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Electrochemical Characteristics of Coated and Uncoated Aluminium in 0.5 M H₂SO₄ Solution

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Abstract:

The electrochemical corrosion behaviour of coated and uncoated Al samples were studied in 0.5 M H₂SO₄ using open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization (PDP) techniques. OCP measurement revealed that the coated Al exhibited lower susceptibility to dissolution in the electrolyte solution, compared with the uncoated Al. Based on EIS analysis; this barrier decreased the quantity of charge which can be stored in the Al/electrolyte interface, and increased the charge transfer resistance. Potentiodynamic polarization confirmed that the coating definitely increased the corrosion resistance of the Al sample by lowering both the cathodic and anodic half reactions in the acid solutions.

1. Introduction

Aluminium and its alloys are materials of choice in many industrial applications such as in building, electronic devices, automobiles, and aviation etc. The immense industrial application of aluminium and its alloys is due to the low density, attractive appearance, high thermal and electrical conductivities and most importantly good corrosion resistance. Importantly, the corrosion resistance of aluminum is attributed to the tendency of aluminium to form a compact passive adherent oxide film on the surface which creates a formidable barrier between the aluminum surface and the aqueous solution (Zhang, and Hua2010). Unfortunately, however, this passive oxide film is amphoteric and would not guarantee an increased corrosion resistance during the corrosion of aluminum in acid and alkaline solutions (El-Maghraby 2009, Hurlen *et al.* 1984, Oguzie *et al.* 2007).

The application of coatings on metal surfaces is a veritable means of increasing its corrosion resistance. For organic coatings, the mechanism of increasing the metal corrosion resistance is by increasing the hydrophobicity of the metal surface and decreasing the interaction of the metal surface with the aqueous solution. For instance, Wei *et al.*, (1995) reported that the application of doped or undoped polyaniline coatings on cold rolled steel (CRS) could increase the corrosion resistance of the steel substrate under various conditions. Similarly, Stankovic *et al.*, (2005) employed detailed electrochemical techniques (such as polarization and electrochemical impedance spectroscopy) complimented with thermo gravimetric technique and observed that an electrodeposited epoxy coating could greatly improve the corrosion performance of aluminum in 3% NaCl solution. The authors further reported that the performance of the epoxy coating on aluminium were significantly higher than when applied on other substrates such as steel and phosphatized steel. This indicates that aluminum could serve as a good substrate for the application of epoxy coatings. Nevertheless, reports on the corrosion performance of epoxy-coated aluminum are still scarce in acidic solutions. It is envisaged that in an acid solution, the barrier

properties of the epoxy coating could decrease the tendency for the dissolution of the protective aluminum oxide, thus, increasing the corrosion resistance of the metal in such medium.

In the present work, we investigate the electrochemical properties of an epoxy – coated aluminum metal in 0.5 M H₂SO₄ solution. We hope that the results from this work may contribute to the growing knowledge of the behaviour of epoxy coatings on aluminum, especially, in acid solutions.

2. Experimental

2.1. Material Preparation

Pure aluminum coupons with dimension 10 X 10 X 1 mm³ were supplied by First Aluminum Company Ltd., Rivers state, Nigeria. The pure aluminum coupons had composition: Cu [0.1%], Si [0.5%], Fe [0.6%], Mn [0.1%], and Al [99%]. In comparison, epoxy coated aluminum coupons were also provided by the same manufacturer. The dimensions of the epoxy coated aluminum coupons were 10 X 10 X 1.5 mm³. The coated and uncoated Al coupons were used as supplied without grinding the surface. The samples were pre-treated by cleaning with acetone and ethanol followed by rinsing with distilled water and drying in warm air.

The electrochemical measurements were carried out with a conventional three electrode cell of 400 ml capacity using a PARSTAT 263 potentiostat/Galvanostat. The coated and uncoated Al samples served as the working electrode (WE), prepared by embedding in a resin and exposing only a working area of 10 mm². A saturated calomel electrode (SCE) connected through a Luggin's capillary, served as the reference electrode (RE), while a graphite rod served as the counter electrode (CE). The corrosion agent was 0.5 M H₂SO₄ solution, prepared by diluting BDH analytical grade concentrated H₂SO₄ with distilled water.

2.2. Electrochemical Measurements

The experiments were carried out in an unstirred and naturally aerated 0.5 M H₂SO₄ solution at 30±2 °C. Measurements were performed at the end of 1 h of immersion in the acid solution. The electrochemical techniques employed for the corrosion testing included open circuit potential, electrochemical impedance spectroscopy (performed over a frequency range of 100 kHz–10 MHz with signal amplitude perturbation of 5mV) and potentiodynamic polarization (carried out in the potential range of -0.25 V/E_{ocp} to +1.7 V/SCE with a scan rate of 0.333 mV/s). Each test was run in triplicate to ensure the reproducibility of the systems.

3. Results and Discussion

3.1. Electrochemical characterization

3.1.1. Open Circuit Potential Result

In Figure 1, the variation of open circuit potential for the coated and uncoated Al samples in 0.5 M H₂SO₄ solution is provided. The OCP values provide information on the susceptibility of the exposed metals to dissolution in electrolyte solutions under equilibrium conditions. The potential of both Al samples continuously decreased with time during the scan. From the plots, it can be seen that the coating had only slight influence on the value of OCP for the Al sample. The OCP value was slightly more positive for the coated Al sample than for the uncoated sample; indicating that the coating decreased the tendency of the Al substrate to be dissoluble in the acid solution. This must definitely be attributed to the barrier properties of the coating on the Al sample. Nevertheless, the continuous decrease in the potential values with time for both samples indicates that the formation of a corrosion resistance layer on Al could be hindered in the acid solution, without or with the epoxy coating.

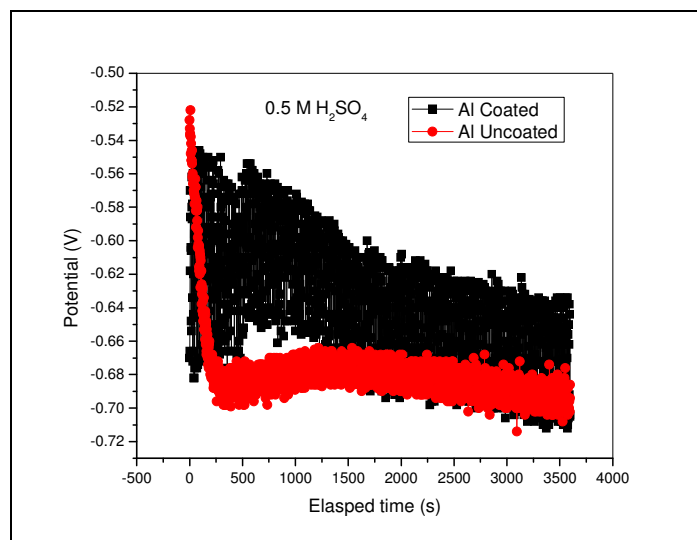


Figure 1: Variation of OCP with time for coated and uncoated Al samples in 0.5 M H₂SO₄ solution

3.1.2. Electrochemical Impedance Spectroscopy Measurement

The Electrochemical impedance spectroscopy provides information about the rate and mechanism of the electrochemical reaction occurring at the metal surface/electrolyte interface. The impedance results were expressed in the Nyquist and BODE phase angle formats. The Nyquist plots show a capacitive loop followed by an inductive loop for the coated and uncoated Al samples in the 0.5 M H_2SO_4 acid solution as shown in Figure 2(a). The size of the capacitive loops was greater for the coated Al sample, than for the uncoated; an indication of a higher corrosion resistance for the coated Al sample. The occurrence of an inductive loop for both samples may indicate certain non-Faradaic processes, such as adsorption and desorption of corrosion products, occurring at the sample/electrolyte interface (Abdel-Gaber *et al.*, 2008; Umoren *et al.*, 2010). The authors stated that the inductive loop is synonymous with a degrading corrosion product layer. This gives more credence to the instability of the Al corrosion product layer formed in an acid solution. The Phase angle plots Figure 2(b) show two time constants which implies that the electrochemical process occurring at the Al sample surfaces can be explained using two basic phenomena, namely the process occurring in the electric double layer formed due to storage of charges at the sample/electrolyte interface, and another process occurring beneath the charged layer i.e. directly in the Al substrate/electrolyte interface (Harvey and Schweinsberg 2005, Onyechu *et al.*, 2014). The similar shapes of the impedance plots for both coated and uncoated Al samples indicates that the coating does not disturb the electrochemistry of the Al sample, but greatly improves the corrosion resistance of the Al sample in the acid solution. In order to relate the impedance behaviour of the samples with electrical elements, the equivalent circuit model shown in Fig.2(c) was used to model the impedance results obtained for the coated and uncoated Al samples in the 0.5 M H_2SO_4 solution, after fitting with Zsimpwin software.

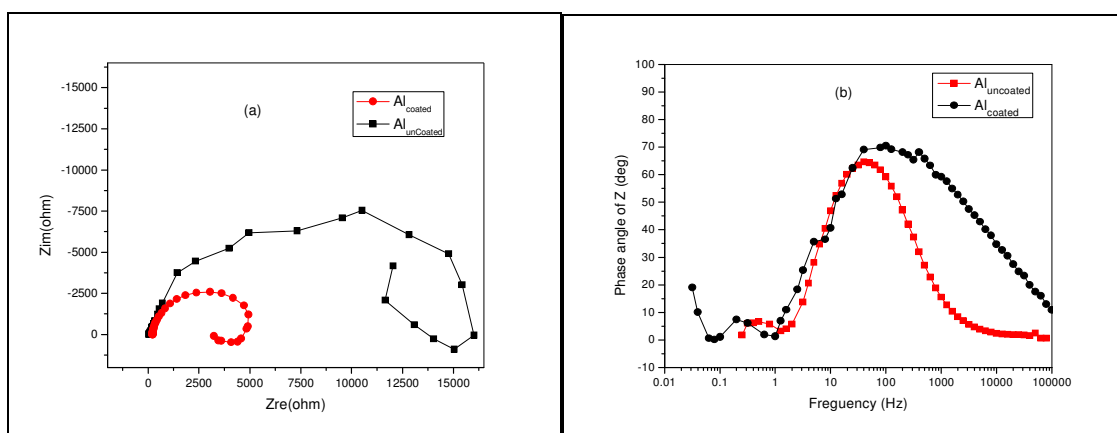


Figure 2: (a) Nyquist and (b) Bode Phase angle plots for coated and uncoated Al samples in 0.5 M H_2SO_4 solution

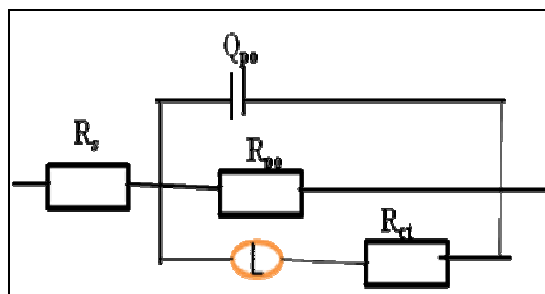


Figure 3: Equivalent circuit model for the impedance behaviour of the coated and uncoated Al in 0.5 M H_2SO_4 solution

Material	$R_s(\Omega cm^2)$	$R_{po}(\Omega cm^2)$	$R_{ct}(\Omega cm^2)$	Q_{po}	L
Coated Al	50.33	2.0×10^4	4.5×10^6	8685	20
Uncoated Al	50.04	5321	3.1×10^6	4.1×10^4	1.1×10^4

Table 1: Equivalent circuit parameters for coated and uncoated Al samples in 0.5 M H_2SO_4 solution

The R_s is the solution resistance, Q_{po} and R_{po} , respectively, show the values of capacitance of charge and the resistance of the charge layer to penetration of the electrolyte solution. On the other hand, the inductance, L, and charge transfer resistance, (R_{ct}) characterize the processes beneath the store of charges. The result shows that the Q_{po} value was lower for the coated Al sample compared to the uncoated sample, while the R_{po} was greater for the coated sample than for the uncoated. Similarly, the value of inductance was greater for the coated Al sample than for the uncoated. It may indicate that the coating can modify the electrochemistry of the Al sample by reducing the penetrations of electrolyte into the substrate–electrolyte interface, thus, decreasing the rate of the corrosion in the acid solution. This can also be evidenced by the higher value of R_{ct} , for the coated Al sample than the uncoated Al sample.

3.2.3. Potentiodynamic Polarization Measurement

The corrosion of metals in aqueous solutions is well known to be an electrochemical process. The potentiodynamic polarization measurement, therefore, provides information on how the coating can modify the cathodic and anodic half reactions occurring at the metal surface/electrolyte interface. The polarization curves obtained for the coated and uncoated Al samples in 0.5 M H₂SO₄ solution is as shown in Fig.4. The corrosion potential E_{corr} and corrosion current density, i_{corr} , were extrapolated from the intersection of the anodic and cathodic Tafel slopes drawn ± 10 mV around the OCP. The E_{corr} and i_{corr} values for the coated and uncoated Al samples are respectively -696.453 mV and -698.895 mV in the 0.5 M H₂SO₄ solution. The corresponding current densities were 2.239×10^{-3} A/cm² and 4.136×10^{-5} A/cm² respectively for the coated and uncoated Al samples. The result indicates that both the cathodic and the anodic curves of the coated Al sample show a lower current density than the uncoated Al sample. The i_{corr} value is highly related to the corrosion rate of the corroding sample. This behaviour confirms that the coating could reduce the corrosion rate of the Al sample in the 0.5 M H₂SO₄ solution.

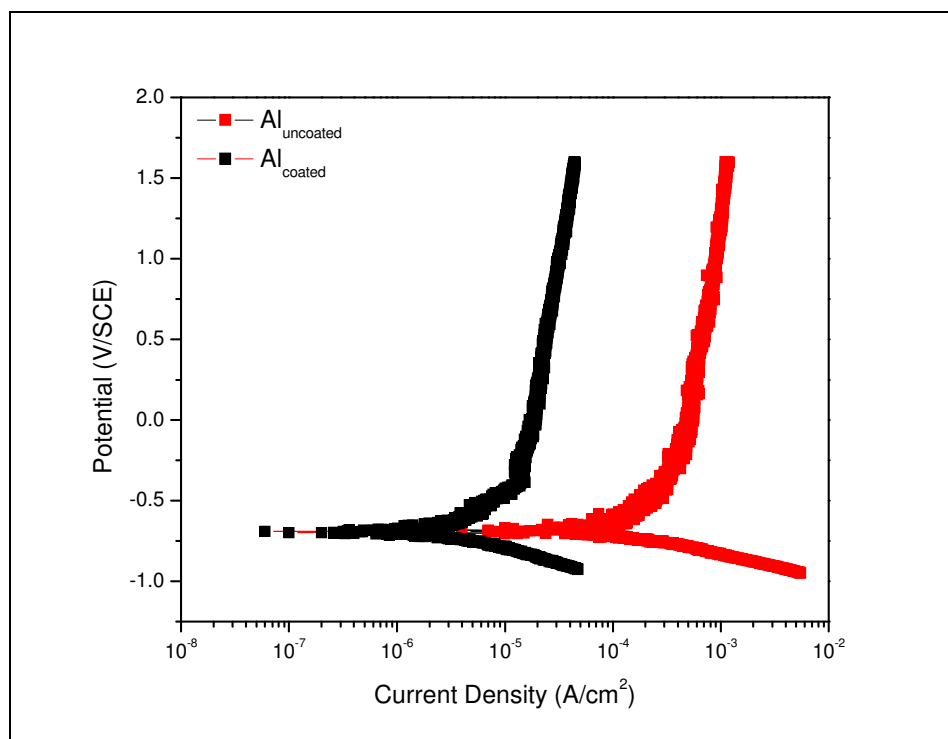


Figure 4: Potentiodynamic polarization curves for coated and uncoated Al samples in H₂SO₄ solution.

Material	E_{corr} (mV)	I_{corr} (μA)	β_{c} (mV/dec.)	β_{a} (mV/dec.)
Uncoated Al	-698.895	2.239×10^{-3}	-61.503	153.980
Coated Al	-696.453	4.136×10^{-5}	-180.122	766.233

Table 2: Polarization parameters for coated and uncoated Al in 0.5 M H₂SO₄.

4. Conclusion

The electrochemical characteristics of a coated and uncoated Al sample has been investigated in 0.5 M H₂SO₄ solution. The epoxy coating does not change the corrosion mechanism of the Al sample but could increase the inertness of the Al sample towards dissolution in the acid solution. The effect is the reduction in both cathodic and anodic half – reactions occurring at the Al surface/H₂SO₄ interface.

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