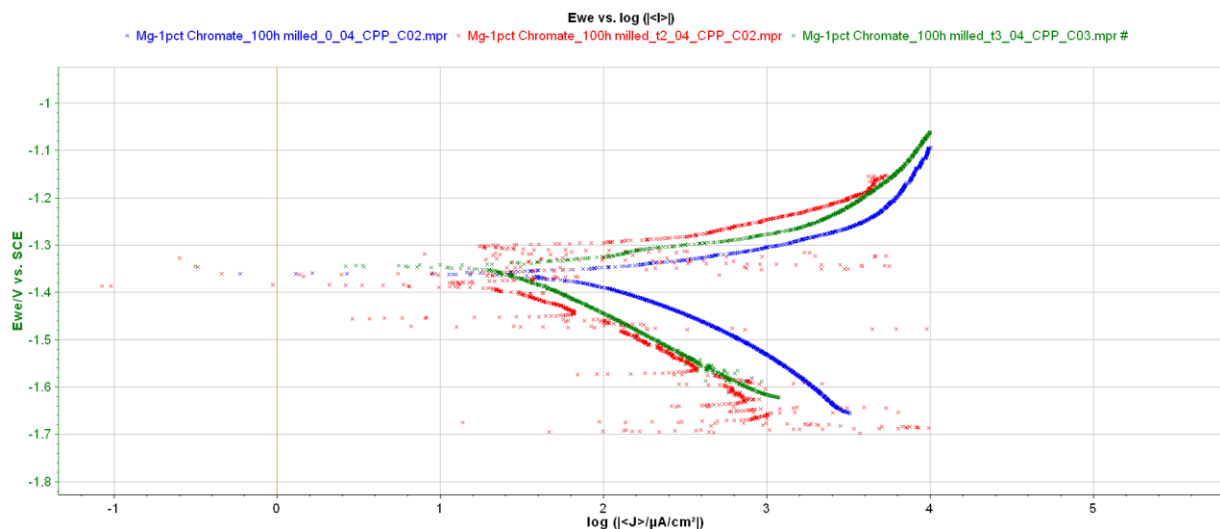


Figure 8: CPP test for three trials of Magnesium 1% Sodium Chromate.

Cyclic potentiodynamic polarization tests were plotted by measuring potentials ( $E_{pit}$ ) against current density. In the potentiodynamic scan, the potential is varied from its initial potential ( $E_i$ ) in the positive direction to its final potential ( $E_f$ ). The initial point represents the open circuit potential, where the sum of the anodic and cathodic reactions occurring on the electrode surface is zero [8]. The initial increase, when reaching a current density of  $0 \mu A/cm^2$ , represents the oxygen reduction reaction. The continued increase of potential reaches a point where there is no change in the reaction rate, where current density is  $0 \mu A/cm^3$ .  $E_{pit}$  can be measured at the highest current density in passive region where there is no change in reaction rate. The potential becomes sufficiently positive for another reaction to take place, typically a water reduction reaction [8]. The polarization resistance can be calculated from the ratio of the applied potential to the applied current ( $\Delta E/\Delta I$ ). The plot shows both the anodic and cathodic reaction. The corrosion rate could be calculated from the polarization resistance. Figure 8 shows the CPP test for Mg- 1%  $Na_2CrO_4$ .  $E_{pit}$  is found to be -1.35 V for Trial 1, -1.3 V for Trial 2, and -1.34 for Trial 3. An average of -1.34 volts can be assumed for Magnesium 1% Sodium Chromate. Table 2 shows the calculation



for polarization resistance, where the change in applied potential is divided by the change in current. The polarization resistance can be approximated to be around 0.06 kΩ.

Table 2: Calculation of polarization resistance for Mg- 1% Na<sub>2</sub>CrO<sub>4</sub>.

Mg 1pct Chromate											
Trial 1	Initial	Final	Change	Trial 2	Initial	Final	Change	Trial 3	Initial	Final	Change
E (V)	-1.6	-1.15	0.45	E (V)	-1.55	-1.19	0.36	E (V)	-1.6	-1.1	0.5
I (μA/cm <sup>3</sup> )	-2000	8000	10000	I (μA/cm <sup>3</sup> )	-400	4000	4400	I (μA/cm <sup>3</sup> )	-800	8000	8800
		R <sub>p</sub>	0.045 kΩ			R <sub>p</sub>	0.082 kΩ			R <sub>p</sub>	0.057 kΩ

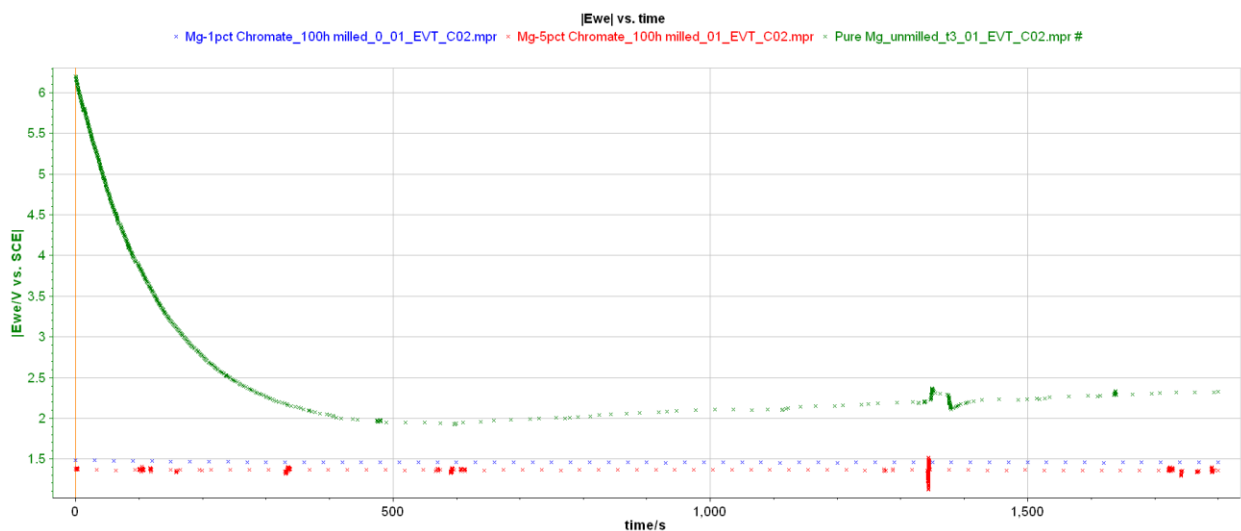


Figure 9: First EVT test of Magnesium with increasing amounts of Sodium Chromate, 1 wt. % sodium chromate, and 5 wt. % sodium chromate. Green represents Pure Magnesium, blue represents Magnesium-1 wt. % Sodium Chromate, and red represents Magnesium 5 wt. % Sodium Chromate.

Figure 9 shows the EVT testing for Pure Mg, Mg- 1% Na<sub>2</sub>CrO<sub>4</sub>, and Mg- 5% Na<sub>2</sub>CrO<sub>4</sub>. Multiple trials of pure magnesium were run, and all exhibited a period of time before a stationary potential was reached. Pure Mg reached an estimated stationary potential of 2.1 V. Mg- 1 wt. % Na<sub>2</sub>CrO<sub>4</sub> has an open circuit potential value of 1.5 V while Mg- 5 wt. % Na<sub>2</sub>CrO<sub>4</sub> has a potential of 1.4 V. A decrease in potential, in reference to the reference electrode, can be observed as sodium chromate is added.

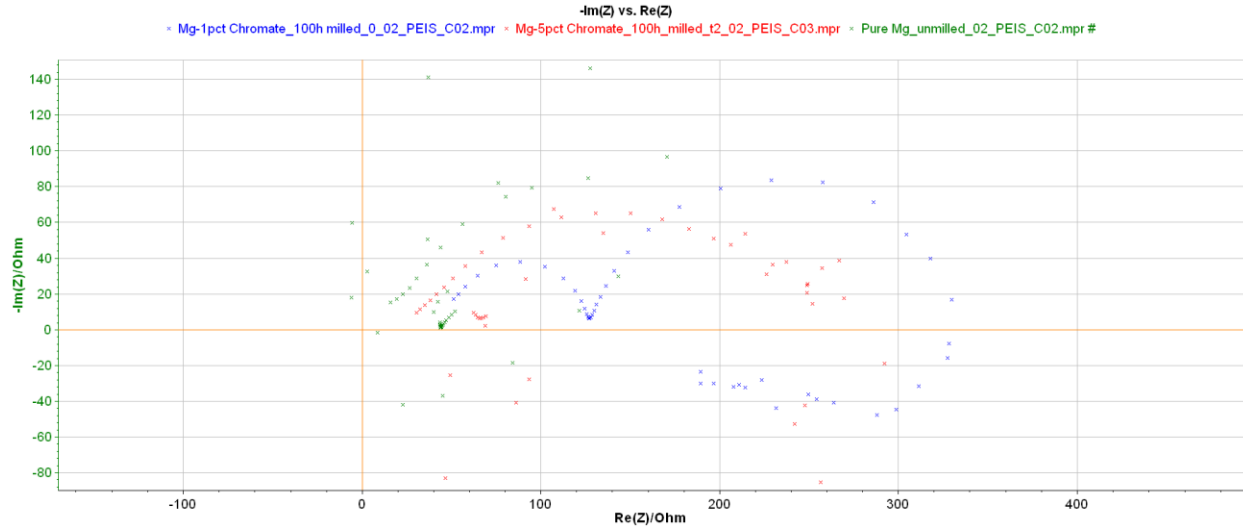


Figure 10: PEIS technique of Magnesium with increasing amounts of Sodium Chromate, 1 wt. % sodium chromate, and 5 wt. % sodium chromate. Green represents Pure Magnesium, blue represents Magnesium 1wt. % Sodium Chromate, and red represents Magnesium 5 wt. % Sodium Chromate.

Figure 10 shows the PEIS technique for Pure Mg, Mg- 1-wt%  $\text{Na}_2\text{CrO}_4$ , and Mg- 5 wt. %  $\text{Na}_2\text{CrO}_4$ . All three trials show scattered points, but Pure Mg has the largest diameter of its semi-circle, which correlates to the polarization resistance. The larger the diameter, the higher the polarization resistance. Excluding outliers, the semi-circle of Pure Mg reaches 100  $\Omega$ , with a real impedance range of 20  $\Omega$  to 180  $\Omega$ . Mg 1%  $\text{Na}_2\text{CrO}_4$  shows two main semi-circles, the second one having a large diameter than the first. The two semi-circles indicate an impedance increase dependent of the amplitude, which overall indicates increasing frequencies. The first, smaller semi-circle ranges from 50 to 130  $\Omega$ , while the second ranges from 130  $\Omega$  to 330  $\Omega$ . The first semi-circle reaches an imaginary impedance of 30  $\Omega$  and the second semi-circle reaches an imaginary impedance of 80  $\Omega$ . Mg- 5%  $\text{Na}_2\text{CrO}_4$  has the smallest diameter with an initial reading at 25  $\Omega$ . The plot shows an increasing dependence on potential as the concentration of sodium chromate increases.

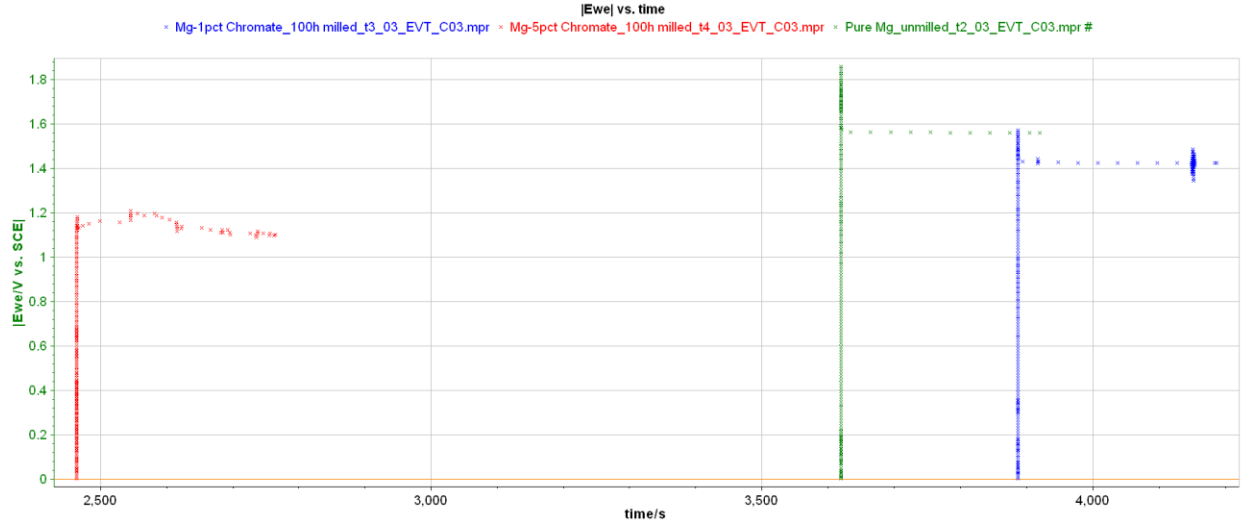


Figure 11: Second EVT test of Magnesium with varying amounts of Sodium Chromate, 1 wt. % sodium chromate, and 5 wt. % sodium chromate. Green represents Pure Mg, blue represents Mg- 1 wt. % Sodium Chromate, and red represents Mg- 5 wt. % Sodium Chromate.

The EVT test following the PEIS method is shown in Figure 11. Pure magnesium shows a potential measurement of 1.58 V. Mg- 1%  $\text{Na}_2\text{CrO}_4$  gives a value of 1.42 V. Mg- 5%  $\text{Na}_2\text{CrO}_4$  reaches a stationary potential of 1.1 V. As the weight percent of sodium chromate increases, the stationary potential decreases. As expected, the second EVT test follows the same trend as the first EVT test.

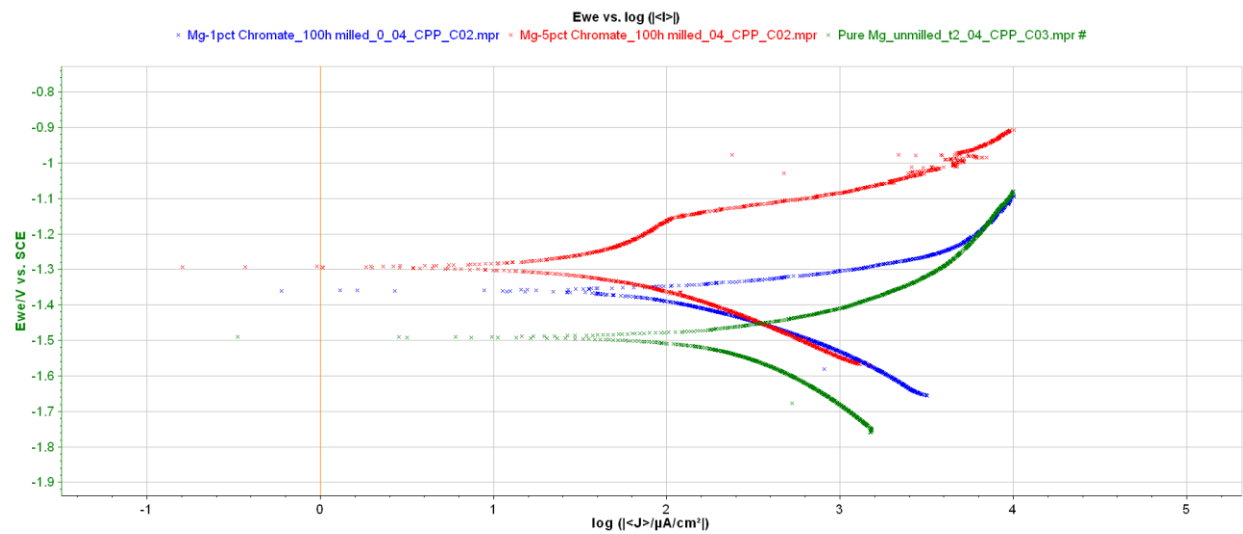


Figure 12: CPP test of Magnesium with varying amounts of Sodium Chromate, 1 wt. % sodium chromate, and 5 wt. % sodium chromate. Green represents Pure Mg, blue represents Mg 1% Sodium Chromate, and red represents Mg 5% Sodium Chromate.

Figure 12 shows the CPP test of Pure Mg, Mg-1 wt. %  $\text{Na}_2\text{CrO}_4$ , and Mg-5 wt. %  $\text{Na}_2\text{CrO}_4$ . Pure Mg shows no clear region where potential increases with no change to the reaction rate, thus  $E_{\text{pit}}$  cannot be

measured. Mg- 1 wt. %  $\text{Na}_2\text{CrO}_4$  gives a value of -1.3 V, while Mg- 5%  $\text{Na}_2\text{CrO}_4$  has a value of -1.14 V. There is a clear trend of higher potentials at higher concentrations of sodium chromate, with changing current. The polarization resistance of Pure Mg and Mg- 1%  $\text{Na}_2\text{CrO}_4$  are both calculated to be 0.057 k $\Omega$ . The polarization resistance of Mg- 5%  $\text{Na}_2\text{CrO}_4$  is calculated to be 0.070 k $\Omega$ . It can be concluded that polarization resistance is affected at higher concentrations of sodium chromate.

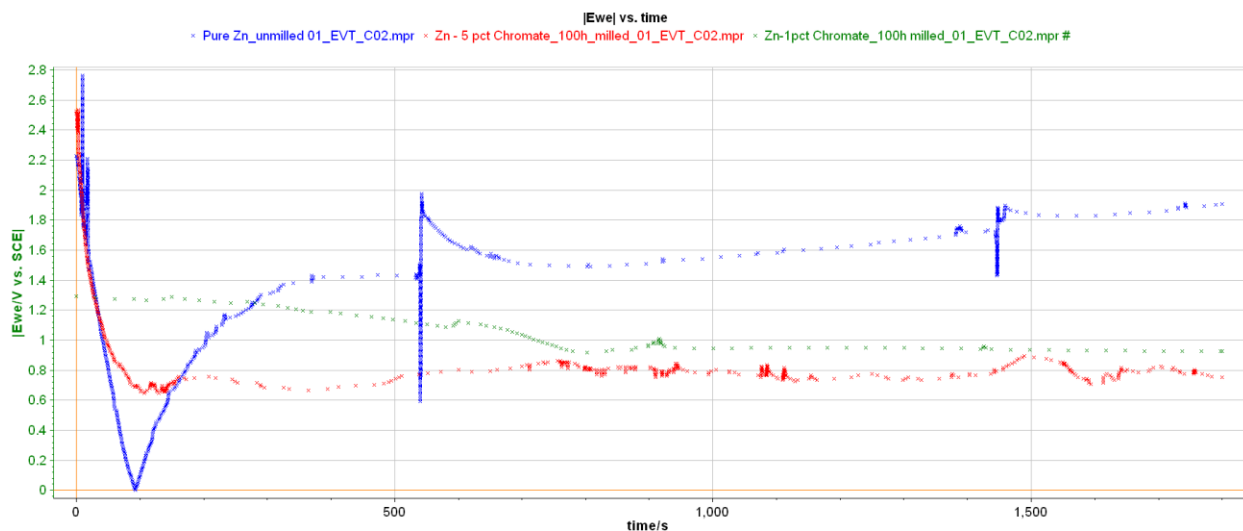


Figure 13: First EVT test of Zinc with varying amounts of Sodium Chromate, 1 wt. % sodium chromate, and 5 wt. % sodium chromate. Blue represents Pure Zn, green represents Zn- 1% Sodium Chromate, and red represents Zn- 5% Sodium Chromate.

Figure 13 shows the EVT graph for Pure Zn, Zn- 1 wt. %  $\text{Na}_2\text{CrO}_4$ , and Zn- 5 wt. %  $\text{Na}_2\text{CrO}_4$ . Interference can be observed for all three tests, but pure zinc visibly has the highest potential. The potential of pure zinc can be approximated to be 1.8 V, although the trend shows the potential slowly increasing. Zn- 1%  $\text{Na}_2\text{CrO}_4$  shows the least amount of disturbance and stabilizes at 0.92 V. Zn- 5%  $\text{Na}_2\text{CrO}_4$  gives a stationary potential of 0.75 V. The impedance of the sample increases as the amount of sodium chromate increases. The zinc samples show an overall lower voltage compared to the magnesium samples.

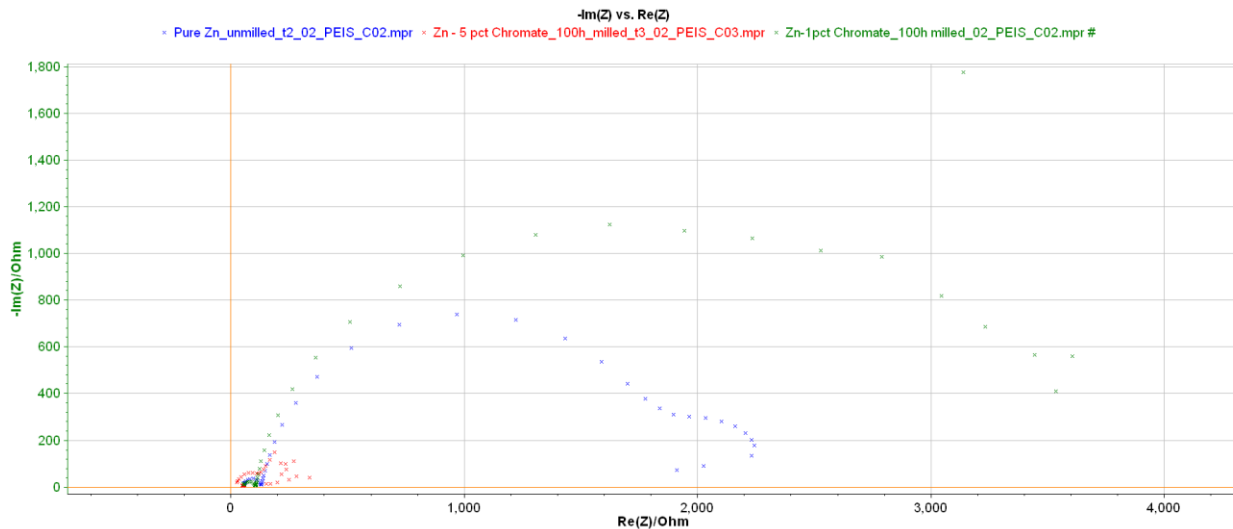


Figure 14: PEIS technique of Zinc with varying amounts of Sodium Chromate. Blue represents Pure Zn, green represents Zn- 1% Sodium Chromate, and red represents Zn- 5% Sodium Chromate.

Figure 14 shows the PEIS technique for Pure Zn, Zn- 1%  $\text{Na}_2\text{CrO}_4$ , and Zn- 5%  $\text{Na}_2\text{CrO}_4$ . Zn- 5%  $\text{Na}_2\text{CrO}_4$  gives a very small diameter, relative to Pure Zn and Zn 1%  $\text{Na}_2\text{CrO}_4$ . Zn- 5%  $\text{Na}_2\text{CrO}_4$  reaches an imaginary impedance of 100  $\Omega$ . The impedance of Zn- 5%  $\text{Na}_2\text{CrO}_4$  ranges from 50 to 350  $\Omega$ . Pure Zn shows a larger diameter, reaching approximately 750  $\Omega$ . The real impedance ranges from 120 to 2000  $\Omega$ . Zn- 1%  $\text{Na}_2\text{CrO}_4$  gives the largest diameter, with the max value reaching 1100  $\Omega$ . The range of Zn- 1%  $\text{Na}_2\text{CrO}_4$  is 100 – 3500  $\Omega$ . No clear trend is shown, as Zn- 5%  $\text{Na}_2\text{CrO}_4$  is expected to produce the largest semi-circle. As it is difficult to characterize the behavior of a non-linear system, further trials would need to be completed.

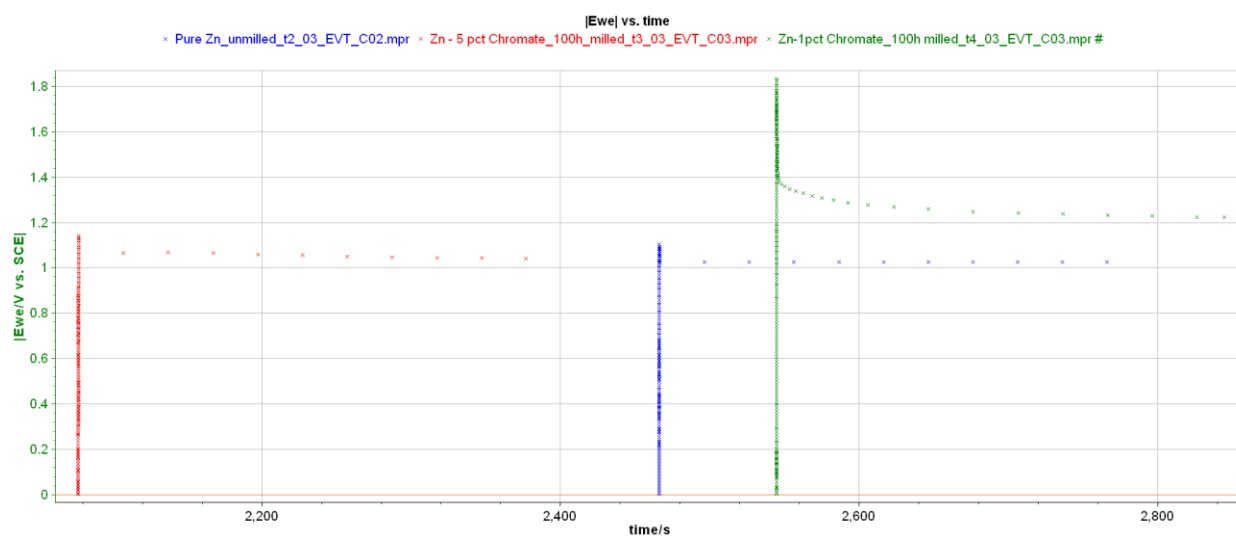


Figure 15: Second EVT test of Zinc with varying amounts of Sodium Chromate. Blue represents Pure Zn, green represents Zn- 1% Sodium Chromate, and red represents Zn- 5% Sodium Chromate.

The second EVT of Pure Zn, Zn- 1%  $\text{Na}_2\text{CrO}_4$ , and Zn- 5%  $\text{Na}_2\text{CrO}_4$  is shown in Figure 15. The potential of Pure Zn is measured at 1 V, Zn- 1%  $\text{Na}_2\text{CrO}_4$  at 1.2, and Zn- 5%  $\text{Na}_2\text{CrO}_4$  at 1 V. Multiple trials of each sample show varying potential values ranging between 1- 1.3 V. No clear trend is observed as the potential appears to stabilize at similar values for each sample (Fig. 15).

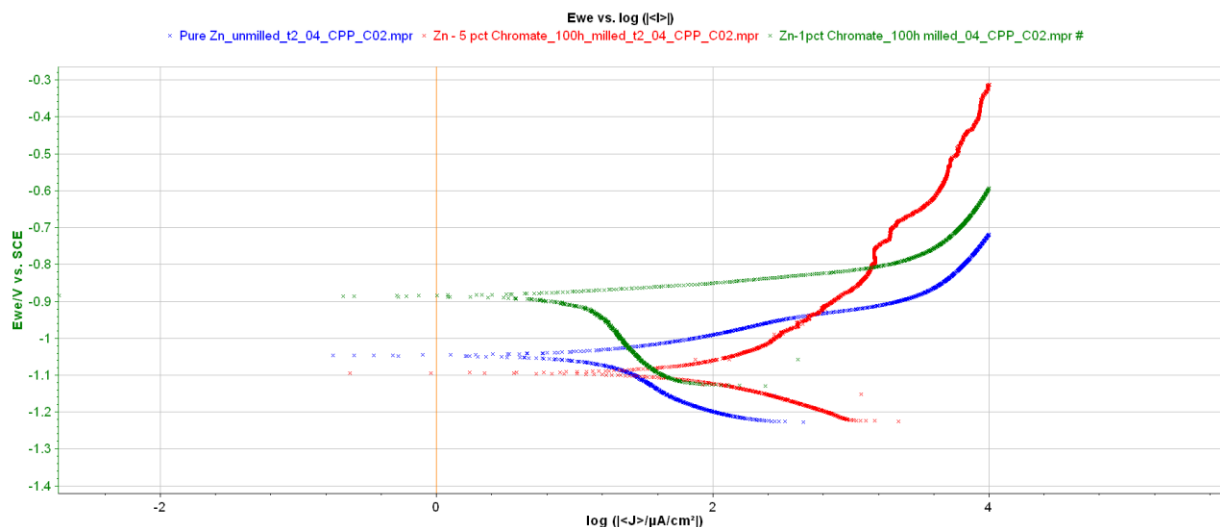


Figure 16: CPP test of Zinc with varying amounts of Sodium Chromate, 1 wt. % sodium chromate, and 5 wt. % sodium chromate. Blue represents Pure Zn, green represents Zn 1% Sodium Chromate, and red represents Zn 5% Sodium Chromate

Figure 16 shows the CPP test of Pure Zn, Zn 1%  $\text{Na}_2\text{CrO}_4$ , and Zn 5%  $\text{Na}_2\text{CrO}_4$ .  $E_{\text{pit}}$  of Pure Zn can be measured to be -0.93 V while Zn- 1%  $\text{Na}_2\text{CrO}_4$  gives a value of -0.87 V, Mg- 5%  $\text{Na}_2\text{CrO}_4$  shows no clear region with no reaction rate, but with disregarding a slight current increase the  $E_{\text{pit}}$  value can be measured at -0.75 V. Zinc shows a similar trend of higher potentials at higher concentrations of sodium chromate, with changing current. The polarization resistance of Pure Mg was calculated to be 0.049 k $\Omega$ .  $R_p$  of Mg- 1%  $\text{Na}_2\text{CrO}_4$  was calculated to be 0.053 k $\Omega$ . The  $R_p$  of Mg- 5%  $\text{Na}_2\text{CrO}_4$  was calculated to be 0.087 k $\Omega$ . The graph shows an increase of polarization resistance as the amount of sodium chromate increases.

## Conclusions

Zinc and magnesium powders with added sodium chromate were produced through high-energy ball milling. Pure samples of zinc and magnesium were compared to sample of added sodium chromate at two weight percentages (1 wt. % and 5 wt. %). The characteristics of the samples were analyzed through optical microscopic imaging. Corrosion behavior was analyzed via EVT, PEIS, and CPP testing. Predictably,

the corrosion performance significantly improved as the concentration of sodium chromate increased in both zinc and magnesium. A recommendation to further solidify the trend of corrosion behavior would be to run hardness tests. The next steps of the process would be to mix the powdered samples with paint and apply to a metal substrate for testing.

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## Appendix A: Raw data plots of trial comparisons

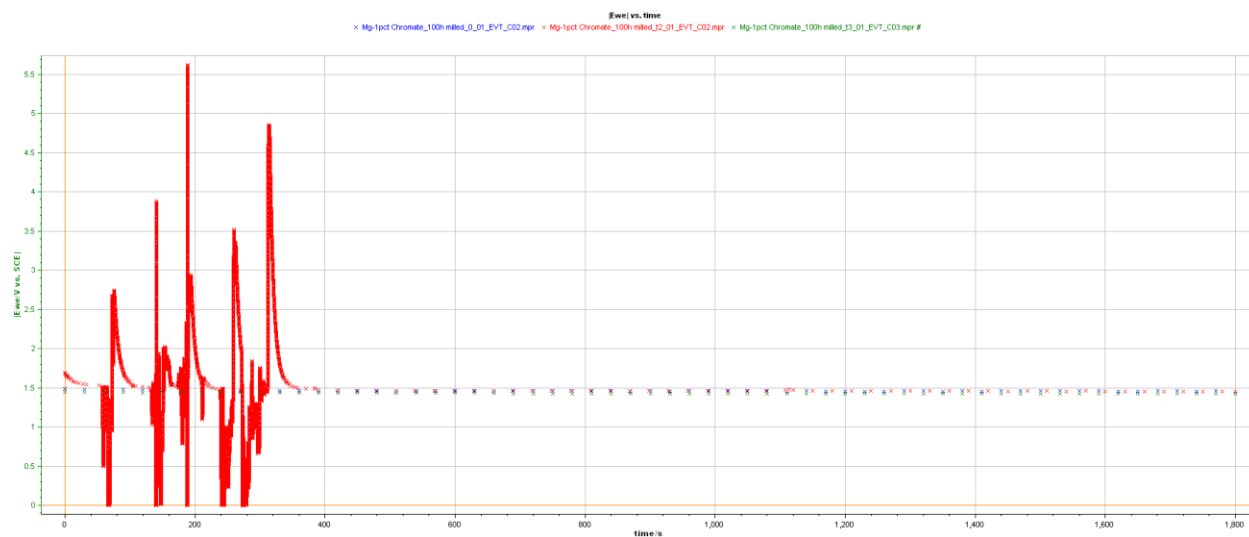


Figure 17: Primary EVT test of Mg 1%  $\text{Na}_2\text{CrO}_4$



Figure 18: Primary EVT test of Mg 5%  $\text{Na}_2\text{CrO}_4$

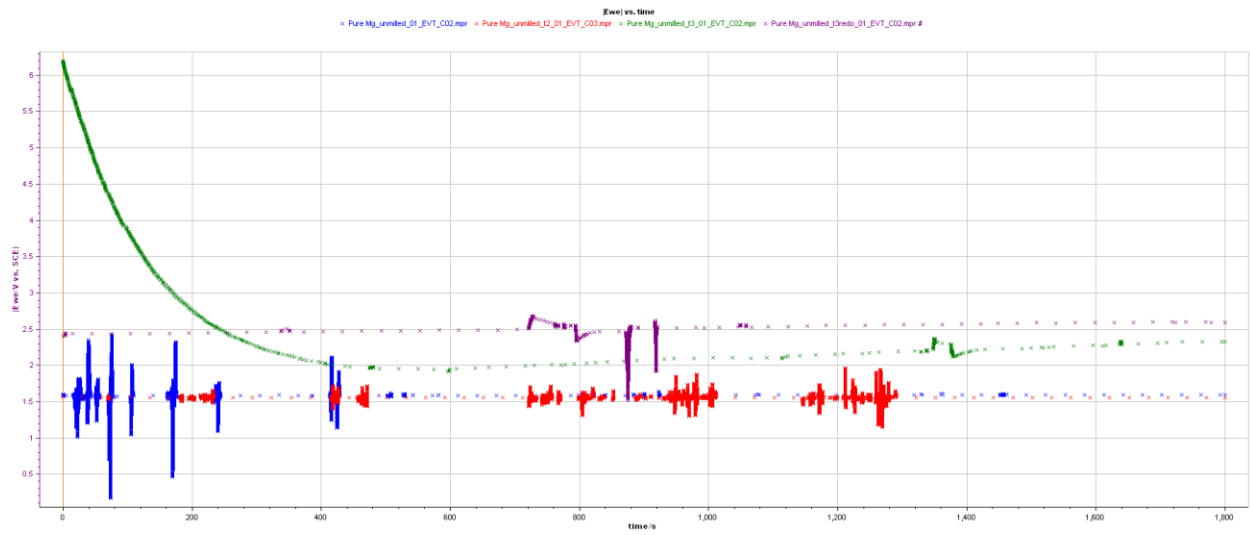


Figure 19: Primary EVT test of Pure Mg



Figure 20: Primary EVT test of Pure Zn

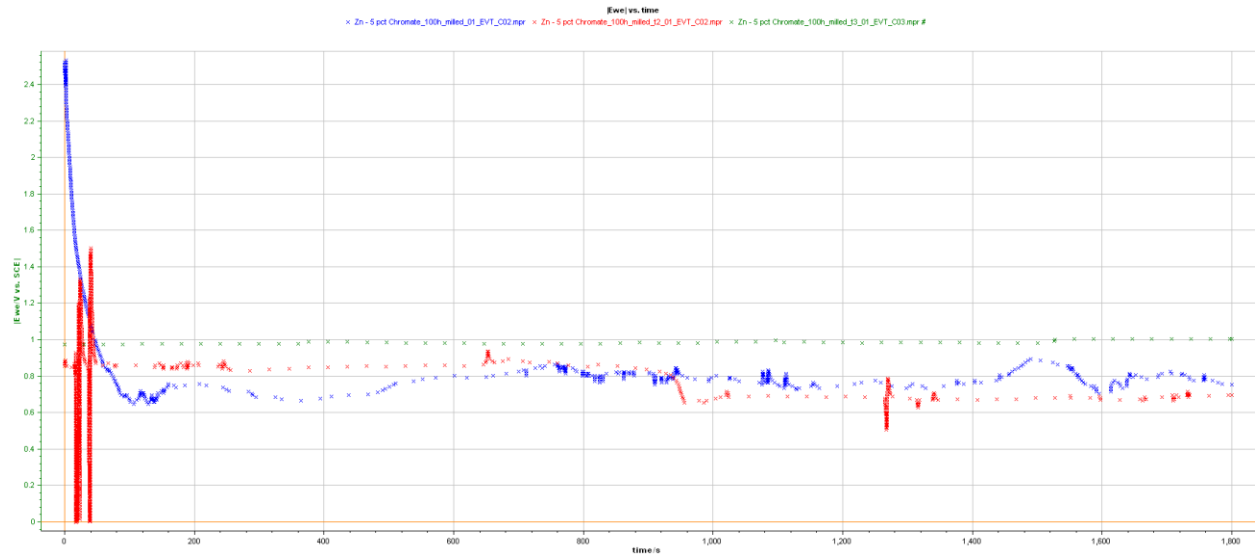


Figure 21: Primary EVT test of Zn 5%  $\text{Na}_2\text{CrO}_4$

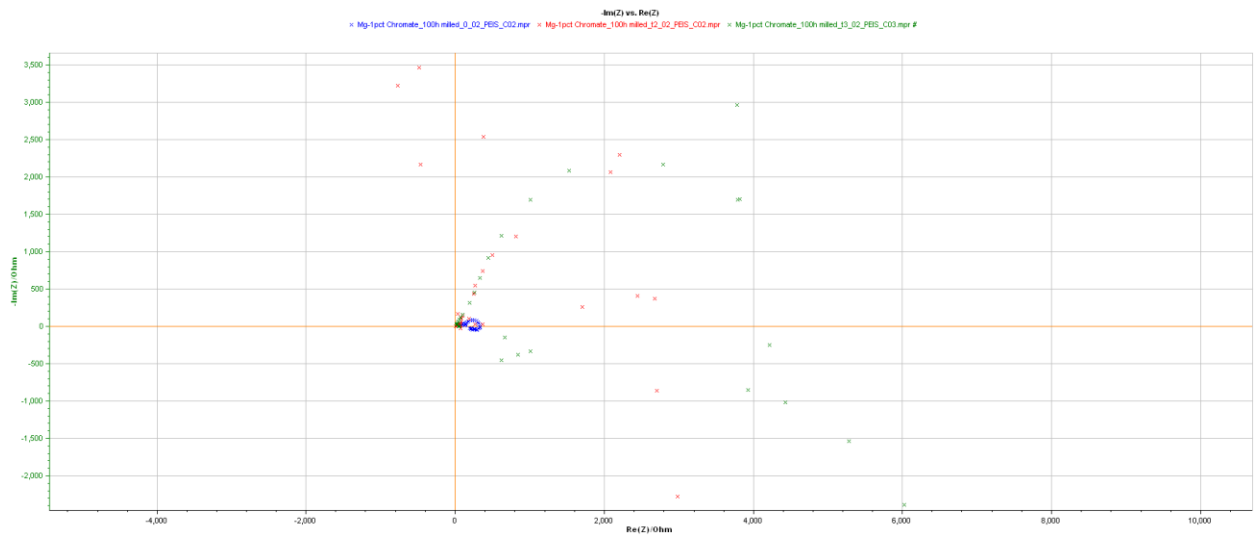


Figure 22: PEIS test of Mg 5% of  $\text{Na}_2\text{CrO}_4$

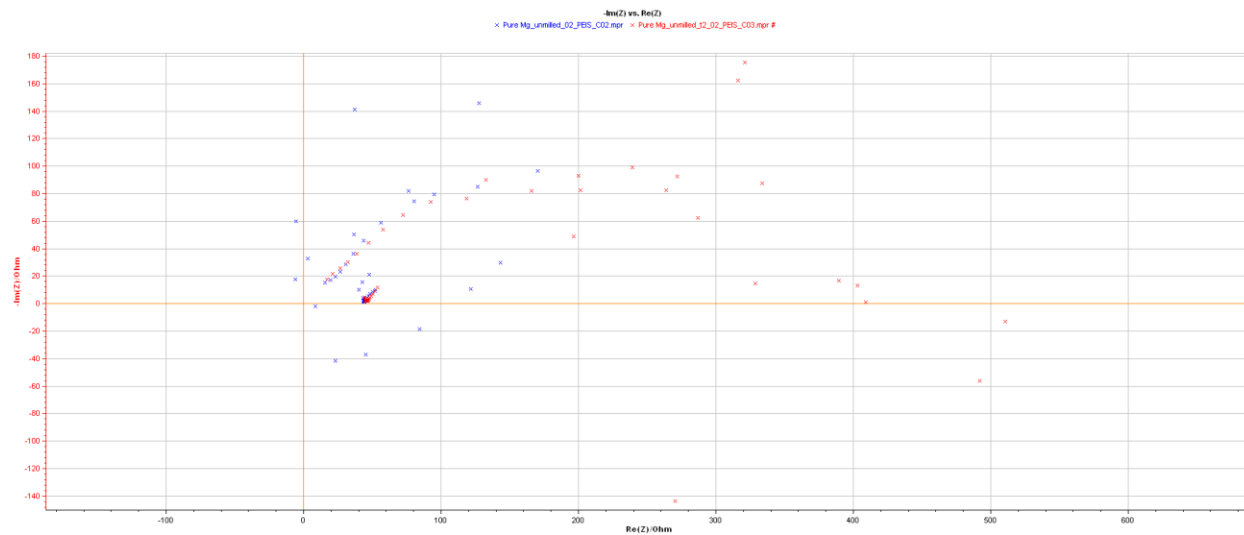


Figure 23: PEIS test of Pure Mg

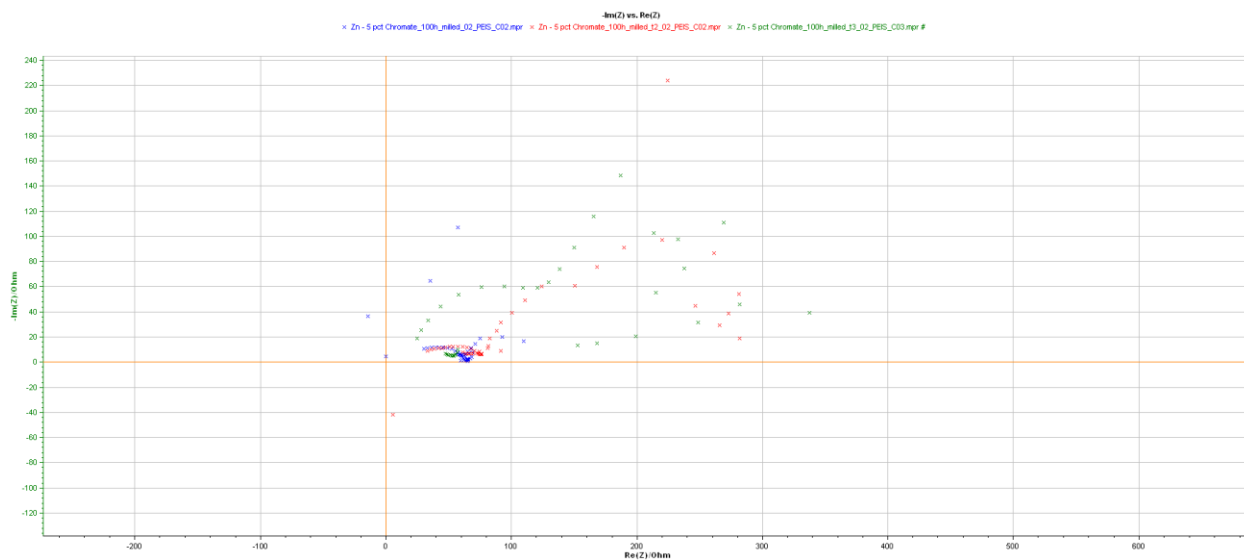


Figure 24: PEIS test of Zn 5% Na<sub>2</sub>CrO<sub>4</sub>

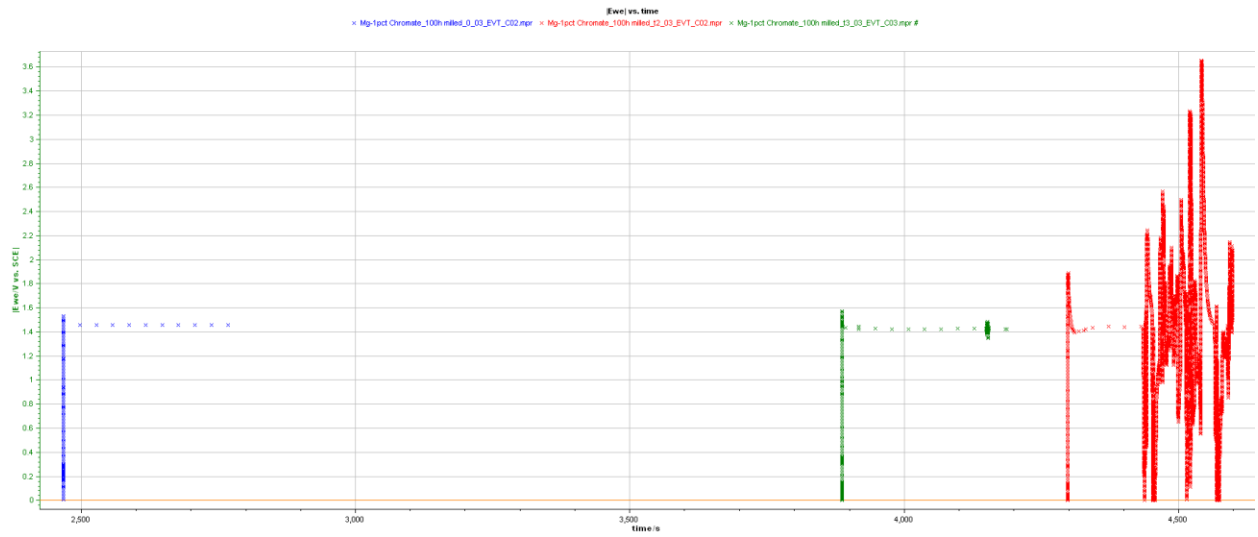


Figure 25: Secondary EVT test of Mg 1%  $\text{Na}_2\text{CrO}_4$

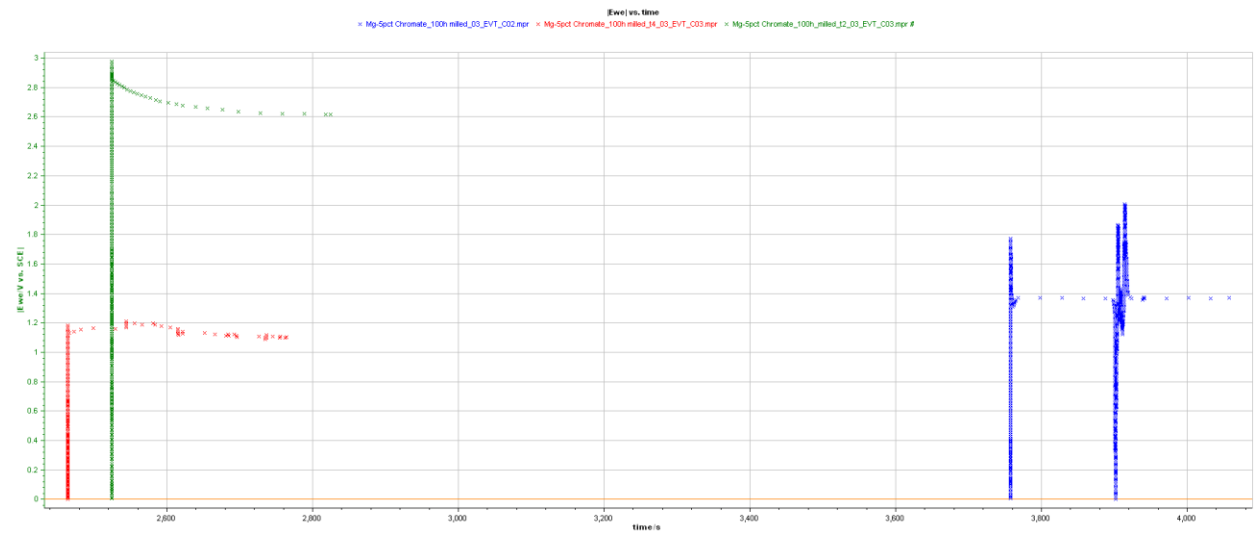


Figure 26: Secondary EVT test of Mg 5%  $\text{Na}_2\text{CrO}_4$

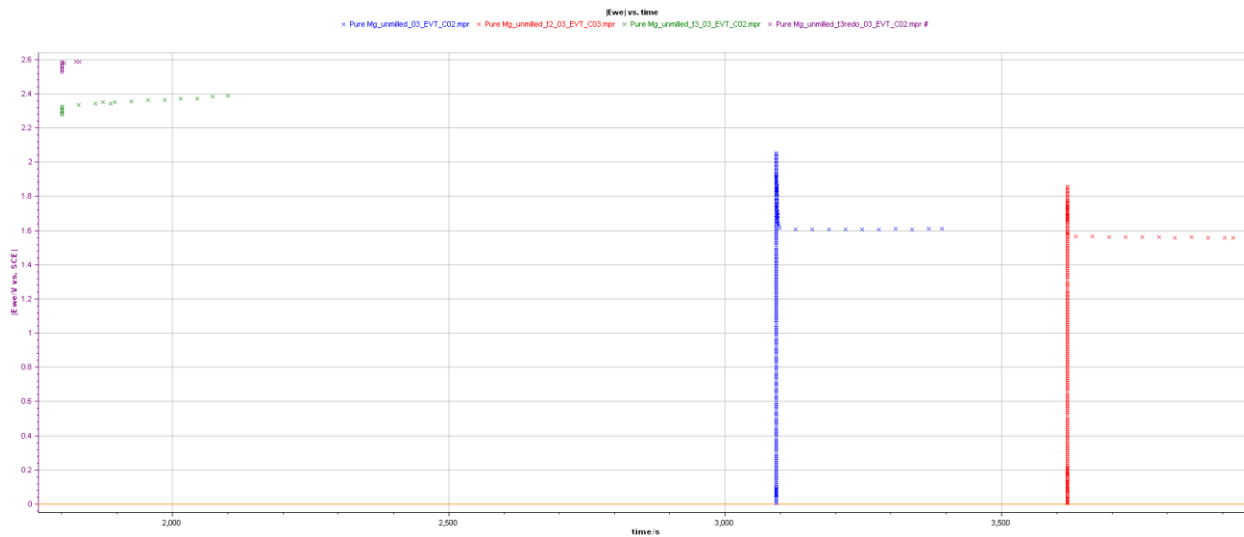


Figure 27: Secondary EVT test of Pure Mg

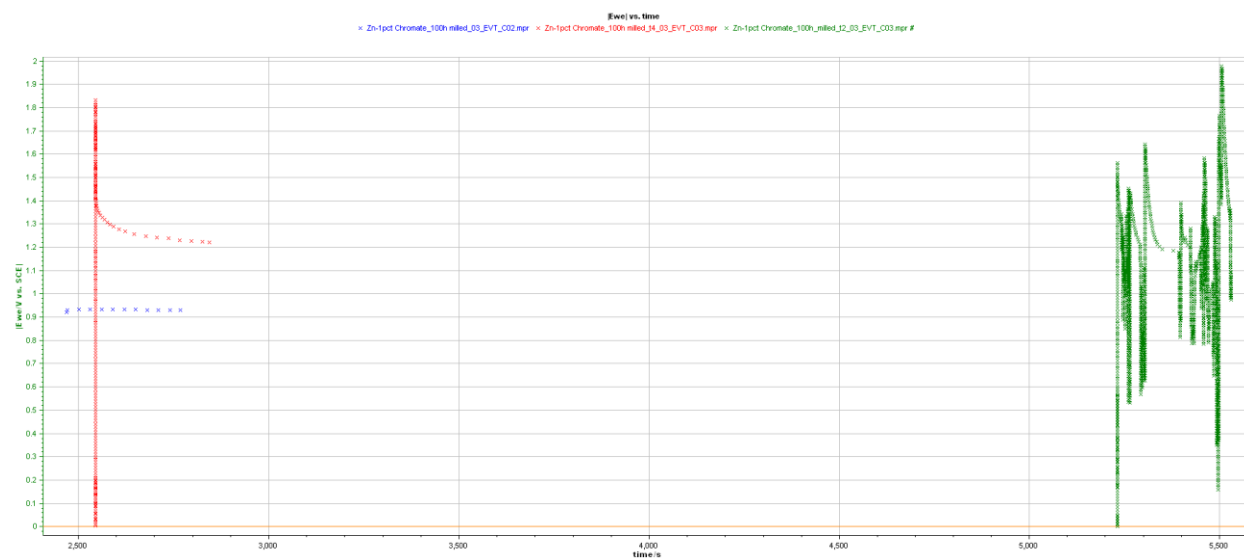


Figure 28 Secondary EVT test of Zn 1% Na<sub>2</sub>CrO<sub>4</sub>

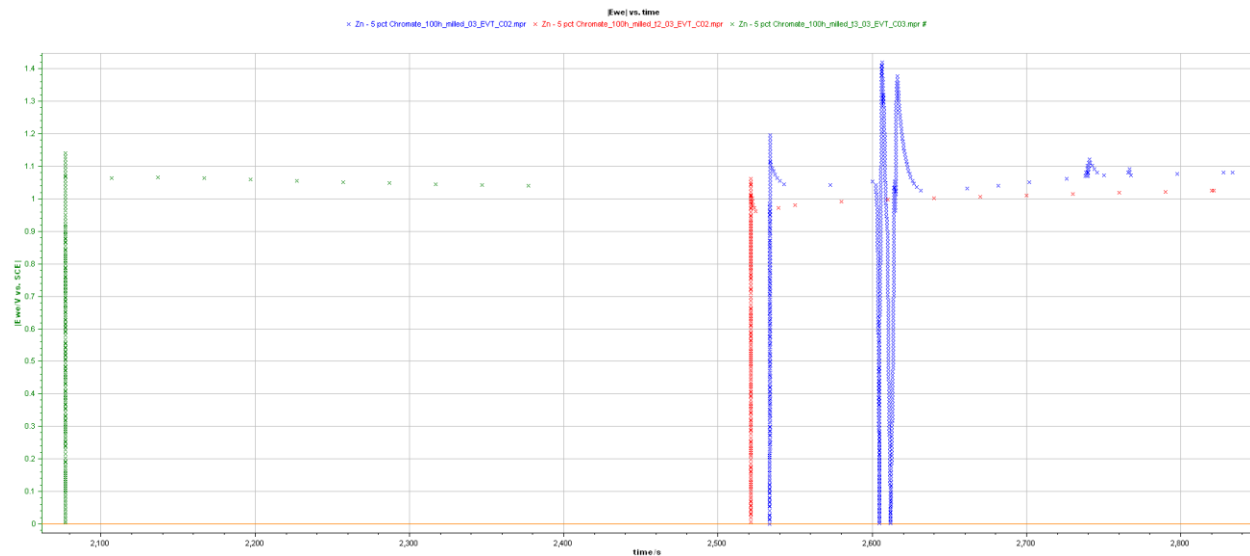


Figure 29: Secondary EVT test of Zn 5%  $\text{Na}_2\text{CrO}_4$

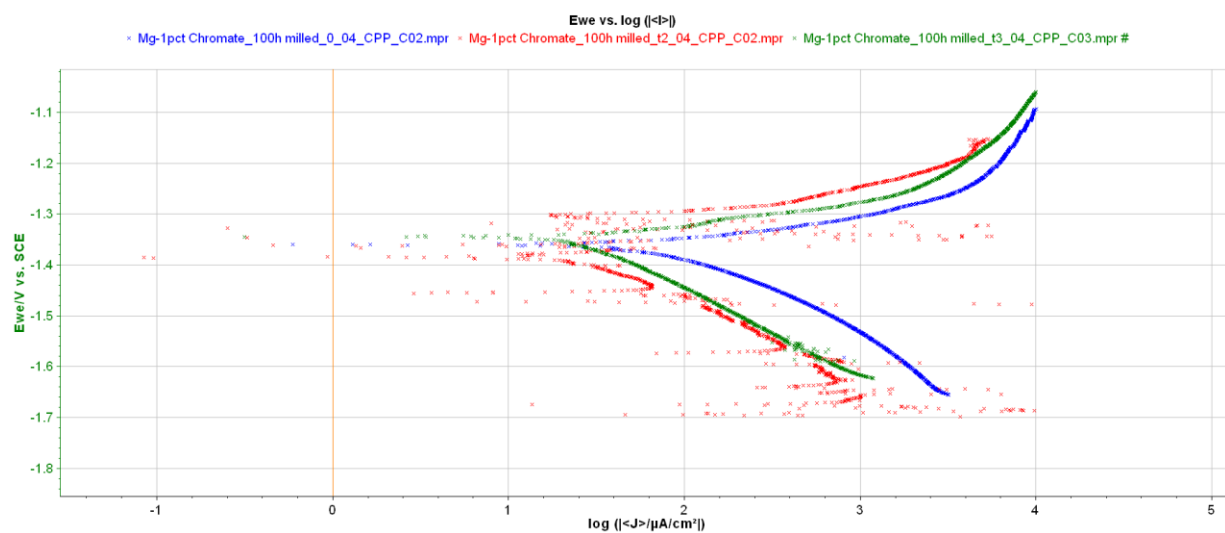


Figure 30: CPP test of Mg 1%  $\text{Na}_2\text{CrO}_4$



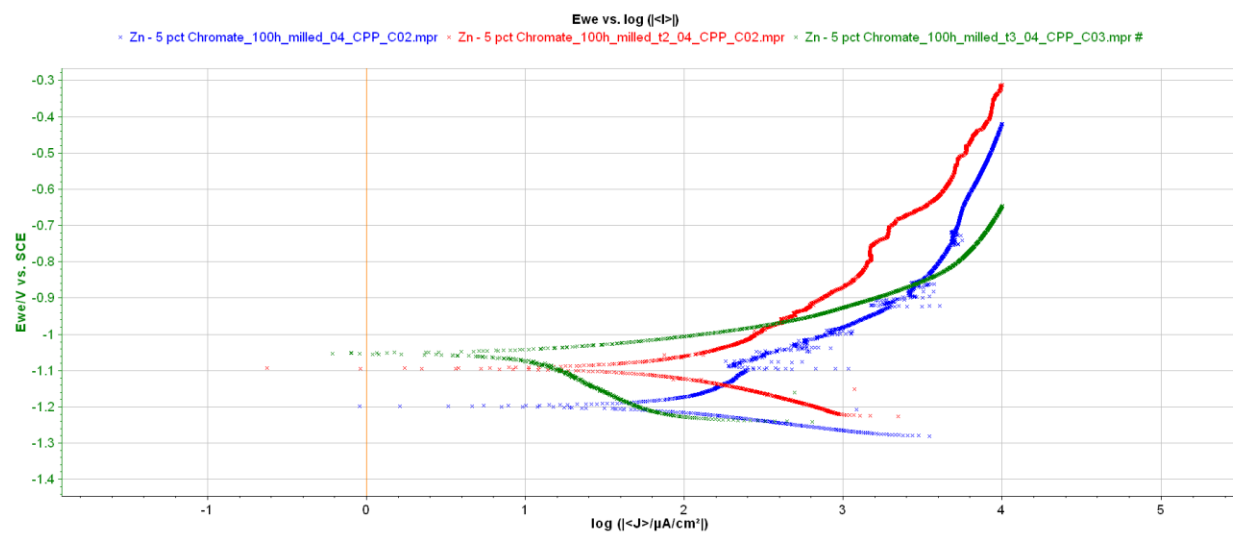


Figure 31: CPP test of Zn 5%  $Na_2CrO_4$

## Appendix B: Raw Data Tables

Table 3: Sample areas of each trial used for testing.

	Trial 1	Trial 2	Trial 3	Trial 4
	Area (cm <sup>2</sup> )			
Pure Mg	0.1597	0.369383	0.2149305	
Mg 1 wt%	0.279	0.329532	0.2367312	
Mg 5 wt%	0.1739	0.12796		0.1480868
Pure Zn	0.1977	0.224623	0.1850313	
Zn 1 wt%	0.2933	0.196821		0.1222535
Zn 5 wt%	0.2961	0.204418	0.2384546	

Table 4: Calculation of polarization resistance from CPP testing.

### Mg 1pct Chromate

Trial 1				Trial 2				Trial 3			
	Initial	Final	Change		Initial	Final	Change		Initial	Final	Change
E (V)	-1.6	-1.15	0.45	E (V)	-1.55	-1.19	0.36	E (V)	-1.6	-1.1	0.5
I (μA/cm <sup>3</sup> )	-2000	8000	10000	I (μA/cm <sup>3</sup> )	-400	4000	4400	I (μA/cm <sup>3</sup> )	-800	8000	8800
	Rp		0.045 kΩ		Rp		0.082 kΩ		Rp		0.057 kΩ

### Mg CPP

Pure Mg				Mg 1% Na <sub>2</sub> CrO <sub>4</sub>				Mg 5% Na <sub>2</sub> CrO <sub>4</sub>			
	Initial	Final	Change		Initial	Final	Change		Initial	Final	Change
E (V)	-1.8	-1.25	0.55	E (V)	-1.6	-1.1	0.5	E (V)	-1.55	-0.93	0.62
I (μA/cm <sup>3</sup> )	-1600	8000	9600	I (μA/cm <sup>3</sup> )	-800	8000	8800	I (μA/cm <sup>3</sup> )	-800	8000	8800
	Rp		0.057 kΩ		Rp		0.057 kΩ		Rp		0.070 kΩ

### Zn CPP

Pure Zn				Zn 1% Na <sub>2</sub> CrO <sub>4</sub>				Zn 5% Na <sub>2</sub> CrO <sub>4</sub>			
	Initial	Final	Change		Initial	Final	Change		Initial	Final	Change
E (V)	-1.23	-0.72	0.51	E (V)	-1.13	-0.6	0.53	E (V)	-1.22	-0.35	0.87
I (μA/cm <sup>3</sup> )	-500	10000	10500	I (μA/cm <sup>3</sup> )	-200	9800	10000	I (μA/cm <sup>3</sup> )	-1000	9000	10000
	Rp		0.049 kΩ		Rp		0.053 kΩ		Rp		0.087 kΩ

## Appendix C: Experimental Parameters

Devices ☒ Turn to OCV between techniques  $\mu$ [

VMP-300 - USB0

Rest for  $t_R$  = 0 h 30 mn 0.000 0 s  
 Limit  $|dE_{we}/dt| < dE_R/dt$  = 0.0 mV/h  
 Record every  $dE_R$  = 10.0 mV  
 or  $dt_R$  = 30.000 0 s  
 E Range = -2 V; 2 V  
 Resolution = 100  $\mu$ V

Experiment

Advanced Settings  
 Cell Characteristics  
 External Devices  
**Parameters Settings**

1 - EVT  
 2 - PEIS  
 3 - EVT  
 4 - CPP

▶ || ⏮ ⏭

Figure 32: Experimental parameters for first EVT test.

Devices ☒ Turn to OCV between techniques  $\mu$ [

VMP-300 - USB0

Excitation signal mode Single sine

Set  $E_{we}$  to  $E$  = 0.000 0 V vs.  $E_{oc}$   
 for  $t_E$  = 0 h 0 mn 0.000 s  
☐ Record every  $dl$  = 0.000 mA  
 or  $dt$  = 0.000 s

Scan from  $f_i$  = 1.000 MHz  
 to  $f_f$  = 10.000 mHz  
 with  $N_d$  = 6 points per decade  
 in Logarithmic spacing  
 sinus amplitude  $V_a$  = 10.0 mV ( $V_{rms} \sim 7.07$  mV)  
 wait for  $p_w$  = 0.10 period before each frequency  
 average  $N_a$  = 2 measure(s) per frequency  
 drift correction ☐  
 Repeat  $n_c$  = 0 time(s)

E Range = -2 V; 2 V  
 Resolution = 100  $\mu$ V  
 I Range = Auto  
 Bandwidth = 8 (~ 11mn19s / scan)

Go back to seq.  $N_s$  = 0 (9999 ends technique)  
 for  $n_f$  = 0 time(s) (0 for new sequence)  
☐ increment cycle number

Experiment

Advanced Settings  
 Cell Characteristics  
 External Devices  
**Parameters Settings**

1 - EVT  
 2 - PEIS  
 3 - EVT  
 4 - CPP

▶ || ⏮ ⏭

Figure 33: Experimental parameters for PEIS testing.

Devices ☒ Turn to OCV between techniques  $\mu$

VMP-300 - USB0

Rest for  $t_R$  = 0 h 5 min 0.000 0 s  
 Limit  $|dE_{we}/dt| < dE_R/dt$  = 0.0 mV/h  
 Record every  $dE_R$  = 10.0 mV  
 or  $dt_R$  = 30.000 0 s  
 E Range = -2V; 2V  
 Resolution = 100  $\mu$ V

Experiment

Advanced Settings

Cell Characteristics

External Devices

Parameters Settings

1 - EVT  
 2 - PEIS  
 3 - EVT  
 4 - CPP

▶ || N ||

Figure 34: Experimental Parameters for second EVT test.

Devices ☒ Turn to OCV between techniques  $\mu$

VMP-300 - USB0

Rest for  $t_R$  = 0 h 0 min 0.000 0 s  
 Limit  $|dE_{we}/dt| < dE_R/dt$  = 0.0 mV/h  
 Record every  $dE_R$  = 0.0 mV  
 or  $dt_R$  = 0.100 0 s

Scan  $E_{we}$  with  $dE/dt$  = 1.000 mV/s  
 from  $E_i$  = -0.200 V vs. Eoc  
 to  $E_L$  = 0.500 V vs. Ref  
 Limit  $|I| > I_p$  = 2.790 mA after  $t_b$   
 $t_b$  = 0.100 0 s from scan beginning  
 Record <1>  
 over the last 25 % of the step duration  
 average N = 5 voltage steps  
 E Range = -2V; 2V  
 Resolution = 100  $\mu$ V  
 I Range = 10 mA  
 Bandwidth = 8

☐ Hold  $E_L$  Until  $|I| > I_p$  (if I limit not previously reached)

☐ End scan to  $E_f$  = 0.000 V vs. Eoc  
 Limit  $|I| < I_f$  = 0.000  $\mu$ A

( $dE/dt \sim 100 \mu$ V / 100 ms)  
 ( $dEN \sim 500 \mu$ V)

Figure 34: Experimental parameters for CPP testing.

Devices

+

-

↕

⌂

⚙

VMP-300 - USB0

Experiment

Advanced Settings

**Cell Characteristics**

External Devices

Parameters Settings

+

-

↕

↔

🔑

1 - EVT

2 - PEIS

3 - EVT

4 - CPP

Cell Description

Electrode material

Initial state

Electrolyte

Comments

Electrode surface area

0.279

cm<sup>2</sup>

Characteristic mass

0.001

g

...

Battery

Corrosion

Equivalent Weight

0.000

g/eq.

Density

0.000

g/cm<sup>3</sup>

Reference Electrode

SCE Saturated Calomel Electrode

...

Offset potential vs. Normal Hydrogen Electrode: 0.241 V

Figure 35: Cell Characteristics parameters for full experimental sequence. Electrode surface area comes from measured area in ImageJ.