

Effect of Cerium Doped on the Poly(3-(Trimethoxysilyl)propyl methacrylate) Characteristic as Corrosion Protection Material of Carbon Steel

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Abstract. The hybrid polymer precursor was synthesized from monomer of 3-(trimethoxysilyl) propyl methacrylate (TMSPMA) using sol-gel method and doped with inhibitor of Cerium Nitrate Hexahydrate with a concentration of 0.2%. The synthesized material was coated on a carbon steel surface by solution casting technique and followed by a photopolymerisation process. Corrosion tests were performed by using Electrochemical Impedance Spectroscopy (EIS) in 3.5% NaCl at the critical temperature of 75°C. Result of EIS data and their fitting analysis using an equivalent circuit model shows that a coating of poly(TMSPMA)-Cerium on the surface of carbon steel form a layer of protection and caused increasing of impedance value significantly. The impedance is higher compared to the carbon steel that coated with poly(TMSPMA) only.

1. Introduction

Coating technique has been widely used for protection corrosion of metal surfaces. The coating materials for that purpose need to have good mechanical strength and hydrophobicity [1]. The application of hybrid polymer as coating material to protect steel and other metals from corrosion attack have been reported [2,3]. Besides, inhibitor is also widely used for corrosion protection [2, 4]. Lanthanides have been identified as good corrosion inhibitor since they have low toxicity and can be used as cathodic inhibitor [4]. Amongst the lanthanide, Cerium is widely used as an inhibitor for corrosion protection in industrial application [5].

We synthesized coating material using hybrid polymer precursor of 3-(trimethoxysilyl) propyl methacrylate (TMSPMA) and doped with Cerium inhibitor for corrosion protection of carbon steel, and measured the material performance using Electrochemical Impedance Spectroscopy (EIS).

2. Experiments

The precursor of hybrid polymer were polymerized from monomer TMSPMA using sol-gel method as described previously [6, 7]. The inhibitor of Cerium Nitrate Hexahydrate was doped into the polymer precursor with a concentration of 0.2% in order to obtain poly(TMSPMA)-Ce. Before coated with the poly(TMSPMA)-Ce precursor, the carbon steel (API 5L X65) surfaces were polished and cleaned with acetone and dried on air. The synthesized poly(TMSPMA)-Ce precursors then dissolved with ethanol and added with 1% Irgacure-819 as an initiator. The polymer precursors were coated on the surface of carbon steel, then prebaked and photopolymerized using UV light. Beside carbon steel/poly(TMSPMA)-



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Ce, we also prepared carbon steel coated with the poly(TMSPMA) named as carbon steel/poly(TMSPMA) and carbon steel covered with Cerium then followed by poly(TMSPMA) that named as carbon steel/Ce/poly(TMSPMA).

The corrosion tests were done using EIS measurements that performed in the electrochemical cell and equipped with temperature controlled apparatus. The electrochemical cell consists of three electrodes that are carbon steel as a working electrode, platinum as an auxiliary electrode, and calomel as reference electrode. The EIS measurements were conducted in 3.5% NaCl electrolyte at a critical temperature of carbon steel corrosion of 75°C [6]. Electrochemical cells that has been assembled then placed on a magnetic stirrer and connected to a water bath and a computer pre-installed software Gamry Reference 3000. The EIS characterization was done by varying the frequency range of 20 mHz to 100 kHz. The potentiostat voltage was varied on a range of -10 mV to +10 mV with a sweep rate of 0.2 mV/s, and AC voltage of 10 mV.

3. Results and Discussion

The synthesized precursors of hybrid polymer poly(TMSPMA) has yield of 89% and apparent as transparent gel-like. Addition of Cerium Nitrate Hexahydrate with a concentration of 0.2% does not change the color of the hybrid polymer precursor.

EIS characterization performed on carbon steel that has been coated with poly(TMSPMA) and poly(TMSPMA) which was blended with Cerium inhibitor are meant to measure an improvement passivation character of the poly(TMSPMA) that combined with Cerium. This characterization generate Nyquist curve that shows the value of the impedance of the electrodes and Bode curve showing the relationship between frequency and phase. The EIS data in form of Nyquist curves, Bode curves, and Bode phase curves are shown in figure 1 and figure 2, respectively.

The Nyquist of Carbon steel/poly(TMSPMA) layer has a semi-circle shape, that behaves like passive protection since the poly(TMSPMA) is an isolator. The Nyquist curve of Carbon steel/Ce/poly(TMSPMA) has a same pattern as Carbon steel/poly(TMSPMA)-Ce, that has two semi-circular shape and shows capacitive loop. Both of them show characteristic of Cerium that performed inhibition-like protection as indicating by downward looping curve that has correlation with inductive characteristic. Capacitive loop shows the charge transfer in the corrosion process, whereas inductive loop suggesting possible adsorption-desorption process of the inhibitor molecule. An adsorption will occur when an inhibitor molecule is absorbed and bound at carbon steel surface, and desorption will occur when inhibitor apart from the surface [8].

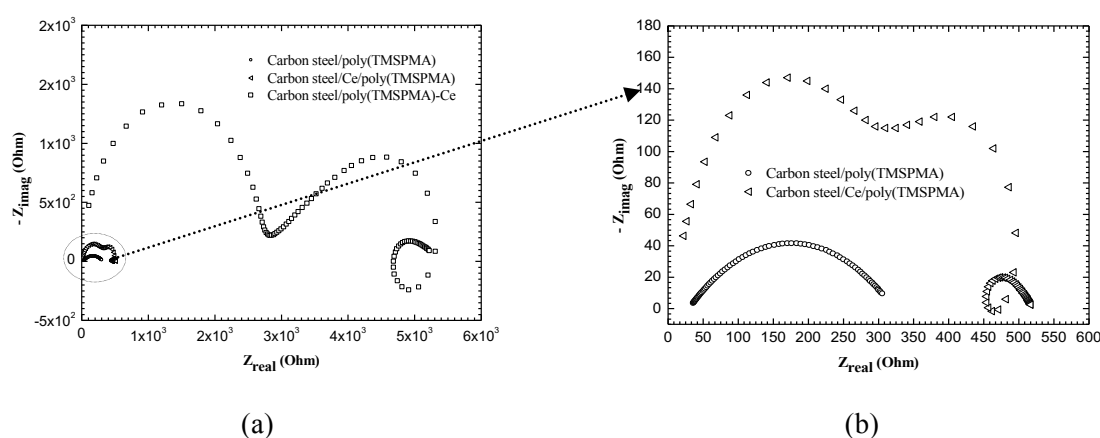


Figure 1. EIS Nyquist curves of the protected carbon steel (a), and its zooming (b)

Figure 2(a) show modulus impedances and phase of all of coated carbon steels in the measurement range of EIS scanning frequency. The total impedances of carbon steel have significantly increased with addition of Cerium on the hybrid polymer. High modulus impedance value indicates higher resistance value of the coated carbon steel. The Bode curves that have higher impedance values at a low frequency indicate a passivity of the carbon steel surface due to coating materials. The phase curve in figure 2(b) shows difference phase response at higher frequency.

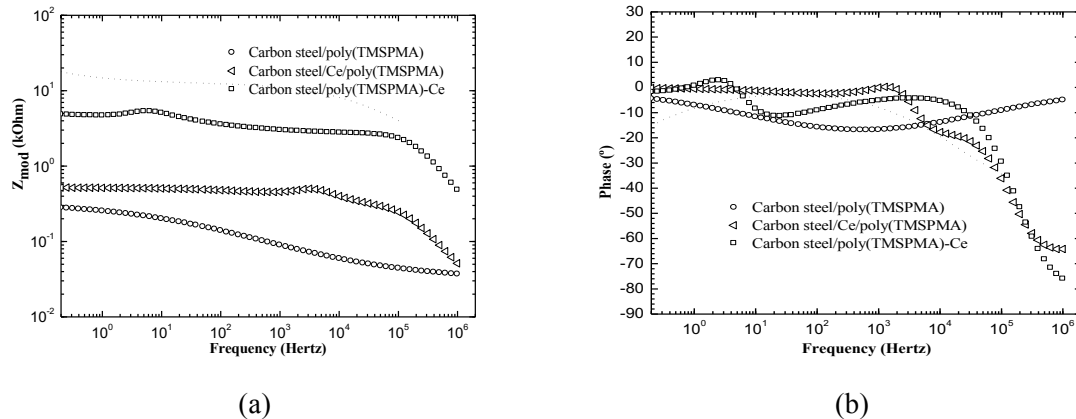


Figure 2. EIS Bode-plot of the protected carbon steel, (a) Modulus impedance, and (b) Phase

Fitting the data is the first step to be able to analyze characteristics of corrosion protection resulting from EIS measurements. We employ data fitting using equivalent circuit modeling that utilizes Gamry Echem Analyst software which is integrated with the equipment Reference Gamry-3000. The initial fitting was done using a series of double resonance, which makes the RC circuit made of two series. However double resonance circuit seem not able to follow the data points. The model of equivalent circuit should represent protection characteristics as passive protection or as inhibit protection. In an inhibit protection, an inductive characteristic should be added in the equivalent circuit model. A number of semicircle curve in the Nyquist curve indicates the number of resonating equivalent circuit. The Nyquist curve of Carbon steel/poly(TMSPMA) is not an ideal semicircular because the curve experienced 'depression' with center below the Z_{real} axis. It shows the behavior frequency dispersion associated with the irregularities of the surface of the electrode [8]. Therefore to do a fitting of this data element, additional Constant Phase Element (CPE) is required to facilitate the fitting process. Elements of the capacitor to the second loop is replaced with CPE to improve performance of fitting. In addition, the inductor elements are added as well because there are data points form an arch. Based on these consideration, we propose equivalent circuit as shown in figure 3.

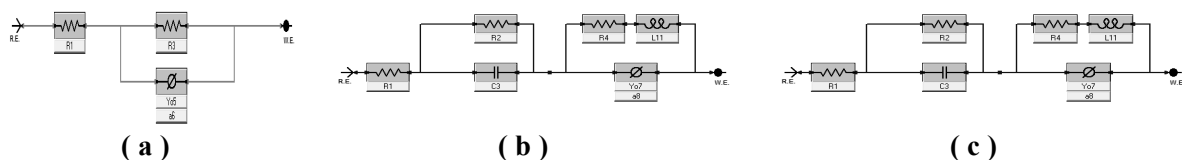


Figure 3. Equivalent circuit model for data fitting, (a) Carbon steel/poly(TMSPMA), (b) Carbon steel/Ce/poly(TMSPMA), and (c) Carbon steel/poly(TMSPMA)-Ce.

Fitting on the Nyquist curve will automatically provide fitting of Bode curve and Bode phase curve. Bode curves can be used to analyze changes of impedance magnitude and phase of the system in response to changes of the input signal frequency. The fitting results of each component value in the equivalent circuit model are listed in table 1. The resistance value of the Carbon steel/poly(TMSPMA)-

Ce is higher than the Carbon steel/poly(TMSPMA) and the Carbon steel/Ce/poly(TMSPMA). This is due to a protective layer of blend poly(TMSPMA)-Ce. The capacitance value of the carbon steel/poly(TMSPMA)-Ce is lower than the Carbon steel/Ce/poly(TMSPMA). It implies that the smaller the capacitance value, the better protection. Overall, the characterization of electrodes with different coatings have been able to reveal the characteristics of poly(TMSPMA) and Cerium inhibitors as a coating material to minimize corrosion of the carbon steel. Only required optimization of the carbon coating on steel to increase resistance to corrosion. Also deposition of Cerium on the surface of carbon steel forms a passive layer since Cerium has more negative potential than steel, resulting in a cathodic protection on the carbon steel. Adding of 0.2% corrosion inhibitor of Cerium improved film's corrosion performance and barrier properties compared to samples without inhibitor.

Table 1. The parameter values of EIS data fitting results

Carbon steel /poly(TMSPMA)	Carbon steel /Ce/poly(TMSPMA)	Carbon steel /poly(TMSPMA)-Ce
R1(ohm) = 290.5	R1(ohm) = 1.243×10^{-6}	R1(ohm) = 5.326×10^{-8}
R3(ohm) = 31.29	R2(ohm) = 230.0	R2(ohm) = 2585.0
Yo5(S*s^a)= 6.259×10^{-4}	R4(ohm) = 285.0	R4(ohm) = 2805.0
a6 = 0.352	C3(farad) = 1.631×10^{-9}	C3(farad) = 3.461×10^{-10}
	Yo7(S*s^a)= 3.590×10^{-5}	Yo7(S*s^a)= 9.570×10^{-5}
	a8 = 0.501	a8 = 0.350
	L11(henry)= 4.470×10^{-2}	L11(henry)= 150.0

4. Conclusions

We have successfully prepared corrosion protection materials of hybrid polymer precursors from monomer of TMSPMA doped with Cerium inhibitor. Addition of Cerium inhibitor into the hybrid polymer precursors does not change the physical condition of precursors that is still clear gel and viscous. The result of corrosion test use EIS experiment showed that coating material protection corrosion poly(TMSPMA)-Cerium on the carbon steel increased impedance value significantly.

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