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Cathodic Electrodeposion of Nanotitania along with the Epoxy Based Coating and Evaluation of its Anticorrosion Properties

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ABSTRACT

The effect of nano-TiO_2 *particles on the corrosion properties of epoxy based coatings was investigated so that the nano titania particles were co-deposited together with epoxy resins on standard phosphated steel panels by cathodic electrodeposition technique. To evaluate its anticorrosion properties, the coating containing nano titania were compared with plain coating regarding to their immersion stability in 3.5% NaCl solution for 2880 hours (120 days). The scanning electron microscopy micrographs showed that the nano titania particles were dispersed appropriately within the coatings. Moreover, electrodeposition process was performed at a pH value of about 6.0 which lies below the isoelectric point of nano titania for the nano titania could be electrodeposited cathodic. The electrochemical impedance spectroscopy technique was used to investigate the corrosion properties of coatings. The resulted Nyquist graphs and Bode plots showed that the high corrosion resistance of the nano titania has caused an improvement in the correlating epoxy layers even after 120 days of immersing in 3.5% NaCl solution. Prog. Color Colorants Coat. 7(2014), 227-235 © Institute for Color Science and Technology.*

1. Introduction

Organic coatings are widely used to protect metallic materials against corrosive environments [1-2]. The protective performance of coatings generally depends on their barrier properties and adhesion to the substrate. In the most cases, the absence of any defects in the coatings reveals their barrier properties by separating corrosive media from the substrate [3-5].

Nanostructure materials (1-100 nm) are known for their outstanding mechanical and physical properties due to their extremely fine grain size and high grain boundary volume fraction. Nowadays, incorporation of nano-size pigments and fillers in the coating is very common. Because of their inherent small size and particle morphology, many of the problems associated

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*Corresponding author: ranjbar@icrc.ac.ir with conventional pigments such as poor adhesion, reduced coating flexibility, low impact resistance, low optical transparency, inferior abrasion and scratch resistance, early delamination and increase in coating viscosity are significantly improved [5-6].

Electrodeposition is an application technique whereby the metal substrate is coated through an electrical field. This application method offers superior corrosion performances by the aid of processes and materials that are environmentally friendly and economically efficient [6-9]. In this way, very high adhesion and saponification resistance is obtained and therefore the corrosion resistance of the electrocoat is guaranteed. In cathodic electrodeposition process, the positively charged particles migrate to the cathode (substrate) and deposit at its surface [6]. After cross-linking, a molecular network containing urethane linkages are formed which has high adhesion to the metal surface. The film that is formed by electrodeposition is homogeneous, smooth and covers all parts of the object with virtually the same thickness, even at the edges [7-11]. However, there are little studies concerning electrodeposition coatings modified by nanotitania particles.

In this research work, the corrosion resistance of the cathodic electro coatings modified by nanotitania particles is investigated using electrochemical impedance spectroscopy (EIS).

2. Experimental

2. 1. Materials

Titanium dioxide (P25) as a powder with a mean particle size of <50 nm was purchased from Degussa Co. Resin dispersion and a pigment paste (CATHOGUARD 500) were obtained from BASF Co. and mixed in a ratio of 6:1. The resin dispersion and the pigment paste had a solid content of 40±2% and 66±2%, respectively. The mixture was diluted using DI water (electrical conductivity < 10 μS/cm) to a weight solid content of 20 percent.

Nanotitania was added to resin component before adding pigment paste and further dilution. The paint films were deposited on phosphated steel panels at 160±20 Volts for 3 minutes at an active anode to cathode ratio of 1:6. The films were then rinsed by DI water. DSC thermogram and curing behavior of the coatings were studied using DSC technique after that they were baked for 20 minutes at 165˚C in an electrical laboratory oven (Memert Co.). The dry film thickness of all samples was adjusted at 20±1 micron.

2. 2. Equipments and instrumentation

Deposition of nanotitania and the morphology of the coatings were investigated using a LEO 1455VP scanning electron microscope. An IVIUM Technologies electrochemical impedance spectrometer was used to study the electrochemical and corrosion behavior of the coatings. The coated panels were immersed in 3.5% NaCl solution for 2880 hours (120 days), after which the corrosion behavior of the coating was characterized via EIS technique. A three electrode cell arrangement was used for measurements. The working electrode was a coated steel panel.

The auxiliary electrode was made of graphite and the reference electrode was a saturated calomel electrode. The volume of the test electrolyte glass cell was 400 cm^3. The impedance measurements were carried out within the frequency range of 30kHz to 10 mHz, using a 5mV amplitude of perturbation voltage.

3. Results and discussion

3. 1. Characterization of coatings

Figure 1 shows the SEM surface micrographs of the electro-deposited resin coating containing 3 wt% of nanotitania particles. As can be seen, the nanotitania particles are well dispersed in the coating. Electrodeposition is performed at a pH value of 6.0 which lies below the isoelectric point of nanotitania (6.4).

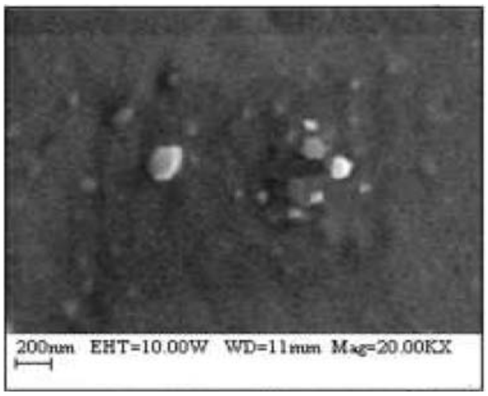

Figure 1: Scanning electron micrograph of the electrodeposited resin containing 3wt% nanotitania particles.

Since the nano TiO_2 particles at this medium have positive electrical surface charge, they could migrate to the cathode surface and deposit there [7-11]. During the electrodeposition process, water is electrolyzed at the cathode surface resulting in formation of hydrogen gas and hydroxyl ions.

As the migrating particles get closer to the cathode surface they are exposed to hydroxyl ions generated by the electrolysis of water. The hydroxyl ions neutralize the cations of the coatings and also the nanotitania particles then particles lost their water disperseability so coagulated on the cathode surface resulting in formation of the film.

3. 2. EIS measurements

The Nyquist graphs and Bode plots of two samples are shown in Figures 2 and 3, respectively.

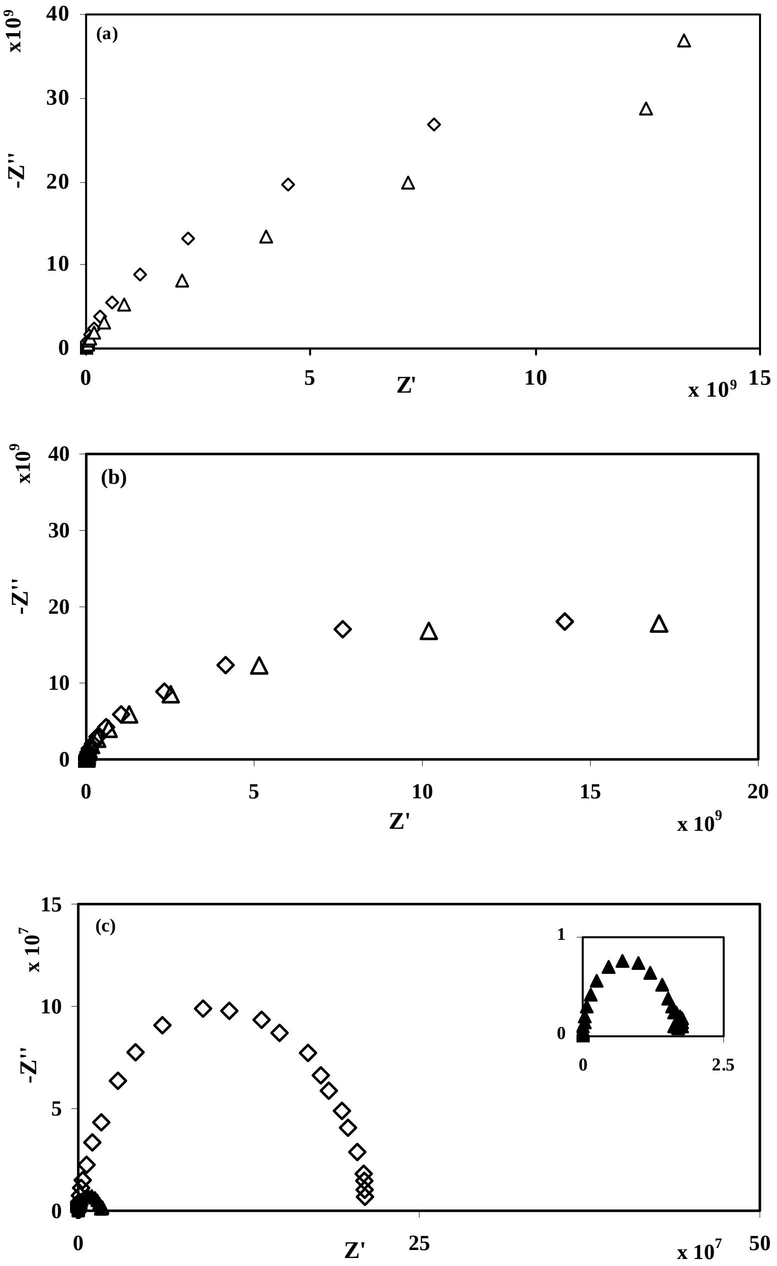

Figure 2: Nyquist plots for different immersion times in 3.5% NaCl solution; after (a) 168 hours, (b) 360 hours, (c) 720 hours, (d) 1080 hours, (e) 1440 hours, (f) 2880 hours immersion (Δ: neat coating and ◊: nanotitania filled coating).

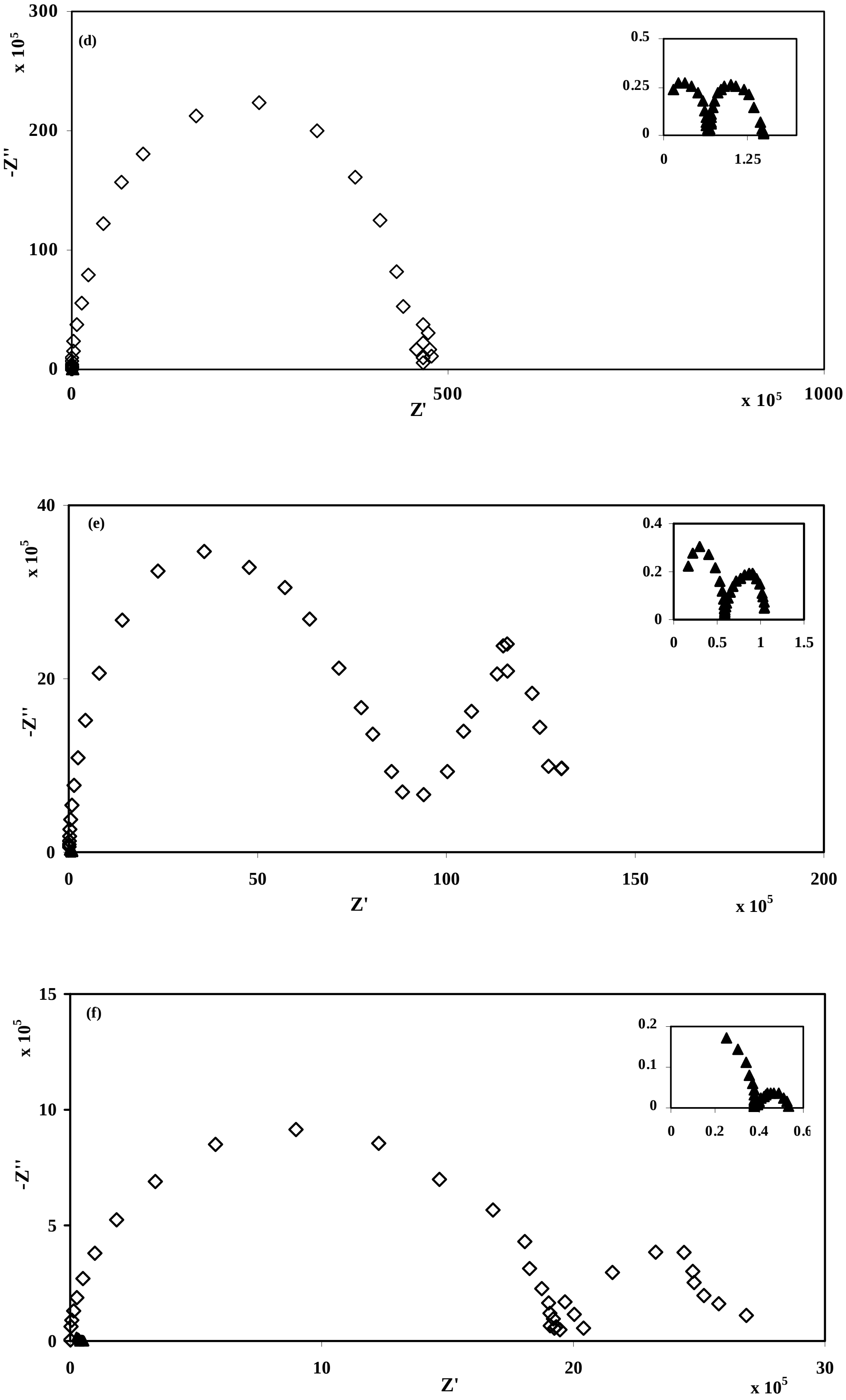

Figure 2: Continued.

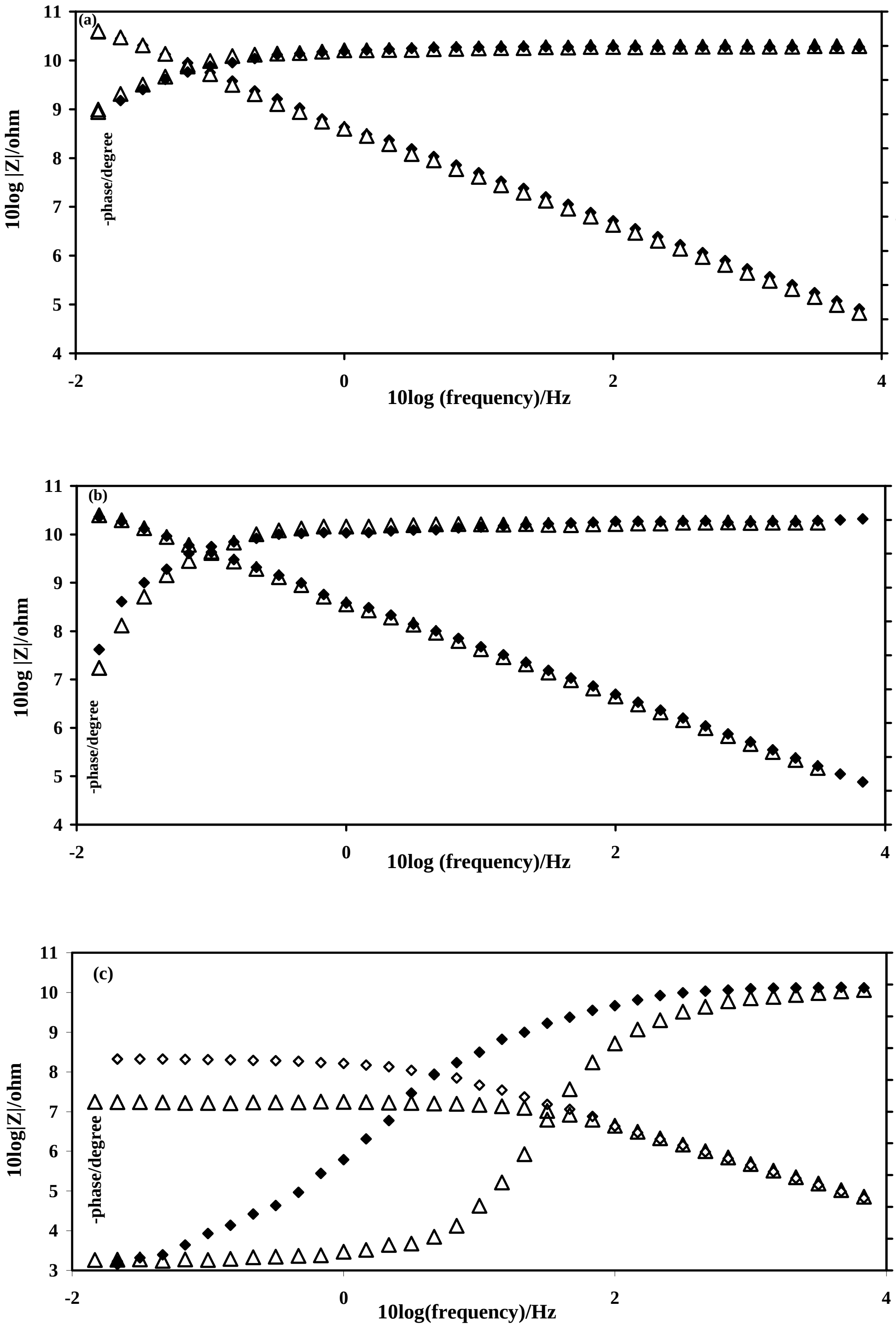

Figure 3: Bode plots for different immersion times in 3.5% NaCl solution; after (a) 168 hours, (b) 360 hours, (c) 720 hours, (d) 1080 hours, (e) 1440 hours, (f) 2880 hours immersion (Δ: neat coating and ♦: nanotitania filled coating).

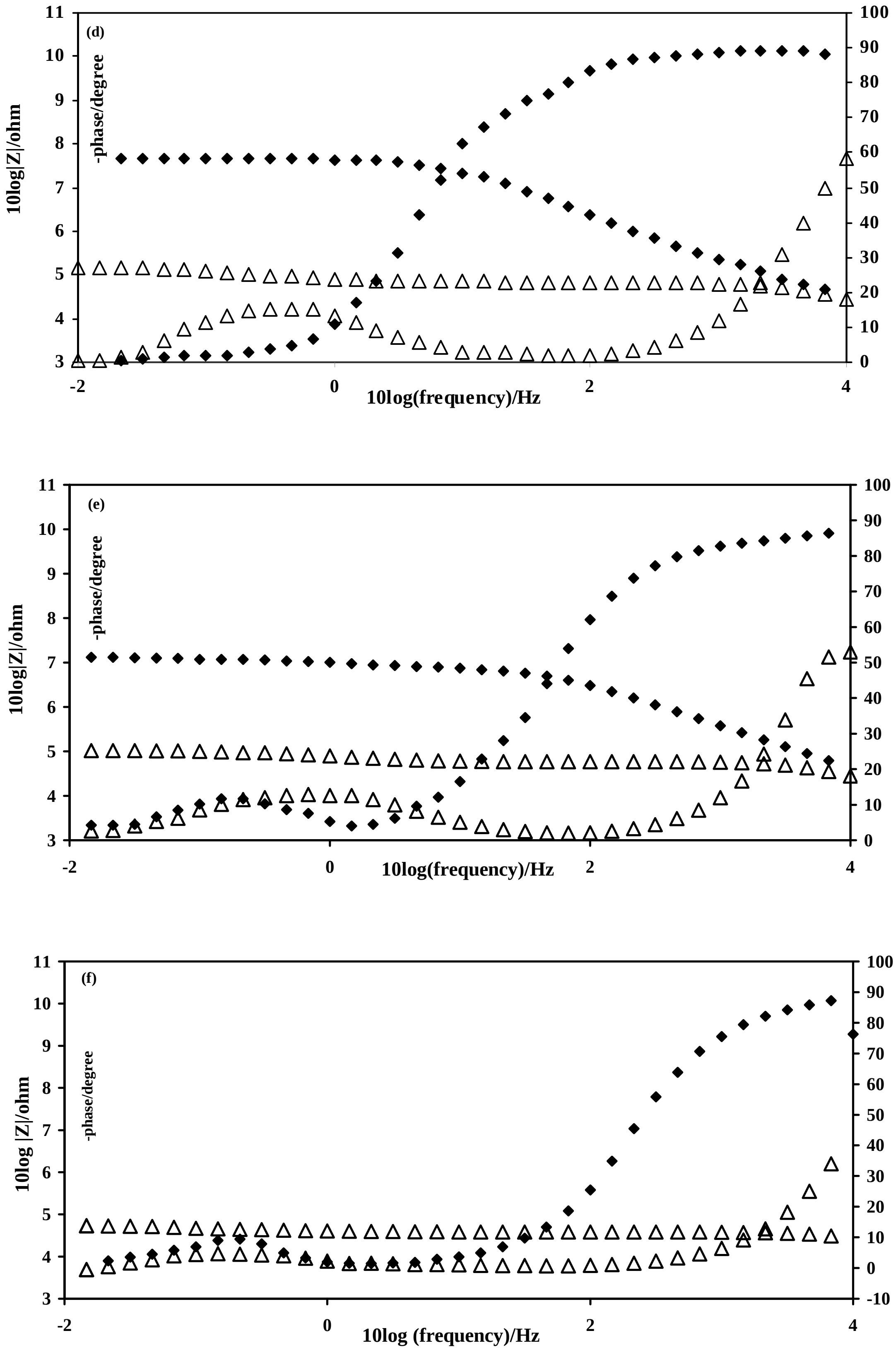

Figure 3: Continued.

It is obvious that the impedance spectrum changes in the presence of nanotitania particles in the coating. Initially, both neat coating and nanotitania filled coating show a very high resistance (>10^{10} Ohms) at low frequencies. The behavior of both coatings before immersion resembles that of a high quality protective coating.

In order to quantify the electrochemical parameters of the coatings, an equivalent circuit was considered as a model for their electrochemical behavior. The equivalent circuit considered in this study, Randle's model, is shown in Figure 4.

In Randle's model the resistance (R_p) is a measure of the coating barrier properties against the ion diffusion while the capacitance describes the dielectric properties of the coating. The model fits the experimental data in neat coating till 720 hours and in nanotitania-filled coating till 1080 hours. By passing the immersion time, another model could fit the experimental data (Figure 5).

In this model, the corrosion reaction at the coating-metal interface is simulated by a parallel arrangement of a resistor (charge transfer resistance) and a capacitor (electrical double layer).

According to Figure 2, further immersion shows two semicircles over the frequency range indicating two time constant character. The high frequency semicircle is attributed to coating pore impedance R_p, while the low frequency semicircle is the impedance response associated with the corrosion reaction occurring at the interface through defects and pores in the coating.

During the initial period of immersion, R_p is extremely high. The Bode plot shows a partly straight line with a slope of -1 with high impedance at low frequency (about 10^{10}), and a phase angle of about -90° in a wide range of frequencies (Figure 3). This indicates that the coating behaves like a capacitor.

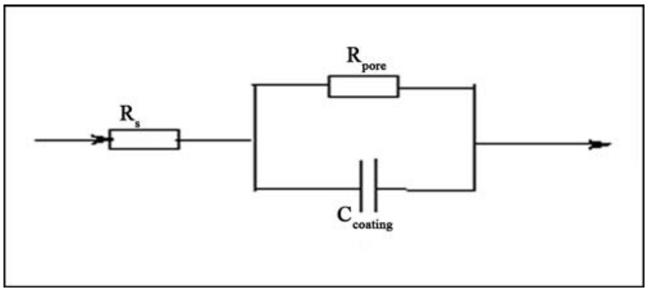

Figure 4: Randle equivalent circuit for an intact coating.

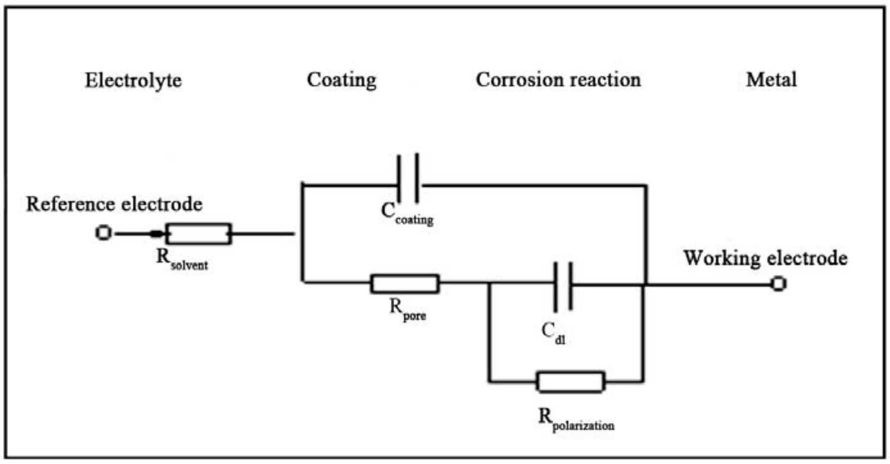

Figure 5: Electrical equivalent circuit for corroding coated metals.

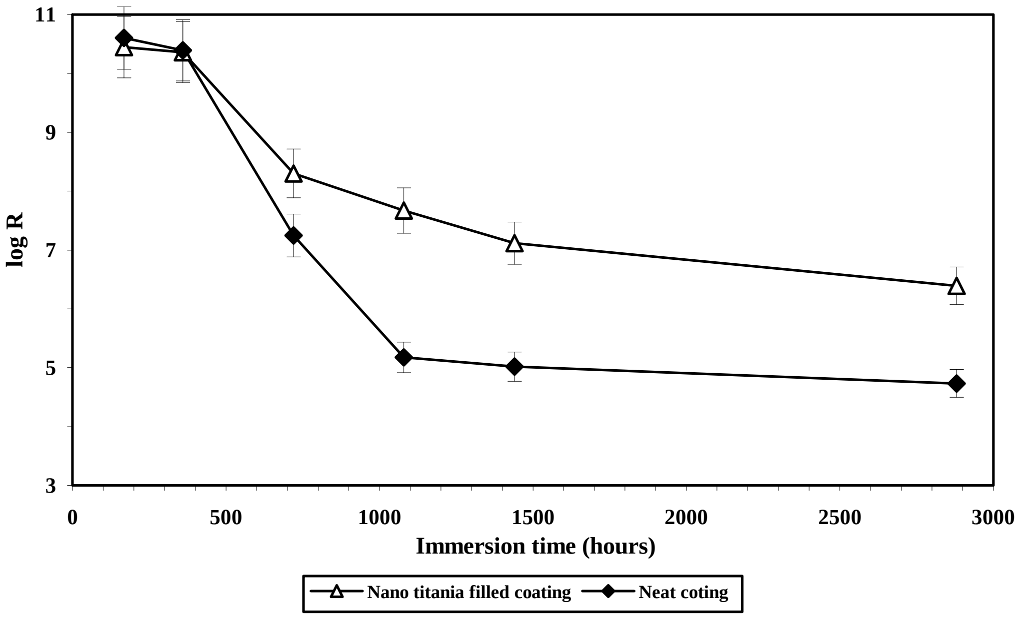

Figure 6: Pore resistance of coatings during the immersion in a 3.5 wt% NaCl electrolyte.

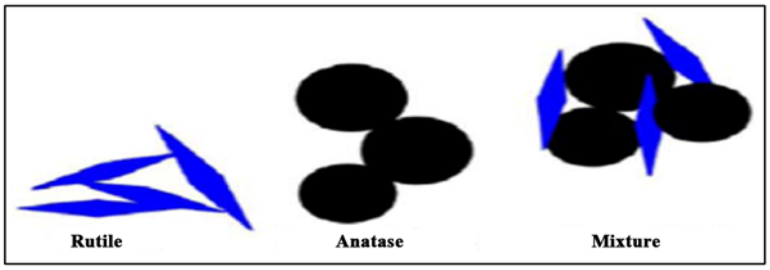

Figure 7: Structure of different kinds of titanium dioxide [14].

As Figure 6 shows, at early hours, the coatings act as ideal coatings with high resistance against corrosive environment but after a while, coatings resistance decrease with higher rate in the neat coatings. This could be attributed to the fact that nano-TiO_2 has greater surface activity and small size which result in absorbing more resin on its surface and enhancing the density of the coatings (nanotitania structure is shown in Figure 7). Its structure reduces the transport paths for the corrosive electrolyte to pass through the coating system and hence reducing the corrosion rate [12-15].

4. Conclusion

Nanotitania was used as a non-migrating additive in catholically electrodeposited epoxy-based coatings.

Since the isoelectric point of nano-TiO_2 particles is higher than that of the medium, the nanoparticles have positive electrical surface charge and could migrate to the cathode surface and deposit there. The coatings were then immersed in 3.5% NaCl solution for different durations. The corrosion resistance of the coatings was investigated by EIS technique. It was found that the coating resistance of the nanotitania-filled coatings is much more than the neat coating. The nanotitania-filled coatings maintain their protective property even after 2880 hours of immersion which could be classified even as coatings with good corrosion resistance.

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