Electrochemical Characterization of Corrosion Behavior of Zinc in Different Sodium Chloride Solution by comparing Two Electrode and Three Electrode Setups

Shwe Wut Hmon Aye[1]

[1]West Yangon Technological University, Pathein-Nyaung Tone Street, Yangon, Myanmar

Abstract- Zinc is highly reactive in all kinds of environments and has a natural tendency to form different types of corrosion products with different corrosion rates. Electrochemical studies typically use a conventional three-electrode setup to study the mechanisms and propose advanced corrosion models. However, for certain electrochemical applications a two-electrode configuration is more suitable. In particular, the analysis of atmospheric corrosion with microelectrodes under very thin electrolyte layers would benefit from such a configuration. In this investigation, a two-electrode configuration was compared with a conventional three-electrode cell to study the corrosion behavior of zinc.

The aim of this work is to evaluate the corrosion behavior of zinc and compare the two-electrode and three-electrode setups. The corrosion resistance was compared in different sodium chloride solutions (1 M, 0.1 M, 0.01 M, 0.001 M) using linear sweep voltammetry and electrochemical odd-random phase multisine impedance spectroscopy.

The results reveal that the corrosion current is higher when the chloride concentration was increased in three-electrode setup. In the two-electrode system, the polarization curve is symmetric for the different concentrations. Furthermore, multisine measurement confirmed that corrosion current increased when the concentration increased. Using both electrode setups a clear evolution of the corrosion behavior of zinc with time is observed. The two-electrode setup gives similar impedance values, however only after taking into account the contributions of both electrodes.

Index Terms- Atmospheric corrosion, Zinc, Electrochemistry, Polarization curves

I. INTRODUCTION

Corrosion is the gradual degradation of a material by chemical and electrochemical reactions when a material is exposed to an aqueous or an atmospheric environment. Corrosion occurs because of the natural tendency of metals to react electrochemically with oxygen, water and alternative substances in the atmosphere. Most corrosion phenomena are of electrochemical nature and consist of at least two reactions occurring at the metal-electrolyte interface: the anodic and cathodic reactions. At the anodic electrolyte-metal interface, the metal is oxidized to form positively charged ions that go into solution or form solid compounds such as oxides.

This reaction releases electrons, which in turn, are consumed by one or several cathodic reactions at the cathodic electrolyte-metal interface.

Industrial outdoor exposure tests give general information related to the damage effect of the test material in a specific corrosion environment. These tests take too long to obtain rapid information on the corrosion of the material. Therefore, accelerated tests in controlled atmospheres are preferred. The most used test methods include salt spray tests [ISO 9227:2012]. Yet these tests still offer limited understanding of the underlying corrosion mechanism. In comparison, corrosion measurements in laboratories give wider information on the corrosion mechanism, since different corrosion environments can be tested and much more detailed measurement data can be obtained in well-controlled conditions. Hence, kinetic and mechanistic analysis can be performed in relatively short times. These analyses provide a good estimation of the materials behavior and can be used as starting point for designing corrosion models. However, most laboratory tests are performed under standard submerged conditions, which still differ from real (atmospheric) corrosion conditions.

To study the corrosion of materials, a number of electrochemistry techniques have been developed over the years. Especially linear sweep voltammetry, cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy are widely used to characterize the electrochemical behavior of metals. The conventional setup consists of a potentiostat with a three-electrode cell. In a three-electrode cell the potential of the working electrode (WE) is controlled versus a reference electrode (RE) and the current flows between the working and a counter electrode (CE). Three-electrode configurations are designed so that the experimental data are totally determined by the chemistry of the working electrode [1]; in corrosion this is the studied material. The reference electrode should maintain a constant potential throughout the experiment. The function of the counter electrode is to provide a current of equal magnitude but opposite sign to that at the working electrode; the electron-transfer reaction at the counter electrode will be that which is easiest in the electrolyte solution.

Atmospheric corrosion is considered to take place on a metal surface covered with a thin layer of dilute electrolyte produced by condensation or adsorption [2]. Studies on atmospheric corrosion of metals under thin electrolyte layers have been carried out with dedicated experimental setups [3, 4,

5]. The electrochemical study of corrosion under these thin films is challenging; due to a limited electrolyte volume it is difficult to introduce all probes and electrodes. In this regard, the three-electrode setup is not the most suitable configuration in practice. That is the reason why in this study a two-electrode setup is tested and validated for the study of zinc corrosion. The basic configuration is used with one electrode as the working electrode and the second electrode connected to the reference and counter electrode inputs of the potentiostat.

Zinc and zinc alloys are used in many engineering applications. A main application is the galvanized coating on steel, which prevents oxygen and moisture from reaching the underlying metal and provides cathodic protection to the substrate. The corrosion behavior of zinc depends on the environmental conditions and electrolyte concentrations. The effect of corrosion can be either locally concentrated (pitting, crevice corrosion) or can be extended uniformly over a greater surface (uniform corrosion). The main factors affecting the corrosion rate and type of corrosion are the type of dissolved species, concentration, pH and temperature. They influence the structure and composition of the resulting films and corrosion products on the surface, which in turn control the corrosion process of zinc.

In the corrosion of zinc, Zn^{2+} ions are released from anodic areas and hydroxide ions are formed at cathodic areas due to the oxygen reduction. The precipitation products of the released ions can form a protective layer on the zinc surface in near neutral aqueous solutions under atmospheric conditions. This layer inhibits the corrosion reactions, providing a better corrosion resistance. In the overall process the anodic and cathodic reactions have to balance each other and thus the corrosion rate is limited by the diffusion of oxygen to the cathodic areas. This can be observed in the polarization curves, which show a limiting current during cathodic polarization.

The present study investigates the corrosion behavior of zinc in different sodium chloride solutions by using linear sweep voltammetry and odd-random phase multisine impedance spectroscopy (ORP-EIS) with a conventional three-electrode system and a two-electrode system. The aim of this work is to validate the two-electrode setup as a tool to evaluate corrosion mechanisms. This allows carrying out electrochemical studies in otherwise inaccessible geometries in applications such as microelectrodes, sensors, thin film analysis and batteries.

II. EXPERIMENTAL

A. Sample and solution preparation

The chemical composition of the zinc sheet is titanium 0.06 to 0.2% (weight percent), copper 0.08 to 1.0% (weight percent), aluminum 0.015% (weight percent) and balanced zinc. The thickness of the zinc sheet is 0.75 mm. First, the zinc sample was cleaned in an ultrasonic bath in ethanol for 30 minutes. Then the sample was washed several times with deionized water and dried at 60°C. A working surface of 5.08 cm^2 was left exposed, while the other areas were sealed with tape.

B. Electrochemical measurements

The linear sweep voltammetry measurements were carried out with potentiostat PGSTAT12 (Metrohm

Autolab). The samples were polarized cathodically and anodically from 0 to ±0.6 V versus the open circuit potential, in separated experiments, with a scan rate of 0.1 mV/s. The measurements were performed after one hour of immersion in sodium chloride. Odd random phase multisine impedance (ORP-EIS) [7] was measured with a Wenking potentiostat POS2 (Bank Elektronik) and a National Instruments PCI-4461 DAQ-card. The applied multisine signal is digitally composed with MATLAB R2010a software (Mathworks). MATLAB is also used for processing the collected data and controlling the DAQ-card. The frequency range analyzed was 0.01Hz to 10 kHz and the amplitude of the sinusoidal voltage signal applied, around the open circuit potential, was 3mV rms. The evolution of the corrosion behavior of the zinc plate was recorded with impedance measurements every 30 min for 24 h during constant immersion in the electrolyte. All experiments were conducted in aerated solution.

The data analysis provided by the ORP-EIS includes information about the noise level, the non-stationary behavior and the non-linear behavior [7]. This analysis verifies whether the impedance data have a good signal-to-noise ratio and whether the conditions of stationarity and linearity, necessary for correct experimental data [6], are fulfilled. The standard deviations on the excited and non-excited frequencies are compared to analyze the characteristics of the electrochemical system. The detailed description of the technique and the noise analysis can be found in [7].

For the conventional three-electrode setup, saturated silver-silver chloride electrode was used as the reference electrode, a platinum grid was used as the counter electrode and the zinc plate was the working electrode. For the two-electrode system, one zinc plate was the working electrode and a second (identically treated) zinc plate was the reference and counter electrode.

C. Chemical and electrochemical reactions

In this work, we only consider the reactions explained in this section. It is well known that the corrosion of zinc occurs through the following reactions [8]:

Zinc dissolution reaction

$$Zn \leftrightarrow Zn^{2+} + 2e^- \qquad (1)$$
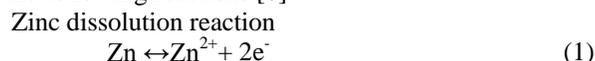
Oxygen reduction at the zinc surface according to the half-cell reaction

$$O_2 + 4e^- + 2H_2O \leftrightarrow 4OH^- \qquad (2)$$

Reaction of the zinc cations and the hydroxide anions producing the zinc hydroxide

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2 \qquad (3)$$

In the presence of sodium chloride, migration of the chloride ions (Cl^-) to anodic sites where zinc hydroxide chloride is formed

$$5Zn(OH)_2 + 2Cl^- + H_2O \leftrightarrow Zn_5(OH)_8Cl_2.H_2O + 2OH^- \qquad (4)$$
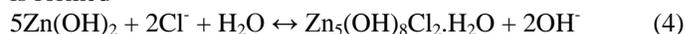
III. RESULTS AND DISCUSSIONS

To characterize the corrosion behavior of zinc, we used two electrochemical techniques; linear sweep voltammetry and multisine impedance. In this study, the corrosion behavior of zinc is characterized by studying the oxidation and reduction reactions. These are represented by zinc dissolution and oxygen reduction, respectively. The reduction of the dissolved oxygen is

limited by oxygen diffusion resulting in a limiting current during cathodic polarization.

A. Linear sweep voltammetry

Polarization curves for the three-electrode setup. Anodic and cathodic polarization curves were performed with the sample exposed to different concentrations of NaCl; 1 M, 0.1 M, 0.01 M and 0.001 M. Figure 1(a) shows the trend for the open circuit potential (OCP) or corrosion potential measured before both the anodic and cathodic polarizations. The OCP shifted to more negative values for higher concentrations. A lower OCP indicates that the metal is less resistant to corrosion. So, as expected, the corrosion resistance is lower for higher sodium chloride concentrations.

Figure 1(b) shows the changes in the polarization curve of zinc with different concentrations of sodium chloride. Since the OCP shifted for the different concentrations, the polarization curves are plotted as a function of the overpotential, which is the difference between the measured potential and the open circuit potential. The curves for positive overpotential (anodic polarization) and negative overpotential (cathodic polarization) are recorded separately.

Anodically, it is clear that the higher the concentration, the steeper the anodic polarization, which indicates strongly enhanced zinc oxidation. Cathodically, the kinetics are limiting and strongly influenced by the diffusion of oxygen to the metal-solution interface. At OCP, the reduction and oxidation currents are equal, so the overall corrosion current is equal to the cathodic limiting current density.
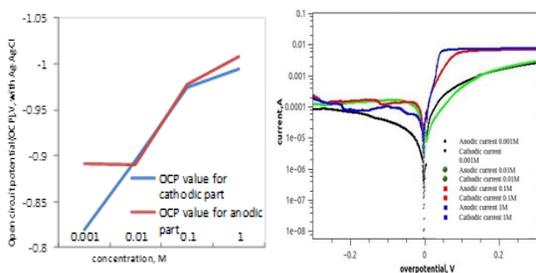
Figure 1. (a) Open circuit potentials for the different concentrations. (b) Cathodic and anodic polarization curves of zinc in different sodium chloride solutions with the three-electrode setup.

It is difficult to have a quantitative discussion on the limiting current for the oxygen reduction (Figure 1(b)), because of the fluctuations in the current. It can be seen that, generally in the potential range from 0 V to -0.2 V, the limiting current was decreased when the concentration was increased. This is due to the fact that the corrosion products block the metal surface, inhibiting oxygen diffusion. Therefore, the limiting current decreases. These results are in agreement with the paper by Yadav et al [9]. For very low chloride concentrations, the solution resistance is so high that the low current cannot be accounted to diffusion limitations. Instead, it is assigned to a high ohmic drop in solution. As a conclusion, the variation of the limiting current was not as high as expected; from the polarization curve we see that mainly the dissolution of zinc is influenced. This is attributed to a lower charge transfer resistance

due to dissolution of the oxide/hydroxide film on the zinc in chloride-enriched environments.

Polarization curves for the two-electrode setup. In the two-electrode setup (Figure 2), the anodic and cathodic polarization currents are symmetrical because the two electrodes are assumed to be identical. For every concentration, both anodic and cathodic regions show comparable current densities. Region I is the region of mixed kinetics between zinc oxidation and oxygen reduction. In this region, we observe the influence of the chloride concentration on the oxidation reaction; a higher slope in the exponential region is linked to higher sodium chloride concentrations. The same behavior was concluded from the polarization curves with the three-electrode system.

In regions II and III, the current is limited by the oxygen reduction reaction. We observe that with a higher sodium chloride concentration a higher limiting current is measured. This is counterintuitive because the saturation concentration and the diffusivity of oxygen decreases in more concentrated NaCl solutions and, therefore, the limiting current would diminish as well, according to the following equation:

$$i_{lim} = j_{lim} \times A = \frac{nFC_sD}{\delta} \times A, \qquad (1)$$

where i_{lim} = limiting current (A), j_{lim} = limiting current density (A/m^2), C_s = concentration of dissolved oxygen (mol/m^3), n = number of exchanged electrons, D = O$_2$ diffusion coefficient (m^2/s), F = Faraday constant, 96485 C/mol, δ = diffusion layer thickness (m), A = electrode surface (m^2).
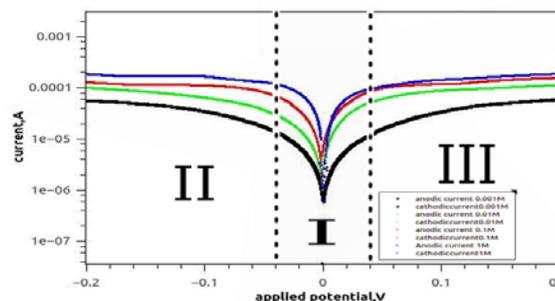
Figure 2. Cathodic and anodic currents for zinc in different sodium chloride solutions with the zinc-zinc two-electrode setup.

A possible explanation of the increase of the limiting current is the increase of the working electrode surface area due to zinc deposition. Although the overall reaction is limited by oxygen reduction, the counter reaction is the oxidation of the second zinc electrode, which brings Zn^{2+} ions in the solution. This means that oxygen reduction is no longer the only reaction in the cathodic part. Oxygen reduction and zinc deposition take place together, at the negatively polarized electrode. With higher NaCl concentrations, more metal of the counter electrode is dissolved, hence the concentration of Zn^{2+} ions is higher and more Zn would be deposited on the working electrode. Due to zinc deposition, the active surface increases; this may increase the limiting current, according to equation (1).

In summary, from both setups it can be concluded that at the initial stages the zinc oxidation reaction is more favored when the concentration is increased. However, the limiting current in the cathodic polarization (corresponding to the oxygen reduction) did not show the expected behavior. Still, similar trends were observed in the kinetic region (close to OCP) of the

cathodic side with both electrode configurations. That confirms the possibility to use the two-electrode cell for kinetic corrosion studies.

B. Impedance spectroscopy

Impedance spectroscopy is a method to study the electrochemistry around the corrosion potential, without having to polarize the sample. With this technique we could eliminate the effect of zinc deposition in the two-electrode configurations.

The corrosion of Zn in NaCl was also investigated with both electrode setups using ORP-EIS. The impedance spectroscopy measurements were performed every 30 min during 24h. There is a clear evolution of the corrosion behavior of the zinc sample during the measurement time, as it can be seen for the Bode plots of the impedance in Figure 3. Over time the modulus of the impedance lowers and the phase curve also reduces and its minimum shifts to lower frequencies, but they seem to stabilize in the last measurements.
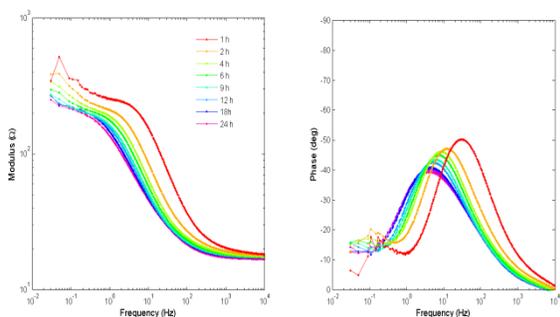
Figure 3. Bode plots of the impedance of zinc in 0.01 M NaCl with the two-electrode cell during 24 h immersion. (a) Modulus. (b) Phase angle.

Zinc presents distinct impedance responses for the different concentrations of NaCl, as shown in Figure 4 for the two-electrode cell. The lower the concentration of the electrolyte, the less attacked the metal and the higher its impedance (Figure 4(a)) and the more the phase minimum shifts to lower frequencies (Figure 4(b)). It is interesting to point out the different magnitude of the impedance at high frequencies for the different solutions, which corresponds to the resistance of the solution: as expected its value diminishes with a higher concentration of electrolyte. A similar trend of the impedance is observed with the three-electrode setup.
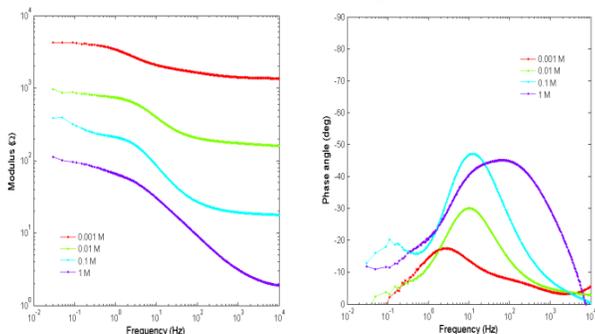
Figure 4. Bode plots of the impedance of zinc in different concentrations of NaCl with the two-electrode cell after 2 h immersion. (a) Modulus. (b) Phase angle.

One of the main advantages of the ORP-EIS technique is the analysis of the linearity and stationary of the

electrochemical impedance. To simplify the interpretation of the noise analysis, three curves are presented together with the impedance measurements, as it is illustrated in Figure 5. If the curves of 'noise + non-stationarities' and 'noise level' overlap, the system is stationary, i.e., time-invariant. If the curves of 'noise + non-linearities' and 'noise level' coincide, the system behaves linearly. In Figure 5(a), for the impedance after 2 h, the noise curves do not fall together, therefore, the electrochemical system is time-variant and non-linear; although the non-linearities can be misinterpreted because of the high level of non-stationarities (3 orders of magnitude higher than the noise). Yet, the impedance after 12 h is stationary and linear, as seen in Figure 5(b). These results show that the zinc corrosion is more time-variant in the first experiments and it varies less with time for longer immersion times. This confirms the behavior observed in the sequence of consecutive measured impedance (Figure 3).
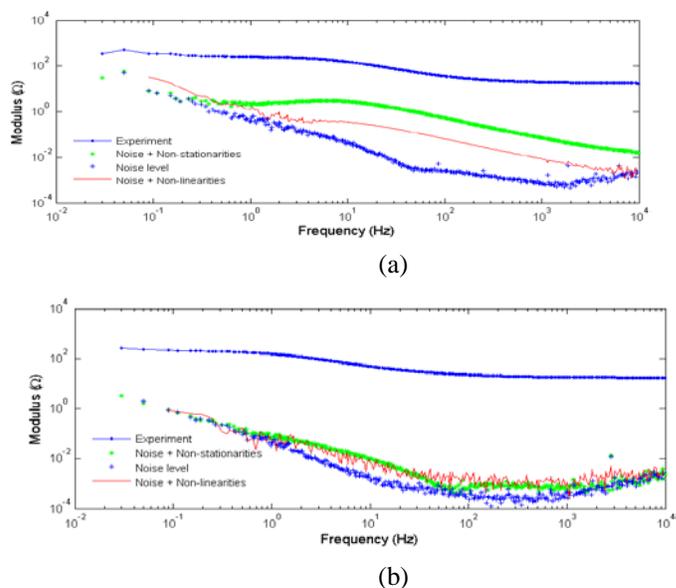
Figure 5. Analysis of the linearity and the stationarity of the impedance measurements of zinc in 0.01 M NaCl with the two-electrode cell: (a) after 2 h; (b) after 12 h.

To better understand the corrosion of the zinc, the impedance data were modeled with the electrical equivalent circuits (EEC) displayed in Figure 6, in which Rs is the resistance of the solution, R1 is the charge transfer resistance, CPE1 is the constant phase element corresponding to the double layer, R2 is the resistance of the oxide layer formed, CPE2 is the constant phase element corresponding to the oxide layer and W is the Warburg impedance caused by the diffusion of species from/towards the electrode/electrolyte interface [2, 10]. The inclusion of the Warburg element (Figure 6 (b)) was needed to model the impedance of zinc in the more concentrated solutions, 1 M and 0.1 M. For the lower concentrations, 0.01 M and 0.001 M; the circuit in Figure 6 (a) was used.

(a)

(b)
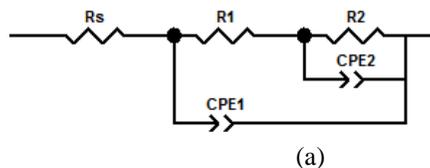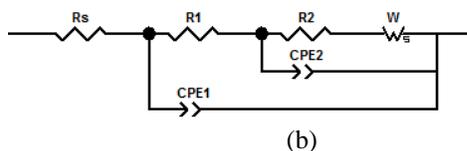
Figure 6. Electrical equivalent circuits used to model the impedance experiments.

The double layer and oxide layer capacitances are, therefore, modeled with a CPE that accounts for the imperfections of the surface. The impedance of the CPE is formulated as a function of the frequency f with the Q and α parameters according to $ZCPE = 1/[Q•(j•2πf)α]$.

The evolution of the parameters for the 24 h immersion in 0.01M NaCl can be seen in Table 1. It is clear that R_1 increases, which indicates that the metal is more resistant to corrosion. R_2 first increases slightly but after 9 h starts to decrease, that is, the resistance of the oxide layer becomes less resistant.

Table 1. Estimated parameters of the EEC for the impedance of zinc in 0.01 M NaCl during 24 h with the two-electrode configuration; all parameter errors are below 15%.

time (h)	R_1 (Ω)	R_2 (Ω)
2	44	619
4	90	660
6	106	677
9	113	684
12	150	675
15	210	616
18	258	553
21	320	435
24	350	381

The impedance data of zinc in different sodium chloride concentrations were also modeled. The calculated resistances of the double layer and the oxide layer after 15 h immersion are displayed in Table 2. In agreement with the trend observed in Figure 4, the resistances of both the double layer and the oxide layer are lower with higher concentrations of NaCl.

Table 2. Estimated resistances for the impedance of zinc in different concentrations of NaCl after 15 h immersion using the two-electrode cell; all parameter errors are below 15%.

[NaCl] (M)	R_1 (Ω)	R_2 (Ω)
1	15	97
0.1	35	166
0.01	210	616
0.001	242	1840

Regarding the impedance measured with each of the electrode configurations, it was observed that the impedance using two electrodes was always higher than the one with the three-electrode cell. This can be easily seen in the modulus of the impedance shown in Figure 7.
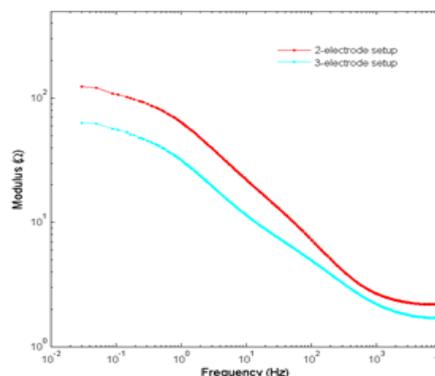
Figure 7. Modulus of the impedance of zinc in 1 M NaCl after 15 h immersion using the two-electrode and three-electrode setups.

This observation is due to the contribution of the CE/electrolyte interface, which cannot be neglected using two identical electrodes. In EIS experiments the total impedance of the circuit WE-CE is measured, that is, the contributions from both electrodes are recorded together. In a conventional three-electrode setup, the CE has a significantly higher surface area than the WE, therefore, its impedance is very low and the total impedance is dominated by the one on the WE. Thus, the only contributions observed with the conventional cell are the electrolyte resistance and the impedance of the WE/electrolyte interface. However, for the two-electrode configuration used in this work, both electrodes have the same area, hence, the impedances on the CE and WE contribute similarly to the total impedance. Since the WE and CE are in a serial circuit, the impedance recorded is the sum of the impedances on both electrodes. This is confirmed with the values of the estimated resistances R1 and R2, which are 1.8-2.3 times higher with the two-electrode cell than with the three-electrode cell.

The two-electrode setup in combination with electrochemical impedance spectroscopy represents an appropriate tool to measure and model electrochemical systems. However, with identical counter and working electrodes, special consideration is required to obtain the proper impedance values. The measured impedance should be corrected to take into account the doubled impedance of the WE/CE system. One practical way is by expressing the impedance per unit area, considering the sum of the areas of the two electrodes.

IV. CONCLUSIONS

Both two-electrode and three-electrode setups show that the oxidation reaction of zinc is more favored with higher NaCl concentrations during the initial stages of corrosion. A similar trend is observed with impedance and polarization techniques. The limiting currents for oxygen reduction are higher with higher concentrations of sodium chloride. Although this is counterintuitive, this effect has been assigned to the deposition of zinc ions. These ions are produced at the zinc counter electrode, after deposition they enlarge the surface area of the working electrode, which results in a higher limiting current. With multisine impedance, higher impedances are measured with lower electrolyte concentrations, showing that the metal is more resistant to corrosion. The same trend is obtained with the two and three-electrode setups. With both electrode setups, the

corrosion of zinc is more time-variant in the first experiments and it varies less with time after several hours of immersion.

When using the two-electrode setup with impedance spectroscopy, the areas of both the working and counter electrodes should be taken into account to calculate the impedance per unit area. Following the conclusions above, the two-electrode setup is validated for the study of the corrosion behavior of materials in inaccessible geometries for applications such as microelectrodes, sensors, thin film analysis and batteries.

ACKNOWLEDGMENT

REFERENCES

[1] D. Pletcher, A first course in electrode processes. Electrochemical consultancy, 1991.

[2] L. Zheng, F. Cao, W. Liu, B. Jia, J. Zhang "Corrosion behavior of pure zinc and its alloy under thin electrolyte layer," Acta Metallica Sinica Letters23 (6), (2010) 416–430.

[3] S. H. Zhang,S. B. Lyon, "Anodic processes on iron covered by thin, dilute electrolyte layers (I)—anodic polarisation," Corrosion Science, 36 (8) (1994) 1289–1307.

[4] M. Stratmann, H. Streckel, "On the atmospheric corrosion of metals which are covered with thin electrolyte layers—I. Verification of the experimental technique," Corrosion Science 30 (6–7) (1990) 681–696.

[5] M. Stratmann, H. Streckel, K. T. Kim, S. Crockett, "On the atmospheric corrosion of metals which are covered with thin electrolyte layers-iii. the measurement of polarisation curves on metal surfaces which are covered by thin electrolyte layers," Corrosion Science 30(6–7) (1990) 715–734.

[6] J.R. Macdonald (Ed.), Impedance Spectroscopy. Emphasizing Solid Materials and Systems, John Wiley & Sons, Inc., 1987.

[7] Y. Van Ingelgem, E. Tourwé, O. Blajiev, R. Pintelon, A. Hubin, "Advantages of OddRandom Phase Multisine Electrochemical Impedance Measurements", Electro-analysis 21 (6) (2009) 730.

[8] F. Rosalbino, G. Scavino, D. Macciò, A. Saccone, "Influence of the alloying component on the corrosion behaviour of zinc in neutral aerated sodium chloride solution," Corrosion Science, 89 (2014) 286–294.

[9] A. P. Yadav, A. Nishikata, T. Tsuru, "Oxygen reduction mechanism on corroded zinc," Journal of Electroanalytical Chemistry, 585 (1) (2005) 142–149.

[10] Y. Hamlaoui, F. Pedraza, L. Tifouti, "Corrosion monitoring of galvanised coatings through electrochemical impedance spectroscopy", Corrosion science, 50 (2008) 1558-1566.

AUTHOR

Author – **Shwe Wut Hmon Aye,** Professor and Head, Department of Metallurgical Engineering and Materials Science, West Yangon Technological University, hmon152@gmail.com.