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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

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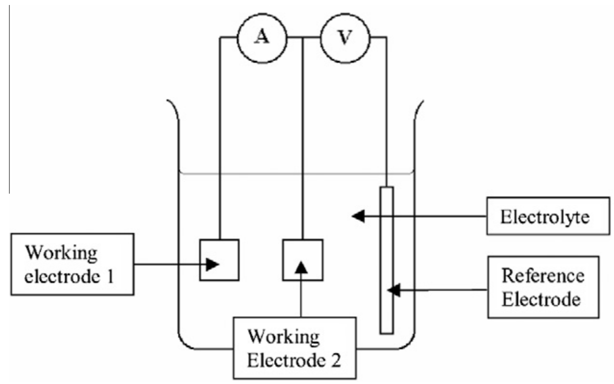


**Figure 1** Electrochemical noise measurement setup.

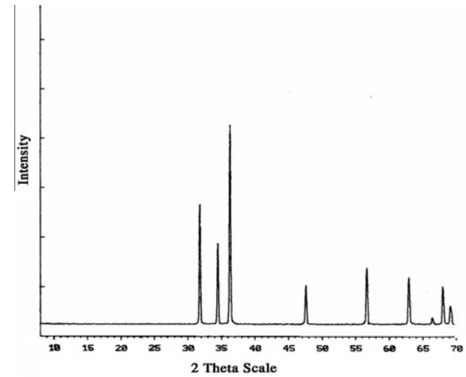


**Figure 2** XRD pattern of prepared ZnO nanoparticle.

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).

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 $cm^2$ 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.

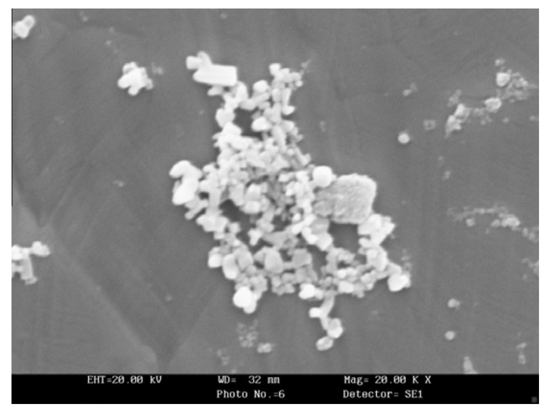


**Figure 3** SEM image of prepared ZnO nanoparticle.

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 $cm^2$) 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

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