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Research paper

Electrochemical Impedance Spectroscopy Evaluation of Organic Coating on Mild Steel

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Abstract

Electro-oxidation of 4-hydroxybenzalaniline in alkaline solution on mild steel surface was successfully carried out using cyclic voltammetric technique. Results demonstrated that brownish colour appeared on the mild steel surface after the cycle of voltammetric study. The presence of film was confirmed by the EIS measurement whereas the Nyquist plots obtained from EIS measurements were fitted with suitable electrical equivalent circuit. The coated mild steel exhibit better polarization resistance than uncoated mild steel.

Keywords: *4-hydroxybenzalaniline; Corrosion; Cyclic Voltammetry; EIS; Electrodeposition; Nacl Solution*

1. Introduction

Corrosion is a problem caused by nature and affects a wide variety of materials not limited to metal [1]. Hence corrosion control must be applied in order to reduce the effect of corrosion. Surface modification via formation of organic passive layers is an alternative approach in developing optimum corrosion protective layers particularly in acidic or marine conditions. Schiff base compound namely 4-hydroxybenzalaniline abbreviated as 4OH is an organic compound which contain electron rich carbon nitrogen double bond. Hydroxyl (-OH) on the ring enables electrodeposition of the compound on mild steel surface. Bao et al. [2] has proposed a mechanism for electrodeposition of phenol where oxygen from OH formed radical and combine with other radical during the electro- oxidation of phenol. The aim of this work is to investigate the effectiveness of the protective film electrodeposited on mild steel surface by cyclic voltammetry technique through electrochemical impedance spectroscopy (EIS). In this work, a 0.1 M 4OH was electrodeposited on mild steel surface by cyclic voltammetry technique and the presence of the film on mild steel surface was confirmed using electrochemical impedance spectroscopy (EIS).

2. Method

The 4OH compound was synthesized by condensation reaction of the appropriate amount of 4-hydroxybenzaldehyde and aniline at 1:1 molar ratio in absolute ethanol. The pale yellowish flakes compound was collected and characterized. The expected chemical structure of synthesized 4OH was illustrated as in Figure 1.

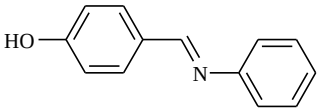


Fig. 1: Chemical structure of 4-hydroxybenzalaniline

The mild steel embedded in epoxy resin exposing its surface area of 0.5 cm2 was prepared via these procedures: mild steel electrode was polished with different grit (120, 220, 320, 500, 600, 800 and 1200) of silicon carbide papers, polished on the diamond cloth with the presence of lubricant blue and diamond spray with grain size of 3µ followed by 1µ to get a mirror like surface and was cleaned in ethanol using ultrasonic cleaner, rinsed thoroughly with deionized water and dried prior to the electrodeposit process.

The conventional three-electrode system was used throughout the electrodeposition process and the EIS measurements, where mild steel is the working electrode (*WE*), silver/silver chloride (Ag/AgCl/KClsat.) as the reference electrode (*RE*) and platinum rod as the counter electrode (*CE*). *RE* was placed inside a Luggin capillary to minimize the ohmic drop and was placed near to the exposed area of *WE*. All the experimental works were performed inside the Faraday cage to reduce interference from the environmental electronic noise. Gamry Instruments Framework Reference 600 potentiostat/galvanostat/ZRA interfaced with a computer via USB was used throughout the studies.

The electrodeposition of 0.1 M 4OH on mild steel surface was implemented in 0.3 M sodium hydroxide (NaOH) solution (70% deionized water: 30% absolute ethanol) using cyclic voltammetry (CV) technique. The solution was freshly prepared prior to use.

The EIS measurements were conducted in order to confirm the presence of insulative organic film on mild steel surface and to measure the performance of the organic film with time during exposure to the electrolyte. The measurement was conducted in 0.5 M NaCl solution at open circuit potential (*E*oc) of 10 mV sinusoidal AC amplitude at the frequency range from 30 kHz to

0.03 Hz after 1 hour of exposure in 0.5 M NaCl solution. The results obtained were fitted with various electrical equivalent circuits (*EEC*) using Gamry Echem Analyst software.

3. Results and Discussion

All physical and chemical result of synthesized 4OH was tabulated in Table 1 and Table 2, respectively. High percent yield of 4OH indicates that almost all starting materials had been converted to form expected product. In addition, the successful of 4OH is proved by the close agreement between experimental and theoretical values of carbon, hydrogen, nitrogen and oxygen.

Table 1: Physical Properties of 4OH

Compound	Molecular formula	Yield (%)	Melting point (oC)
4OH	C13H11NO	87	196-198

Table 2: Chemical Properties of 4OH

Compound	Elemental analysis (%)			
	Experimental (Theoretical)			
	C	H	N	O
4OH	78.95	5.64	7.21	8.2
	(79.16)	(5.62)	(7.1)	(8.12)

The background determination for control purposes was carried out on mild steel electrode in 100 mL 0.3 M NaOH solution containing 30% absolute ethanol (EtOH) and 70% deionized water. Five CV cycles were set at a scan rate of 25 mV/s. The voltammogram presented in Figure 2 shows five linear current-potential responses recorded as the mild steel was scanned five cycles from +0.30 V to +1.40 V and reversed to +0.30 V at a scan rate of 25 mV/s. At about +0.60 V, the increment of current density is directly proportional with potential applied. The growth of current densities corresponding to the oxidation of solvent [3]. There was no changes in color observed on the mild steel surface after five cycles of potential scan.

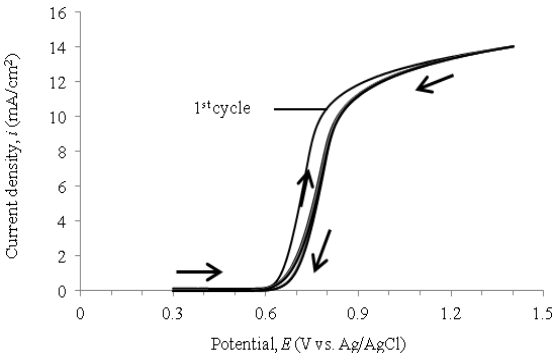


Fig. 2: Cyclic voltammogram of mild steel in 0.3 M NaOH solution

Another two CV were performed confirmed that the increment of current densities was due to the solvent oxidation as shown in Figure 3 and Figure 4, respectively. Based on Figure 3 the current density begins to increase at about +0.40 V than that in Figure 2 as shown in the inset of Figure 3. The anodic wave during the first cycle was associated with the oxidation of ethanol in NaOH solution [4].

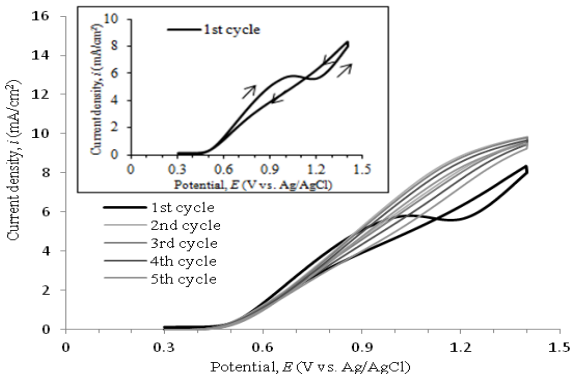


Fig. 3: Cyclic voltammogram of mild steel in 0.3 M NaOH solution containing 100% ethanol

On the other hand, when the same experiment was performed in 0.3 M NaOH solution containing 100% deionized water; the voltammogram as shown in Figure 4 was produced. In this case, it shows almost the same voltammetric profile as in Figure 2. The current density begins to increase at about +0.60 V and was further increased with potential. Bubbles were observed as the potential reached at +0.9 V which indicates the evolution of oxygen [5].

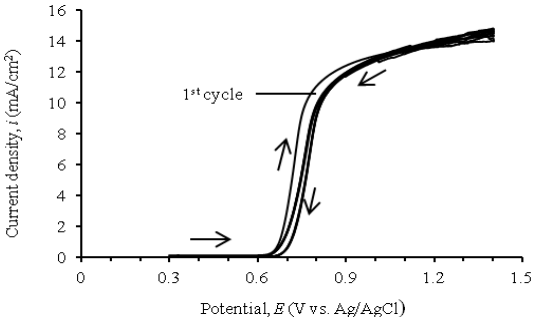


Fig. 4: Cyclic voltammogram of mild steel in 0.3 M NaOH solution containing 100% deionized water

Based on the voltammograms in Figure 3 and Figure 4, it clearly shows that the increase in current densities as shown by voltammogram in Figure 2 corresponds to the solvent oxidation (i.e. deionized water). Hence the addition of ethanol for the solubility purposes has no significant effect towards the electro-oxidation of 0.1 M 4OH.

The addition of 0.1 M 4OH in 0.3 M NaOH solution produced voltammogram as shown in Figure 5. The potential was repeated five times towards anodic direction from +0.30 V to +1.40 V and reversed to +0.30 V at a scan rate of 25 mV/s. On the other hand, the oxidation current density begins at +0.58 V and continues to increase until it reached its maximum oxidation current density at +0.98 V. The mirror like surface of mild steel turned to a shiny brownish colour during the first CV cycle. This indicates that the 4OH compound has been oxidized and electrodeposited on mild steel surface during the first CV cycle. It was observed that during the second and subsequent CV cycles there were no anodic peak current densities recorded on the voltammogram. This phenomenon indicates that the active site on mild steel surface has been covered by the insulative film of organic species [2].

According to the Nyquist plots in Figure 6 recorded from the EIS measurement, the bare mild steel exhibit one semicircle which centre lies under the abscissa as shown in the inset of Figure 6. On the other hand, mild steel electrodeposited with 0.1 M 4OH during the electrodeposition process exhibit two semicircles which centre lies under the abscissa. The centre of semicircles lies under the abscissa which is also known as a depressed semicircle for both samples and is explained by the surface heterogeneity due to surface roughness, impurities or dislocation of fractal structures, inhibitors adsorption and formation of porous layers [6], [7].

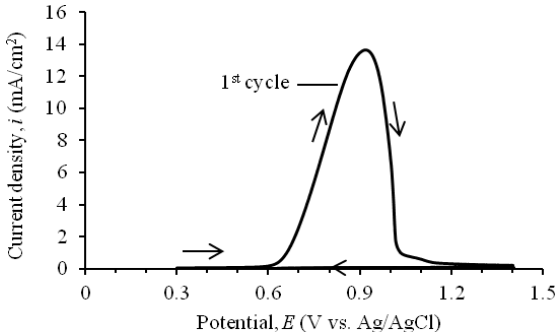


Fig. 5: Cyclic voltammogram of mild steel in 0.3 M NaOH solution containing 0.1 M 4OH

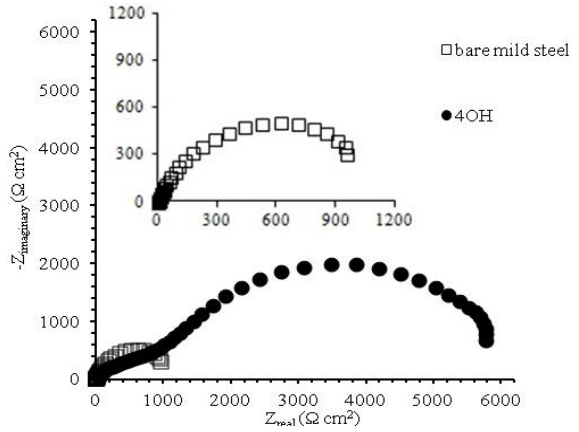
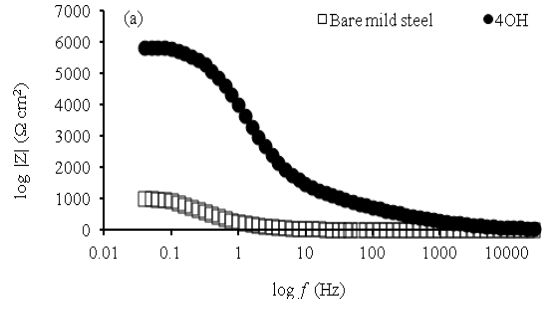


Fig. 6: Nyquist plots of bare mild steel and mild steel treated with 4OH measured in 0.5 M NaCl solution modulus

The Bode modulus in Fig. 7(a) shows that mild steel electrodeposited with 4OH exhibit high total impedance at low frequency as compared to bare mild steel. The Bode phase as shown in Fig. 7(b) demonstrates the presence of two time constants feature for mild steel electrodeposited with 4OH at the high and low frequency region. This is an indication that mild steel electrodeposited with 4OH is resistive in nature and have a deviation in phase angle approaching 50° at high frequency and 40° at low frequency.



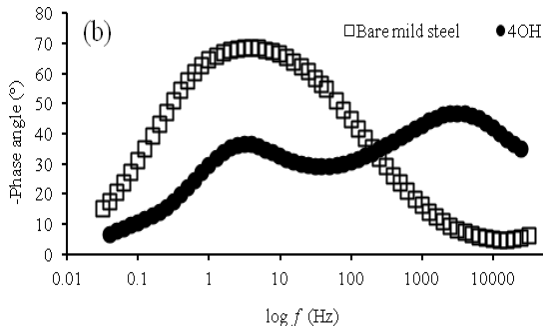


Fig. 7: Bode plot (a) Bode modulus (b) Bode phase of bare mild steel and mild steel treated with 4OH measured in 0.5 M NaCl solution

To further understand the phenomenon that occurred on mild steel surface for both samples (i.e. bare mild steel and mild steel electrodeposited with 4OH after the exposure in 0.5 M NaCl solution for 1 hour, various electrochemical equivalent circuits (*EEC*) were used to fit the obtained impedance spectra.

As for bare mild steel, the *EEC* shown in Figure 8 was used to fit the impedance spectra. The *EEC* consist of solution resistance (R_s) in series with a parallel combination of constant phase element (*CPE*) and a charge transfer resistance (R_{ct}) of mild steel/solution interface. A simple *EEC* was used since no coating on mild steel surface and there was only one semicircle recorded for the measurement. Therefore, the total polarization resistance (R_p) of the mild steel was equal to its charge transfer resistance (R_{ct}). As the impedance of the double layer is not an ideal capacitor in the presence of dispersing effect, a *CPE* was substituted as the capacitor to increase the accuracy of the impedance of the double layer.

On the other hand, *EEC* as shown in Figure 9 was used to fit the impedance spectra of mild steel electrodeposited with 4OH. The *EEC* consist of solution resistance (R_s) in series with a parallel combination of constant phase element (*CPE*) and a film resistance (R_{film}) of solution/film interface which is in series with a parallel combination of constant phase element (*CPE*) and a charge transfer resistance (R_{ct}) of film/metal interface.

Table 3 shows the data obtained from the fitting process. It can be seen that the addition of 0.1 M 4OH during the electrodeposition process increased the polarization resistance value of mild steel. The bare mild steel having one semicircle exhibits polarization resistance of 1154 Ωcm^2. On the other hand, mild steel electrodeposited with 4OH exhibits total polarization resistance of 6386 Ω cm2. The film formed on mild steel surface is insulative in nature since it can impede the flow of current.

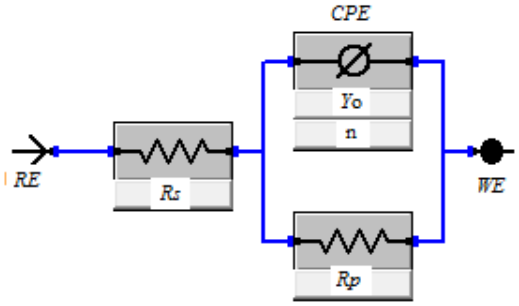


Fig. 8: *EEC* used to fit impedance spectra for bare mild steel exposed in 0.5 M NaCl solution: *RE* = reference electrode, *WE* = working electrode, *Rs* = solution resistance, *Rp* = polarization resistance, *CPE* = constant phase element, n and *Yo* = variable factor of constant phase element.

Table 3: Parameters obtained from the EIS measurement

Sample	*Rs* (Ωcm^2)	R_{film} (Ωcm^2)	$C_{coating}$ ($S.secncm^{-2}$)	n	R_{ct} (Ωcm^2)	C_{dl} ($S.secncm^{-2}$)	n	*Rp* (Ωcm^2)
Bare mild steel	3.7	-	-	-	1154	0.846×10^{-3}	0.81	1154
4OH	25.26	1089	0.010×10^{-3}	0.65	5297	0.041×10^{-3}	0.75	6386

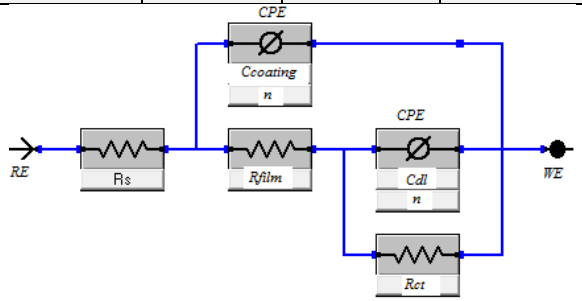


Fig. 9: *EEC* used to fit impedance spectra for mild steel electrodeposited with 4OH exposed in 0.5 M NaCl solution: *RE* = reference electrode, *WE* = working electrode, *CPE* = constant phase element, R_{film} = film resistance, *Cdl* = double layer capacitance, R_{ct} = charge transfer resistance, $C_{coating}$ = coating capacitance, *n* = variable factor of constant phase element.

4. Conclusion

Strong current reduction observed after the first CV cycle indicate that the active site on the mild steel surface has been passivated by the organic layer. The EIS measurements confirmed the presence of an organic layer on the mild steel surface after the electrodeposition process. The equivalent circuit for mild steel electrodeposited with 4OH describes the formation of film on the mild steel surface.

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