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ORIGINAL ARTICLE

Analysis of electrochemical noise data in both time and frequency domains to evaluate the effect of ZnO nanopowder addition on the corrosion protection performance of epoxy coatings

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Abstract Epoxy–ZnO nanocomposite coatings have been developed for corrosion protection of steel. Structural characterization of the prepared nanocomposites was performed using scanning electron microscopy (SEM). The anti-corrosive properties of the coatings were evaluated by electrochemical noise (EN). On the basis of the EN results in both time and frequency domains, the nanocomposite material with low ZnO concentration (0.1% wt.%) was found to be much superior in corrosion protection when tested in aqueous NaCl electrolyte. Finally, EIS measurements were carried out and the data fitted with suitable equivalent circuit. Resistance parameters obtained by both techniques were found to be in relatively good agreement.

1. Introduction

The metallic structural equipment is prone to be attacked by aggressive species such as water, oxygen, and ions in neutral environments. The protection of metals from corrosion has become a very important problem from the economical point of view. Organic coatings have been widely applied to corrosion protection of metallic materials and it is well known that polymer based nanocomposites have the strong anti-corrosive properties (Zhang et al., 2004; Zeng et al., 2002).

Epoxy resins are commonly used as organic coatings for corrosion protection due to their strong adhesion capability to metallic substrates and excellent chemical resistance. However, the serious moisture absorption and volume shrinkage of traditional epoxy resins lead to the diffusion of absorbed water into the epoxy–metal interface and initiate corrosion of the metal substrate particularly in wet conditions. There are various reports concerning improving corrosion resistance of epoxy coatings using nanoparticles. Addition of nanoparticles increases the length of diffusion pathways for oxygen and water (Yeh et al., 2006; Zhang et al., 2007; Hang et al., 2007).

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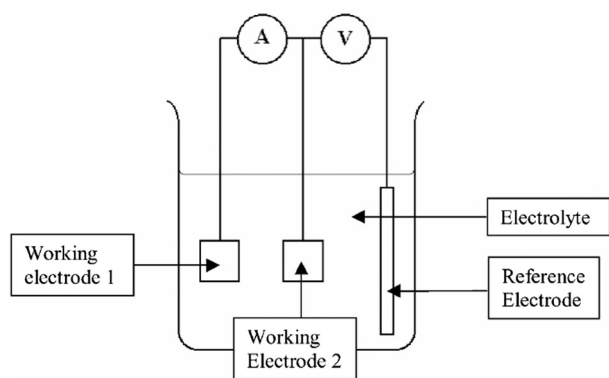
Figure 1 Electrochemical noise measurement setup.

Figure 2 XRD pattern of prepared ZnO nanoparticle.

There are several electrochemical methods to evaluate the corrosion protection performance of coatings, such as EIS (electrochemical impedance spectroscopy), LP (linear polarization) and EN (electrochemical noise). Among them, EN has gained popularity in the recent years and has emerged as a promising technique for corrosion analysis. Protective properties of anti-corrosive coatings have been successfully investigated by electrochemical noise (Sheffer et al., 2004; De Rosa et al., 2002; Greisiger and Schauer, 2000; Woodcock et al., 2005; Gusmano et al., 2007). Electrochemical noise describes the low level spontaneous fluctuations of potential and current that occurs during the corrosion process. EN measurements do not need any externally imposed perturbation to the electrochemical system that could change its specific properties (Girija et al., 2005).

This work examines the influence of ZnO nanoparticles at different concentrations on the anti-corrosion behavior of epoxy coatings in aqueous NaCl solution using EN and EIS methods.
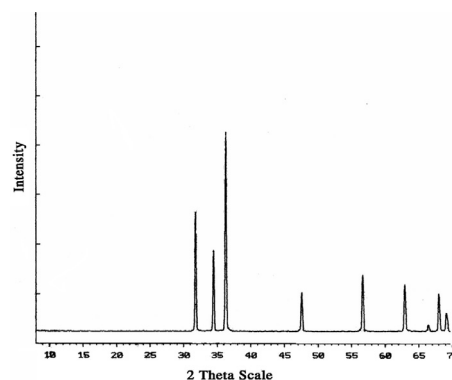
2. Experimental

2.1. Materials
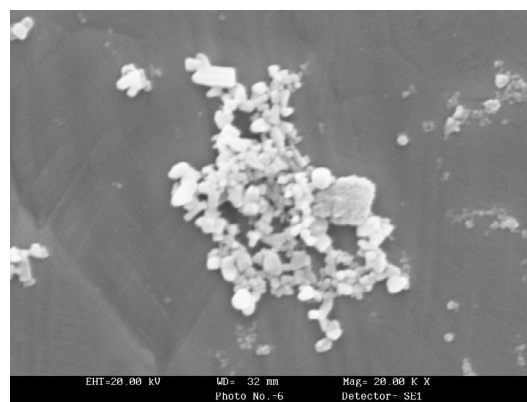
2.1.1. Preparation of ZnO nanoparticles
ZnO nanoparticles were prepared using the precipitation method. $ZnSO_4 \cdot 7H_2O$ was used as the starting material and NaOH as precipitant without further purification. NaOH solution was added dropwise to the vigorously stirred solution to adjust the pH to about 7. After this process, a large amount of white slurry was formed. The resulting slurry was continuously stirred for 12 h, and then washed with deionized water. The wet powder was dried at 100 °C to form the precursor of ZnO. Finally, the precursor was calcined for 3 h in air at a certain temperature (300 °C) to produce the ZnO nanoparticles (Daneshvar et al., 2007).

2.1.2. Steel samples and coatings preparation
Chemical composition of used steel samples determined by SPECTROLAB quantometer was as follows: C 0.2%, Al 0.37%, Si 1.38%, Mn 0.20%, and Fe balance. Steel samples were mounted in polyester in such a way that only 1 cm² of samples was in contact with corrosive solution. Specimens were polished with emery papers no. 400–1200 grade. They were degreased with acetone, washed with distilled water, and finally dried at room temperature.


Figure 3 SEM image of prepared ZnO nanoparticle.

Epoxy resin and curing agent were purchased from Ciba. ZnO nanoparticles were added into the epoxy with proper mixing using a magnetic stirrer. The content of ZnO nanoparticles in the epoxy were 0, 0.1, 1 and 10 wt.%. A curing agent was then added to the mixtures and the solutions were stirred until homogeneity. The liquid paints were coated on a steel substrate by dipping and then dried at 100 °C for 1 h. Test solutions (3.5 wt.% NaCl) were prepared using extra pure NaCl and double distilled water.

2.2. Methods

2.2.1. Electrochemical noise (EN)
Electrochemical noise data were recorded using an AUTOLAB Potentiostat–Galvanostat (PGSTAT30) and GPES (General Purpose Electrochemical Software) version 4.9 007 Beta software. For the electrochemical noise measurements, a three-electrode cell was used: two identical working electrodes (with exposed area of 1 cm²) and the saturated Ag/AgCl reference electrode. The used cell schematic is shown in Fig. 1. Electrochemical current noise was measured between the two identical working electrodes using ZRA (zero resistance ammeters) and simultaneously, the potential noise was measured between coupled working electrodes and the reference electrode. All experiments were carried out in open circuit potential under atmospheric condition in 25 °C. A sampling interval of 0.5 s was chosen over 512 consecutive data points. The frequency domain corresponding to the sampling conditions was evaluated
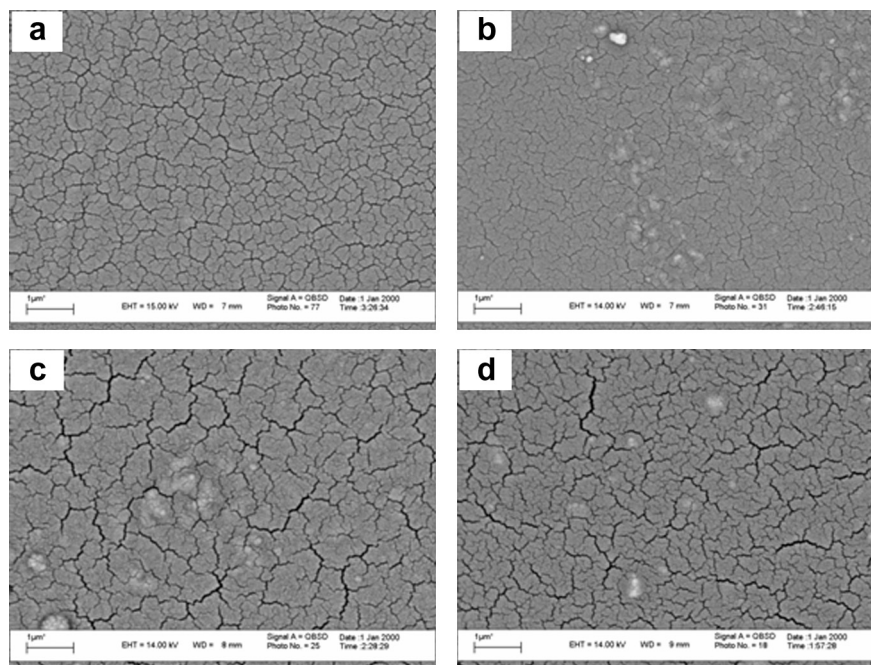
Figure 4 SEM images of epoxy nanocomposites with different content of ZnO nanoparticle: pure epoxy (a), 0.1 wt.% (b), 1 wt.% (c), and 10 wt.% (d).
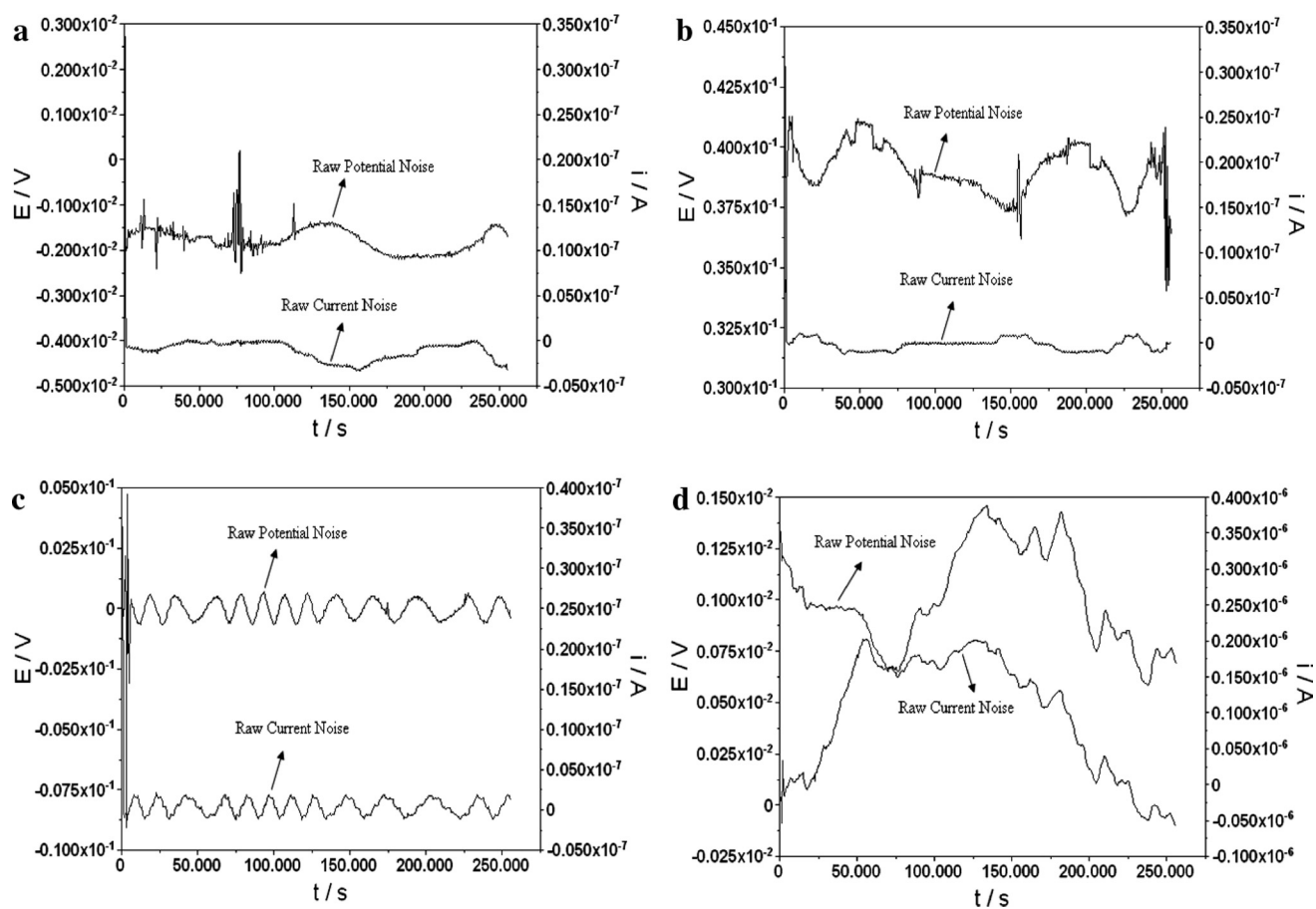
Figure 5 Typical noise records after 90 day immersion: pure epoxy (a), 0.1 wt.% nanoparticle content (b), 1 wt.% nanoparticle content (c), and 10 wt.% nanoparticle content (d).

Table 1 Results obtained by analysis of EN data both in time and frequency domains.

Sample	3 Day	5 Day	12 Day	28 Day	50 Day	64 Day	90 Day	110 Day
Average values of noise resistance, R_n ($\Omega\ cm^2$)								
Pure epoxy	4.34×10^6	3.33×10^6	1.50×10^6	1.01×10^6	8.51×10^5	4.04×10^5	5.00×10^5	1.20×10^5
Epoxy + 0.1%	4.29×10^6	3.69×10^6	2.70×10^6	4.36×10^6	1.26×10^7	1.10×10^7	7.19×10^6	5.16×10^6
Epoxy + 1%	2.34×10^5	1.50×10^5	4.50×10^5	6.69×10^5	6.54×10^5	2.93×10^5	3.14×10^5	4.30×10^5
Epoxy + 10%	5.03×10^4	1.05×10^4	2.47×10^4	6.09×10^4	1.28×10^4	6.72×10^3	6.21×10^3	3.68×10^3
Average values of spectral noise resistance, R_{sn}^0 ($\Omega\ cm^2$)								
Pure epoxy	2.82×10^6	1.38×10^6	5.92×10^5	8.10×10^5	5.35×10^5	1.57×10^5	1.13×10^5	1.27×10^5
Epoxy + 0.1%	2.52×10^6	9.61×10^5	1.10×10^6	1.20×10^6	2.59×10^6	1.87×10^6	2.06×10^6	1.95×10^6
Epoxy + 1%	1.46×10^5	1.11×10^5	1.28×10^5	3.00×10^5	2.08×10^5	2.27×10^5	1.84×10^5	1.69×10^5
Epoxy + 10%	5.25×10^4	3.40×10^4	1.17×10^4	1.17×10^5	3.99×10^3	7.04×10^3	9.88×10^3	5.69×10^3

to be between 1 Hz (f_{max}) and 3.9 mHz (f_{min}) ($f_{max} = 1/2\Delta t$, where Δt is the sampling interval and $f_{min} = 1/N\Delta t$, where N is the total number of data points) (Girija et al., 2005).

2.2.2. Electrochemical impedance spectroscopy (EIS)

EIS measurements were carried out using AUTOLAB Potentiostat–Galvanostat (PGSTAT30). A sinusoidal voltage signal of 100 mV was applied over a frequency range of 10 kHz–5 mHz. All EIS experiments were performed in open circuit potential under atmospheric condition and in 25 °C using a three-electrode cell configuration consisting of a saturated Ag/AgCl electrode as reference electrode, platinum sheet as counter electrode and coated sample as working electrode.

3. Results and discussion

3.1. Nanoparticle and nanocomposite characterization

The average crystallite size (D in nm) of prepared ZnO nanopowder was determined from XRD pattern (Fig. 2) according to the Debeye–Scherrer equation:

$$D = k(\lambda/\beta \cos \theta) \tag{1}$$

where k is a constant equal to 0.89, λ is the X-ray wavelength equal to 0.154056 nm, β is the full width at half maximum and θ is the half diffraction angle (17.61). The average particle size of prepared ZnO was about 14 nm. SEM images of nanoparticles revealed a spherical shape for oxide nanoparticles (Fig. 3).

The morphology of the epoxy–ZnO nanocomposites was observed by SEM as shown in Fig. 4. ZnO nanoparticles can be observed on the coating especially in the presence of ZnO at high concentration.

3.2. Electrochemical noise studies

The potential and current noise of epoxy coated steel samples with different contents of ZnO nanoparticles were simultaneously recorded in 3.5 wt.% NaCl at different immersion times. Each experiment was repeated 4 times and the average statistical results were reported. Examples of typical raw potential and current noise data are shown in Fig. 5.

DC trend can be observed in potential and current records especially in the case of epoxy coating with 10 wt.% of ZnO nanoparticle and therefore, the DC trend of time records was removed before further statistical analysis. Trend removal process was carried out using the Moving Average Removal (MAR) method which has been previously described by Tan
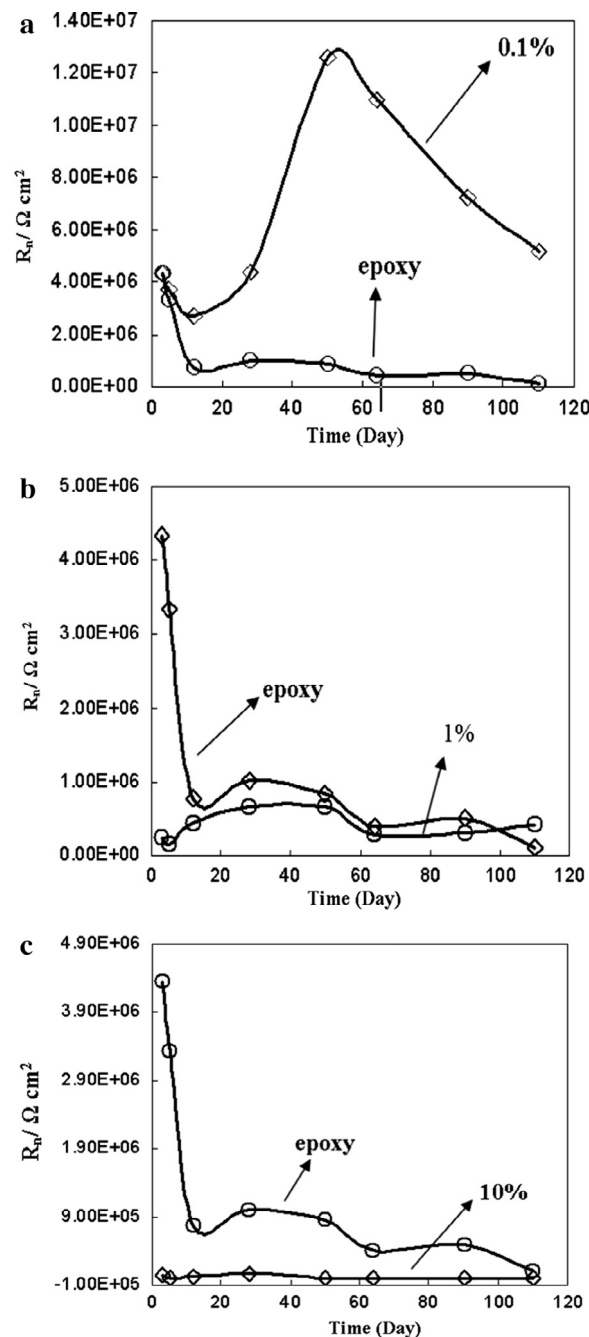
Figure 6 Changes of noise resistance with immersion time for epoxy and epoxy–ZnO nanocomposites with different nanoparticle contents: 0.1 wt.% (a), 1 wt.% (b), and 10 wt.% (c).

et al. (1996). MAR method is capable to remove nonlinear trends from noise records. MAR was carried out by writing a suitable program in MATLAB 6.5. The value of p Ashassi-Sorkhabi and Seifzadeh (2008) was 3 during the trend removal. The noise data were analyzed both in time and frequency domains to calculate noise resistance (R_n) and spectral noise resistance (R_{sn}), respectively.

The noise resistance, R_n, values were determined in the time domain, as the ratio of the standard deviation of potential noise, σV, to that of current noise, σI, ($R_n = \sigma V/\sigma I$). Calculated parameters are given in Table 1. Noise resistance is one of the first quantities derived from EN measurements. In many situations the values of R_n are found to be close to the polarization resistance (Ashassi-Sorkhabi and Seifzadeh, 2008; Ashassi-Sorkhabi et al., 2008). The values of calculated noise resistance are plotted as a function of immersion time (Fig. 6). Three time domains at R_n–t curves can be distinguished, indicating a different step of the electrolyte penetration into epoxy nanocomposites. The initial decrease in R_n corresponds to penetration of electrolyte into the coating to start corrosion. This step duration can be related to the time required for the electrolyte to reach the metal surface and to start corrosion process on the substrate. The first step is followed by increasing of R_n with time (the second step). This increasing in R_n can be explained by the blockage of coating pores with corrosion products of steel. In the final step, noise resistance of coatings is decreased which can be explained by further dissolution or desorption of corrosion products (Misvkovic-Stankovic et al., 1999). It is so important that the analysis of EN data in time domain can produce some data which confirm the logical behavior of epoxy coatings.

The coating with 0.1 wt.% ZnO nanoparticles showed the best corrosion resistance, since the values of noise resistance associated with this content of nanoparticles are significantly higher than those obtained for pure epoxy (Table 1). This can be explained with the increase of the tortuous pathway of oxygen and water due to dispersion of nanoparticles in the epoxy coating (Hang et al., 2007). It is possible to suppose that the life-time protection of the coating with 0.1 wt.% of ZnO nanoparticles will be longer than that of the pure epoxy coating. It is also evident from Fig. 6 and Table 1 that the resistance values of the coatings with high contents of ZnO (1 and 10 wt.%) are less than pure epoxy coating. This fact may be explained by a decrease in physical resistance and also a decrease in coating adhesion to steel substrate.

After the analysis of EN data in time domain, the experimental data were transformed into the frequency domain by fast Fourier transform (FFT). Transformation was performed using the SIGVIEW software. Power spectral density plots were obtained for potential (PSD_V) and current (PSD_I). Spectral noise resistance values calculated are as follows (Gouveia-Caridade et al., 2004):
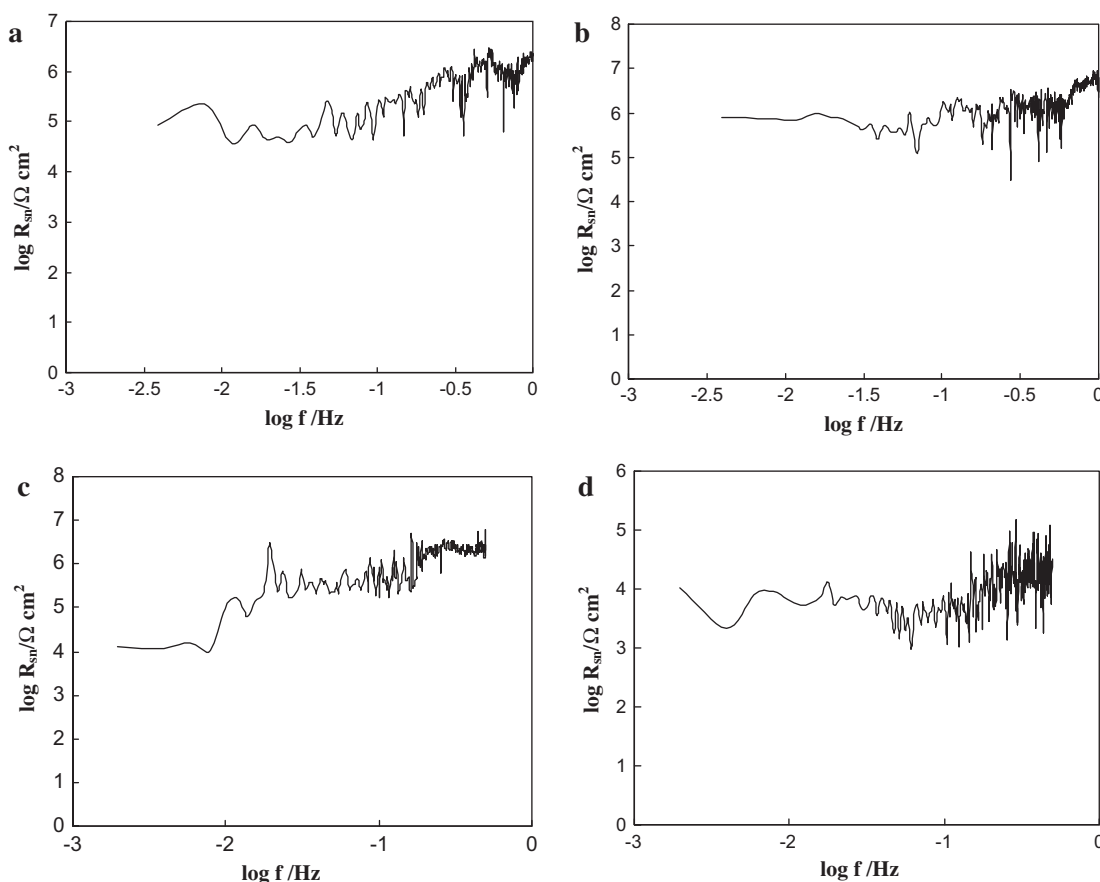
Figure 7 Typical spectral noise plots of epoxy nanocomposites after 90 day immersion in 3.5 wt.% NaCl: pure epoxy (a), 0.1 wt.% nanoparticle content (b), 1 wt.% nanoparticle content (Fig. 7c), and 10 wt.% nanoparticle content (Fig. 7d).

$$R_{sn}(f) = \left[\frac{PSD_V(f)}{PSD_V(f)}\right]^{1/2} \tag{2}$$

The spectral noise resistance, R_{sn}^0, is defined as the dc limit of the spectral noise plot (Gouveia-Caridade et al., 2004):

$$R_{sn}^0 = \lim_{f \to 0}[R_{sn}(f)] \tag{3}$$

In this study, R_{sn}^0 values for each experiment were determined as the average of the 20 data points at lowest frequencies. Some of the typical spectral noise plots (obtained by transformation of Fig. 5 noise records) are shown in Fig. 7. Average R_{sn}^0 values for each sample were calculated using the statistical results of four consecutive repeats (Table 1). Fig. 8 shows the changes of R_{sn}^0 as a function of immersion time for epoxy coatings with a different content of ZnO nanoparticles. Results obtained by analysis of EN data in time and frequency domains were in relatively good agreement.

3.3. EIS studies

Some authors have reported that the EN method is very useful to study the coating protection performance, especially when it used in conjunction with impedance spectroscopy (Mojica et al., 2001; Bierwagen et al., 1998). Epoxy nanocomposites are high resistance coatings, thus making EIS difficult to apply. Some authors have concluded that EIS method can be applied to study high resistance coatings only by applying the high amplitude peak to peak ac signal (Amirudin and Thierry, 1995).

Since the high amplitude signal can damage the coating, EIS studies with high amplitude signal (100 mV) were performed only at the end of EN measurements. Nyquist diagrams of the coated steel samples coated after 110 day immersion in 3.5 wt.% NaCl are presented in Fig. 9. It can be seen that there are two semicircles in the Nyquist plots of the coated samples (small and large semicircles at high and low frequencies, respectively). The Nyquist plot with two capacitive loops is characteristic of a coated metal, one in the high frequency range and the other in the low frequency range. The first loop characterizes the coating layer and the second one indicates the charge transfer through the coating pores (Ashassi-Sorkhabi et al., 2007). An equivalent circuit model with two time constants (Fig. 10) is used for analyzing the EIS plots. Zview2 software was used to calculate the impedance parameters. The calculated impedance parameters are collected in Table 2. As is clear from the Fig. 9 and Table 2 data, the corrosion resistance of epoxy nanocomposites with 0.1 wt.% ZnO nanoparticle content is significantly higher than pure epoxy coating. This result confirms the result obtained by the analysis of EN data both in time and frequency domains. Coating capacitances for different samples are given in Table 2. The coating capacitance determines the total amount of water in the coating. Absorption of water causes an increase in the dielectric constant of the coating with a corresponding increase in the coating capacitance (Naderi et al., 2004). Coating capacitance for studied samples was in the following order:

0.1 wt.% ZnO < Pure epoxy < 1 wt.% ZnO < 10 wt.% ZnO

This fact shows that the epoxy coating with 0.1 wt.% ZnO nanopowder absorb very low amount of water after 110 day immersion and has a very good corrosion protection performance with respect to pure epoxy coating. Comparison of collected data in Tables 1 and 2 shows that the corrosion
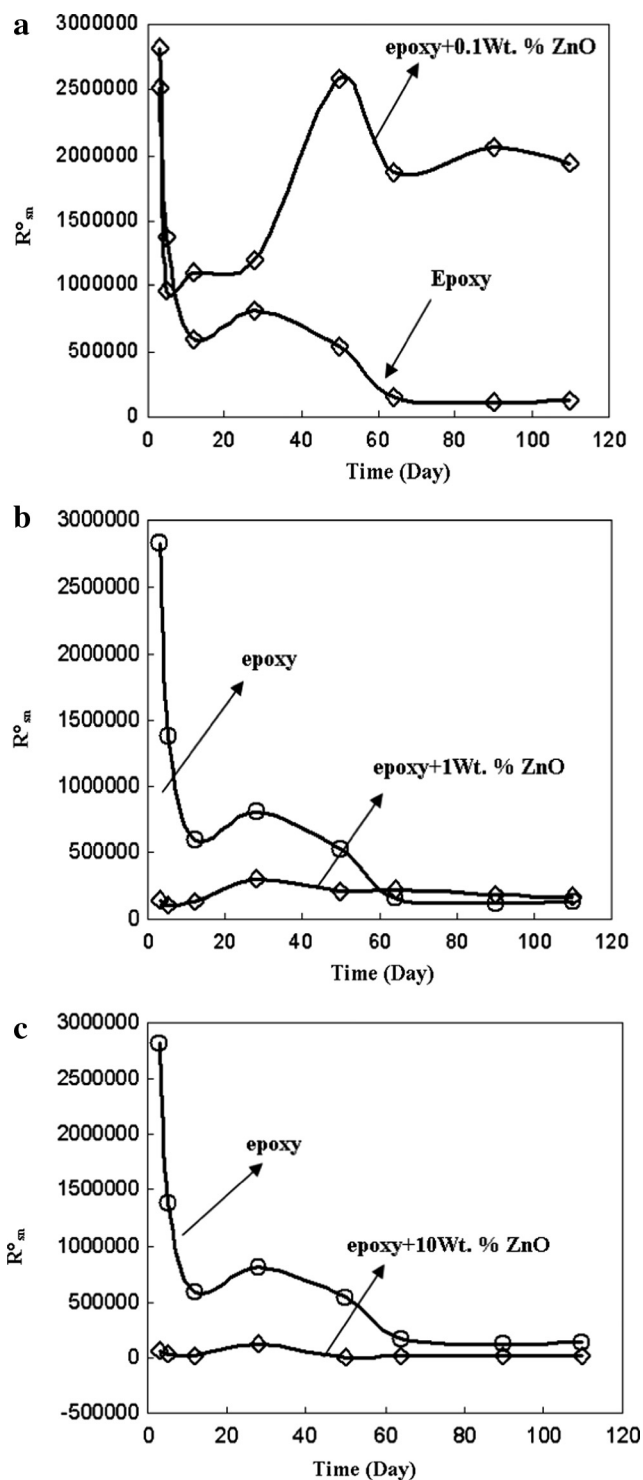

Figure 8 Changes of R_{sn}^0 against immersion time for epoxy nanocomposites with different contents of ZnO nanoparticle: 0.1 wt.% (a), 1 wt.% (b), and 10 wt.% (c).

resistance obtained by EIS method is in good numeral agreement with EN only in the case of low resistance coating (with 10 wt.% ZnO content). This agreement is schematically shown in Fig. 11. This figure represents both the spectral plot and Bode plot for sample with 10 wt.% nanopowder after 110 day immersion in 3.5 wt.% NaCl. As it is clear from the
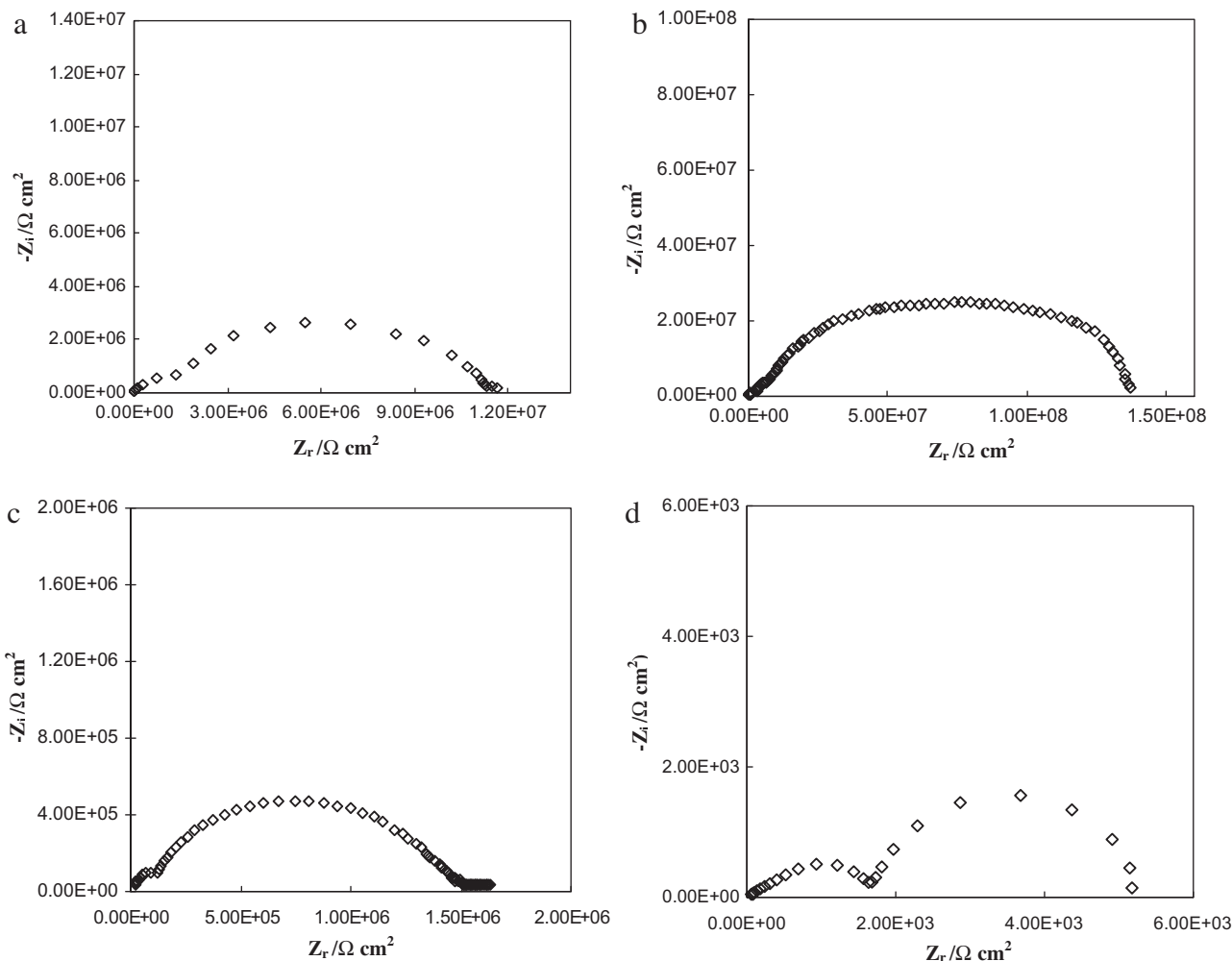
Figure 9 Nyquist diagrams of steel samples coated with epoxy nanocomposites with different nanoparticles contents in 3.5 wt.% NaCl after 110 day immersion. Pure epoxy (a), 0.1 wt.% (b), 1 wt.% (c), and 10 wt.% (d).
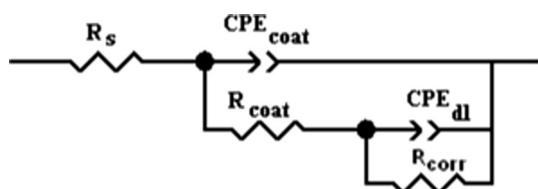
Figure 10 Equivalent circuit used for fitting of EIS data.

figure, the values of spectral noise and impedance for the mentioned samples are close to each other in noise measurement frequency bandwidth. However, a good trend agreement exists between the EIS and EN results for all studied coatings.

4. Conclusion

Corrosion protection performance of epoxy nanocomposites was investigated by EN and EIS methods. Protection performance of epoxy coating is promoted by adding optimum concentration of ZnO nanoparticles. The coating with 0.1 wt.% ZnO nanoparticles possessed the best corrosion resistance among the coatings tested. Results obtained by analysis of noise data both in time and frequency domains were in rela-

Table 2 Impedance parameters obtained by fitting of Nyquist diagrams with suitable equivalent circuit.

ZnO content	R_{coat} (Ω cm^2)	CPE$_{coat}$ (F)	R_{corr} (Ω cm^2)	CPE$_{dl}$ (F)
Pure epoxy	1.53×10^6	3.56×10^{-10}	9.86×10^6	2.80×10^{-9}
0.1 wt.%	3.26×10^6	6.52×10^{-11}	9.78×10^7	1.22×10^{-8}
1 wt.%	4.39×10^4	9.72×10^{-8}	7.06×10^5	9.59×10^{-8}
10 wt.%	1.74×10^3	8.07×10^{-6}	4.03×10^3	3.40×10^{-4}
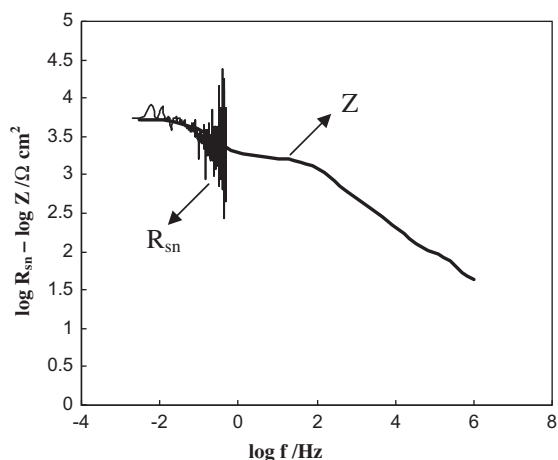
Figure 11 Comparison between the spectral noise and Bode plots of epoxy nanocomposite with 10 wt.% ZnO nanoparticle content after 110 day immersion in 3.5 wt.% NaCl.

tively good agreement. Also there was a relatively good agreement between the electrochemical noise and EIS results.

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