Assessment of Galvanic Corrosion in Molten Salts

Scott Edward Massimi[1,2][https://orcid.org/0000-0002-4400-8093], Liam Witteman[1,2][https://orcid.org/0000-0001-8450-8263], Kristin Gauderman[1], and Kerry Rippy[1,2][https://orcid.org/0000-0001-7154-6543]

[1] National Renewable Energy Laboratory, USA.

[2] Colorado School of Mines, USA.

Abstract. Molten salts are an excellent choice for thermal energy storage materials in concentrated solar power (CSP) plants, yet some salts can cause corrosion of containment alloys that damage plants and increase maintenance costs. Corrosion rates have been characterized for many salt/alloy combinations. However, corrosion rates at junctions of dissimilar alloys in molten salts are relatively poorly characterized. At such junctions, which are common in CSP plants, it is possible that galvanic interactions or other mechanisms could increase corrosion above the industry standard of 20 µm/year. Preliminary reports measured corrosion at dissimilar alloy junctions with a variety of methods, but the results are not uniform. Additionally, some reports have shown that corrosion rates are higher for single alloys than for the same alloys when paired in a galvanic couple, suggesting complex corrosion mechanisms. Here we present a discussion on measuring galvanic corrosion in molten salts that accounts for differences in results between methods and explores the possibility of other mechanisms of corrosion in the system.

Keywords: Molten Salts, Galvanic Corrosion, Zero Resistance Ammeter

1. Introduction

1.1 Dissimilar Metal Corrosion in Concentrated Solar Power Plants

Galvanic Corrosion occurs when two dissimilar metals are in contact while in the presence of an electrolyte. The more noble metal in the pair will act as a cathode and be protected from corrosion, while the less noble will act as an anode and be corroded at an accelerated rate. Concentrated Solar Power (CSP) plants have many locations where dissimilar metals meet in the presence of molten salts; therefore, it is important to understand and be able to accurately measure the rate of galvanic corrosion at these sites. Greater understanding of the corrosion in these systems can lead to developing ways to prevent or mitigate the galvanic corrosion. This can be done by either developing a way to prevent the galvanic corrosion outright, such as with a sacrificial alloy, or by simply avoiding alloy pairings that are shown to have higher corrosion rates. However, accurately measuring galvanic corrosion is not always as straightforward as it may seem.

While attempting to measure galvanic corrosion, our preliminary experiments have had unexpected results. For example, we have seen accelerated corrosion in systems that are designed to mitigate galvanic corrosion, such as with the use of cathodic protection. We have also seen examples where negligible galvanic current is measured in a system where we see accelerated corrosion upon the addition of a dissimilar metal. Further experimentation revealed that the corrosion in these systems is much more complex than originally considered.

For example, corrosion rates of two dissimilar metals were shown to be similarly accelerated in molten salts regardless of the electrical connection between the two. Literature examples have shown similar results, a study by Cody Falconer and coworkers demonstrated that a stainless-steel sample had similar corrosion rates both when electrically connected to and insulated from a nickel 201 sample [1]. This study concluded that the presence of the nickel in the salt was enough to accelerate corrosion of the steel because the nickel was acting as a "sink" for the corrosion products coming from the steel. As the steel was corroding, the corrosion products would deposit on the nickel coupon, therefore pulling them out of solution and creating a concentration gradient and accelerating the corrosion. This is just one example of how galvanic corrosion is not always the culprit, even when it appears to be. Therefore, to accurately measure galvanic corrosion in molten salt, it is important to understand and be cognizant of the other types of corrosion that are happening simultaneously.

There are four main mechanisms of corrosion in molten salt systems. They include intrinsic corrosion, corrosion by oxidizing contaminants, differential solubility, and galvanic corrosion [2]. Intrinsic corrosion is a result of differences in the free energy of formation between the salt and the transition metal corrosion products of the material. This corrosion mechanism is more severe in nitrate/nitrite salts than it is in chloride or fluoride salts. Corrosion by oxidizing contaminants is one of the more commonly studied and prolific mechanisms in molten salts. As the name suggests, this mechanism is defined by corrosive impurities such as HCl or HF corroding the material [3]–[5]. Differential solubility is a corrosion mechanism that is driven by concentration gradients of the transition metal corrosion products in the salt. This can be caused by thermal gradients inducing convection in the molten salt [6], or by the presence of a dissimilar material that acts as a sink for the corrosion products. Falconer et al show how this mechanism can be easily mistaken for galvanic corrosion in relevant systems [1]. Galvanic corrosion is a result of electrical connection between two materials in the presence of an electrolyte, which drives the oxidation of the less noble material.

When attempting to physically measure the effect of a single corrosion mechanism, such as galvanic corrosion, all other mechanisms must be accounted for in experimental design and alternative experiments should be used for comparison. The goal of this article is to examine how galvanic corrosion has been measured in molten salts and suggest ways to account for other corrosion mechanisms or use alternative means, such as electrochemical methods, to achieve more accurate results.

2. Discussion

2.1 Measuring Galvanic Corrosion in Molten Salts with Immersion Testing

One of the more common methods used to measure galvanic corrosion in molten salts is with an immersion test. This is done by submerging a connected pair of metals into a molten salt bath and heating for a set period of time. After subjecting the alloy pairs to the corrosion conditions, the samples are examined for mass loss and chromium (or other alloying metal) depletion to determine the depth and rate of corrosion. This method is important because it allows us to directly measure the corrosion in a sample, while other methods are often measuring it indirectly. It also will show irregularities in the corrosion, making it a good comparison for corrosion during actual application [7]. However, this test is not specific to galvanic corrosion, and the other mechanisms of corrosion should be accounted for in experimental design.

When measuring galvanic corrosion in molten salts it is important to account for the fact that the electrolyte itself is corrosive, even without a galvanic connection. With an immersion corrosion measurement, it is difficult to know how much of the measured corrosion is from galvanic corrosion rather than intrinsic or impurity driven corrosion. Intelligent

experimental design can help determine the difference. For example, if one wanted to measure the rate of galvanic corrosion between Hastelloy C276 and Haynes 230 alloys, they would not only measure the corrosion rate of the galvanically connected samples, but also measure the corrosion rate of the samples independently in the same conditions.

It is also important to account for other dissimilar metal corrosion mechanisms, such as differential solubility. For example, Falconer et al demonstrated that corrosion rates were similarly accelerated both when electrically connected and insulated while submerged in the same molten salt [1]. They attributed the increased corrosion to an activity gradient that was caused by having the different metals in the solution. This is something that can easily be accounted for in galvanic corrosion measurements by measuring the corrosion rate of the alloys that are in the same molten salt crucible but are not electrically connected. If the corrosion rates for this and the galvanically connected experiments are similar, it could suggest that galvanic corrosion is not the main route of corrosion in the system.
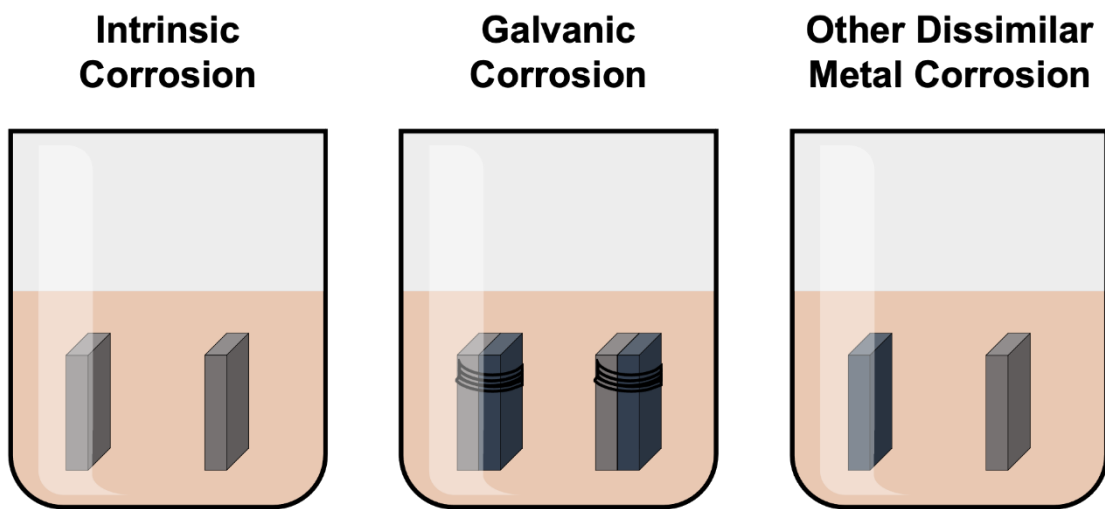

Figure 1. Example of Immersion test, accounting for three different mechanisms of corrosion for a two-alloy system.

2.1.1 Analysis of Galvanic Corrosion Immersion Tests

Analysis of the results from the immersion tests is typically done using two techniques. The first technique is by simply measuring the mass lost from each sample. Measuring the mass of the samples before and after the corrosion test allows for a direct quantification of the corrosion and gives a good indication of how the different experimental conditions are affecting the materials.

The other technique needed to analyze the immersion test is energy dispersive X-ray spectroscopy (EDS), typically done with a scanning electron microscope (SEM). This technique is used to measure and visualize the corrosion of the samples. It is common to see the less noble element in an alloy be selectively depleted in high temperature corrosion environments [8]. This element, usually chromium in the relevant examples [9], is the first to be oxidized and dissolved into the melt. While this presents a problem for the application of these materials, measuring the depth of elemental depletion in a sample is a commonly used way to show the extent of the corrosion.

A cross-sectional analysis of a sample after the immersion test provides important details into the corrosion that took place. As shown in **Figure 2**, Sridharan and coworkers illustrate how elemental depletion, in this case chromium, will show the depth of corrosion in a sample [9]. **Figure 2** shows a line scan analysis of a cross section of 316L stainless steel after an immersion test in a fluoride based molten salt. As the scan gets further from the surface of the 316L that was exposed to the molten salt, the chromium levels rise to the normal atomic composition, from a depleted level that is a result of the corrosion. The corrosion depth can be assumed to be as deep as the chromium depletion is measured.
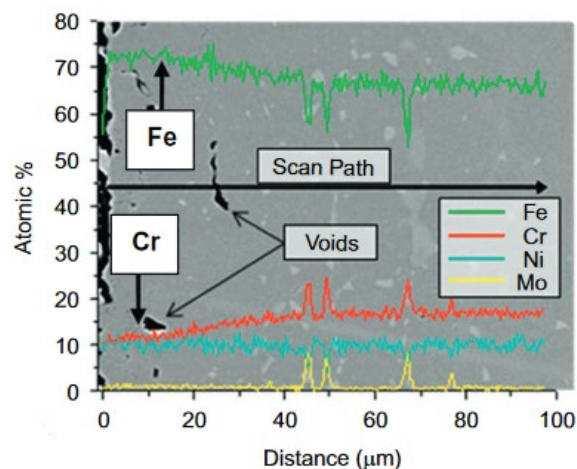

Figure 2. Image of SEM/EDX cross section analysis, showing the depletion of chromium and other alloying elements in 316L stainless steel after exposure to molten fluoride salt.

2.2 Electrochemical Methods for Measuring Galvanic Corrosion in Molten Salts

It must be noted that immersion testing in molten salts are complicated corrosion systems, and many variables influence the corrosion rate. While it is possible to determine the rate of each corrosion mechanism individually, it is much harder to know what is happening in the final system, especially when galvanic corrosion is involved. This is one of the challenges of the immersion testing method. However, there are electrochemical tests that can provide more nuanced information about the corrosion, especially when combined with immersion testing.

One of the more useful techniques uses a zero resistance ammeter (ZRA) to measure the galvanic current between the two samples. By connecting the two metals with a wire that's run through a ZRA, the galvanic current that flows between the alloys can be measured [10]. The measured current can then be used to calculate the corrosion rate. This technique is useful because it only measures the galvanic corrosion in the system, ignoring the effect of other corrosion mechanisms. This allows us to compare the results with the immersion test and start to understand how each other corrosion mechanism contributes to the total.

Another technique that can be used is called a potentiodynamic polarization sweep (PPS) or simply potentiodynamic polarization (PDP). PDP is used to measure the corrosion potential (E_{corr}) and corrosion current (I_{corr}) of an electrode in an electrolyte. This is done by first finding the open-circuit potential (OCP) of the material and then sweeping the applied potential from cathodic to anodic polarization while measuring the current density [4]. The resulting polarization curves are used to find the anodic and cathodic Tafel slopes, the intersection of which provide the E_{corr} and I_{corr} of the material. These values can then be used to estimate the corrosion rate of the material in the electrolyte [11]. While this is traditionally a method that predicts the corrosion rate of a single material, superimposing the Tafel plots of two materials, measured separately, allows to find E_{corr} and I_{corr} of the galvanic couple, or E_{couple} and I_{couple}. The point at which the cathodic and anodic potential of the materials intersect represents where the two materials would be polarized to equal potentials if they were coupled [12]. **Figure 3** illustrates how the corrosion current is determined by superimposing the Tafel plots of two separately measured materials [13]. This information can again be used to determine the corrosion rate of the materials in mm/year. However, this method can only provide an estimate of the galvanic corrosion due to the imprecise nature of calculating Tafel plots. It is still extremely useful for screening large numbers of materials and for comparison with other results.
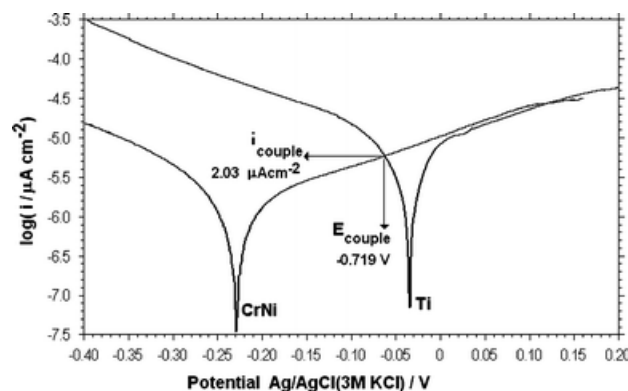

Figure 3. Determination of I_{couple} and E_{couple} from separately measured Tafel plots.

3. Conclusion

While measuring galvanic corrosion can appear as simple as measuring intrinsic corrosion, it is actually more complicated. Accounting for the other mechanisms of corrosion in experimental design can drastically improve the accuracy and reproducibility of results. Control experiments help to decipher the contribution that galvanic corrosion actually has in the total corrosion results. Additionally, the use of electrochemical methods such as ZRA and PDP are useful tools that should be considered when available. And while it can still be difficult to know how corrosion mechanisms interact in the final system, using all tools available can help give a stronger answer.

Data availability statement

This submission is a review of the literature and the opinions formed from that review. The discussion presented is not based on data that was collected independently.

Author contributions

Scott Edward Massimi, Kerry Rippy, Liam Witteman, and Kristin Gauderman: All authors contributed equally to this document.

Competing interests

The authors declare no competing interests.

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