Synthesis of Polypyrrole/CeO$_2$ Nanocomposite and its Application for Improving the Corrosion Protection of Acrylic Waterborne Coating on Mild Steel

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ABSTRACT

In this work, polypyrrole/CeO$_2$ nanocomposite (NC) was synthesized in the presence of methyl orange as a reactive self-degraded soft template. The field emission scanning electron microscopy (FESEM) images indicate that the CeO$_2$ NPs have a nucleus effect and cause a homogenous PPy core–shell type morphology with an encapsulation of the CeO$_2$ core by the PPy shell. The effect of NC on acrylic waterborne coatings for preventing the corrosion of mild steel in 0.50 M HCl solution was evaluated by electrochemical impedance spectroscopy (EIS). The choice of waterborne coatings was made on the basis of environment and human health considerations. The electrochemical impedance data obtained from both blank and coating with polypyrrole/CeO$_2$ nanocomposite samples were fitted with an equivalent circuit containing two time constants. The protection efficiency (PE) was measured from EIS method. According to the obtained PE values the coating with nanocomposite demonstrated higher corrosion resistance compared to blank coating.

Keywords: Nanocomposite; Protection Efficiency; Electrochemical Impedance Spectroscopy

INTRODUCTION

Corrosion of metals is always the major reason of energy and material loss. A generic way to protect metals from corrosion is to apply protective films or coating [1]. The organic coatings currently used in the aerospace industry present very high corrosion protection. However, for environment and human health considerations, the development of waterborne paints as the low-toxicity paints has gained notable importance [2]. The main driving force pushing waterborne systems clearly comes from environmental, safety and health considerations. But advantages in application can also be found, like easy cleaning of the formulation and application equipment with water, as well as the excellent adhesion even to substrates normally difficult to coat, e.g. wet concrete, various metals and plastics [3].

Addition of pigments to coatings is a common industrial practice. Organic coatings with anticorrosive pigments are extensively studied for the protection of metals from corrosion attack [4]. Pigments not only provide aesthetics to the coatings but also help in improving many properties of the coatings such as UV resistance, corrosion resistance and mechanical properties like scratch and abrasion [5]. However, use of these conventional

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pigments is accompanied with various drawbacks in the coating system. For example, problems like poor adhesion, reduced coating flexibility, loss of optical transparency and early delamination are associated with these pigments. Also, the loading level required for conventional pigments is quite high. To overcome these drawbacks and to further improve the performance, incorporation of nano-size pigments and fillers in the coating is a recent practice. Because of their inherent small size and particle morphology many of the above problems are improved [6, 7].

In recent years, electroactive polymers, particularly aromatic conducting polymers, have received much research attention for use as advance materials due to their remarkable physical attributes [8]. Polypyrrole (PPy) is among the group of conducting polymeric materials that have been used most widely because of its good electrical conductivity and environmental stability. In addition, PPy is readily synthesized using a range of aqueous and non-aqueous solvents [9].

Recent investigations have shown that the synthesis of polymers in the presence of nanoparticles (NPs) can increase the polymer surface area [10, 11]. The incorporation of the conducting polymer as the shell in the core–shell structure can increase the surface area of the conducting polymers over that of the bulk polymer. This structure can be obtained from an in situ chemical oxidative polymerization in the presence of nanoparticles [12].

In this work, PPy/CeO$_2$ nanocomposites (NCs) were synthesized in the presence of methyl orange (MO) as a reactive self-degraded soft template. Then, the effect of PPy/CeO$_2$ nanocomposite on acrylic waterborne coatings for preventing the corrosion of mild steel in 0.50 M HCl solution was evaluated by electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL
Materials
The chemicals ammonium cerium (IV) nitrate, citric acid, ammonia solution, hydrochloric acid, chlorofreic and pyrrole, were purchased from Merck. Acrylic resin was obtained from Sun Deco Paint and Resin Company. The employed working electrodes with surface area of 100 mm^2 were prepared from carbon steel with the chemical composition (wt %) of: C (0.17), Mn (1.40), Si (0.50), P (0.045), S (0.045) and Fe (balance).

Synthesis of CeO$_2$ nanoparticles
CeO2 nanoparticles were prepared according to the previously reported procedure [13]. Four grams of ammonium cerium (IV) nitrate (0.01 M) and 4.2 g of citric acid (0.02 M) were dissolved in 50 ml distilled water and stirred vigorously for 20 min. During stirring, ammonia solution was added dropwise and the pH of the solution was raised to about 10. The obtained solution was heated on a hot plate, with constant stirring. After certain period of time, self-combustion takes place. The formed ash was collected in a crucible and then calcinated in the furnace at 300 °C for a period of 3 h. The obtained product was light yellow powder.

Synthesis of Polypyyrole/CeO$_2$ nanocomposite
PPy/CeO$_2$ NCs were prepared via in situ chemical oxidation. The chemical polymerization in the presence of methyl orange was performed by dissolving 0.58 g FeCl$_3$ in 5 mM methyl orange (MO) [14], followed by the dispersion of 0.19 g CeO$_2$ nanoparticles in the mixture. After magnetic stirring for 30 min, 0.2 mL pyrrole monomer was slowly added to the solution. The polymerizations were performed under static conditions for 24 h at 0–5 °C. The precipitate was filtered and

washed repeatedly with distilled water then dried in a vacuum oven at 50 $^\circ$C for 36 h. So, with this method the polypyrole/CeO_2 nanocomposite were synthesized.

Testing the corrosion-resistance properties
The impedance spectra were obtained over the frequency range of 100 kHz–10 mHz and sinusoidal potential perturbation of 10 mV versus OCP. A potentiostat/galvanostat (Autolab Model PGSTAT-302N) using the Nova 1.6 software installed on a personal computer was used in these experiments. EIS measurements were conducted in a conventional three-electrode cell. A platinum rod was used as the counter and a saturated (KCl) Ag/AgCl electrode as reference electrode. The specimens were connected to a copper wire at one end, and then were sealed using epoxy resin, with the other end exposed as the WEs surface. Before coating application, the working surface was polished by wet abrasive papers through 600-2500-grade, washed with distilled water, degreased with ethanol and finally dried in air. A nano-composite coating was formed by adding PPy/CeO_2 NCs powder to the Acrylic resin in concentration 0.1 wt%. The particles were dispersed by using a high speed mechanical stirrer followed by ultrasonication. Clean working electrodes were coated by dip-coating. The withdrawing rate was 18 cm/min and the immersion time in the solution was 100 s. Two kinds of coated working electrodes (without and with Polypyrole/CeO_2 nanacamposite) were cured in air for 7 days and exposed in a 0.5 M aqueous HCl solution. A composition without nanocomposite was prepared as a control sample, so-called blank. The experimental results obtained from the EIS were analyzed with nova software.

The crystal structure and morphology of the products were investigated by field emission scanning electron microscopy (FESEM), model Carl Zeiss Supra 40, equipped with an Energy Dispersive Spectrometer (EDX), from Oxford Instruments for the elemental analysis of the coatings.

RESULTS AND DISCUSSION
Characterization of the PPy/CeO_2 NCs
The FESEM micrograph and EDX spectra of the PPy/CeO_2 NCs synthesized in the presence of MO are shown in Figs. 1 and 2, respectively. The FESEM indicates that the CeO_2 NPs have a nucleus effect and cause a homogenous PPy core–shell type morphology with an encapsulation of the CeO_2 core by the PPy shell. The results yield tubular shape in the PPy CeO_2 NC core–shell structures. The EDX results indicate the weight percentage of Ce in the nanocomposites.

The MO acts as a reactive self-degraded soft template. The formation of the template occurs in an aqueous acidic solution of MO, while its dissolution can occur under mild neutral aqueous conditions. The pH of the aqueous MO solution prior to the addition of $FeCl_3$ is 5.94; therefore, we observed that the MO was completely dissolved. After adding the $FeCl_3$, the pH of solution decreased to 2.9. Under this condition, a flocculent precipitate appeared immediately.

EIS study
The Bode plots of the coatings without nanocomposite (blank) and with nanocomposite were obtained after immersing of the coating samples in 0.5 M HCl solution. Fig. 3 shows the obtained plots at various times after immersion. The results indicate that the log|Z| of the steel coated with nanocomposite is larger than that for the steel coated without nanocomposite.

In order to perform a detailed interpretation of the EIS data, an

equivalent circuit can be proposed. In coated metal samples, the high frequency interval is usually related to dielectric properties of organic coatings, while the low frequency range corresponds to the metal response during the corrosion process [15]. Therefore, the equivalent circuit shown in Fig. 4 has been selected for simulating the response of the studied system.

In the equivalent circuit of Fig. 4, R_s represents solution resistance, that is, the resistance between the working electrode and the reference electrode; Q_c is the constant phase element (CPE) of the coating film and R_{po} is the pore resistance. R_{po} is related to the absorption of water or to the permeability of the coating. The second time constant of the spectra represents the electrochemical process, taking place at the metal-coating interface. Thus, Q_{dl} is the double-layer CPE and can be used as a measure of the paint's loss of adhesion. R_{ct} symbolizes the charge transfer resistance, associated with the kinetic of the corrosion process. This parameter is proportionally inversed to the corrosion rate and to the area where oxidation occurs.

By fitting the spectra in Fig. 3 to the proposed equivalent circuit in Fig. 4,

values of the above-cited parameters have been obtained (Table 1). Table 1 lists the impedance parameters of various coated samples in the absence and presence of nanocomposite (in this table NC refer to cotings with nanocomposite).

The experimental EIS data which were obtained from both blank and blank with nanocomposite samples were fitted to the equivalent circuit depicted in Fig. 4. It can be observed that the fitted data match the experimental data. The points in Fig. 3 represent the experimental data, while the continuous lines represent the best fits.

To comparison for corrosion performance of coatings, the percent protection efficiency values (PE%) was calculated by using below equation [16]:

$$PE\% = \frac{R_{CT}^{'} - R_{CT}}{R_{CT}^{'}} \times 100$$

where $R_{ct}^{'}$ and R_{ct} are the charge transfer resistances of the coating with and without nanocomposite, respectively. According to PE values in Table 1 it can be deduced that the protection efficiency increases with increasing time and reaches a maximum value of 64% at 72 hours after immersion time.
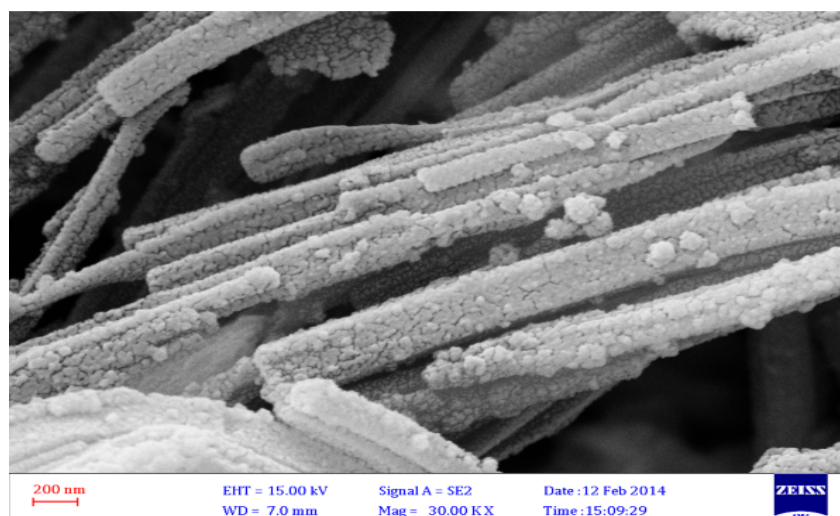
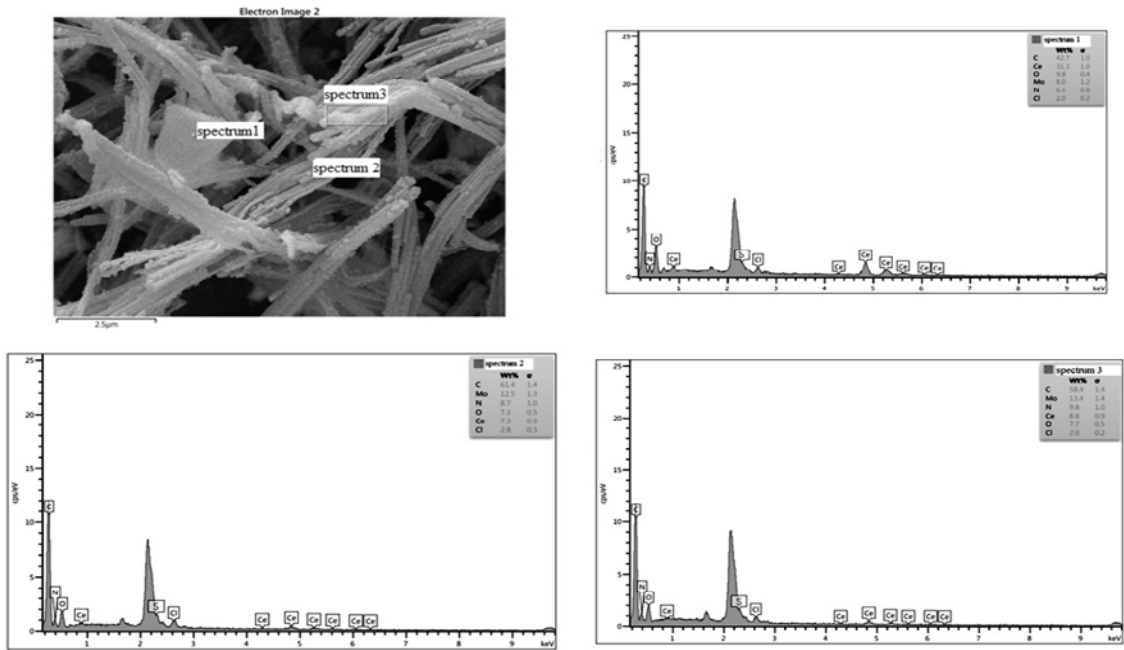**Fig. 1.** FESEM for Polypyyrole/CeO$_2$ nanocomposite.

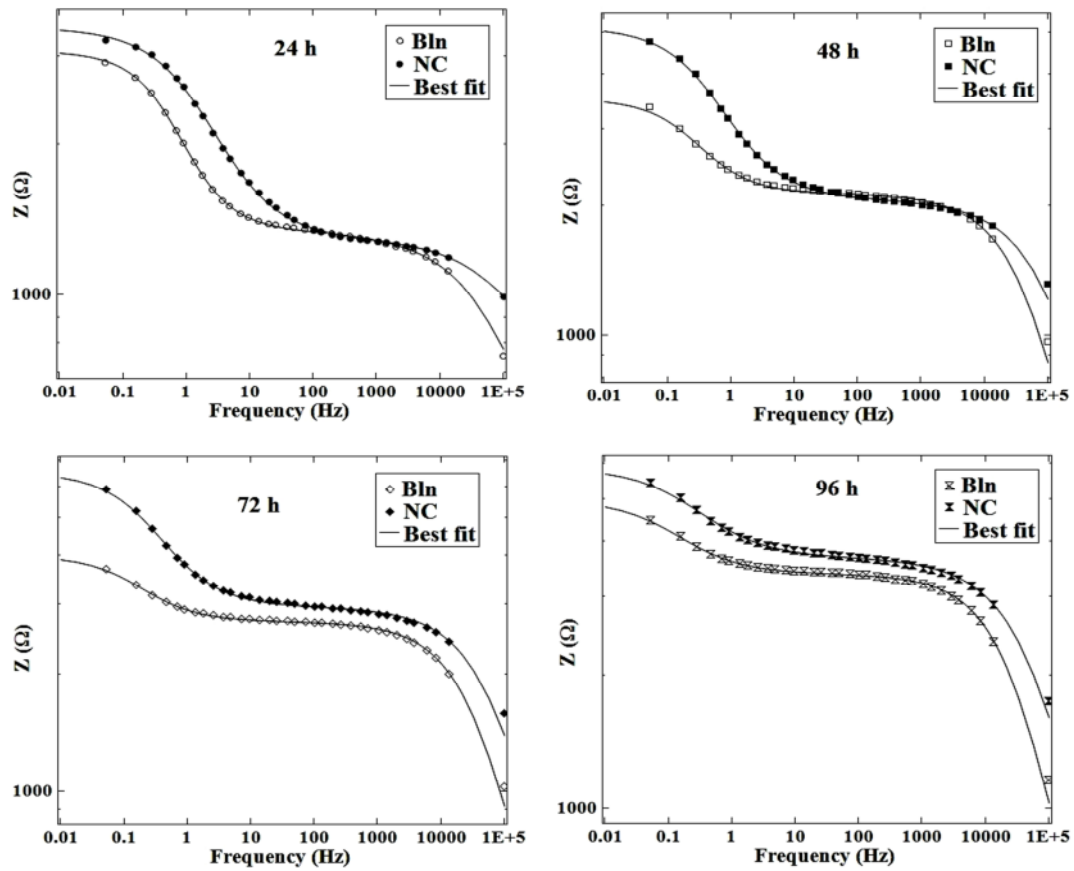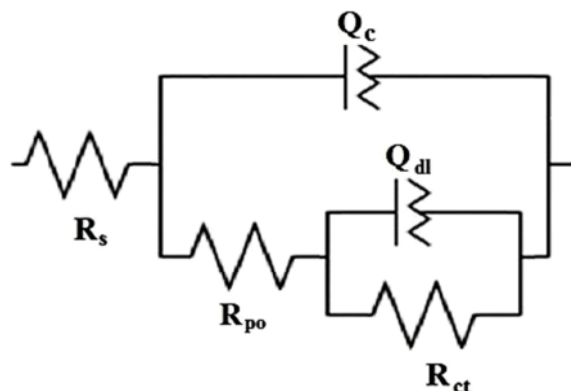**Fig. 2.** EDX spectra of Polypyyrole/CeO$_2$ nanocomposite.

Fig. 3. Bode plots of the coatings without nanocomposite (Bln) and with PPy/CeO$_2$ nanocomposite (NC) at various times after immersion.

Fig. 4. Equivalent circuit.

Table 1. Impedance parameters and the corresponding protection efficiency values.

Time/ h	Coat	R_{po}/kΩ.cm^2	R_{ct}/kΩ.cm^2	PE(%)
24	Bln	2.58	1.75	-
	NC	3.97	2.15	19
48	Bln	2.20	1.40	-
	NC	2.60	3.10	55
72	Bln	2.80	1.30	-
	NC	3.00	3.60	64
96	Bln	3.40	1.60	-
	NC	4.20	2.20	27

CONCLUSIONS

In this study, PPy/CeO$_2$ nanocomposites (NCs) were synthesized in the presence of methyl orange (MO) as a reactive self-degraded soft template. Then, the effect of PPy/CeO$_2$ nanocomposite on acrylic waterborne coatings for preventing the corrosion of mild steel in 0.50 M HCl solution was evaluated by electrochemical impedance spectroscopy (EIS). The protection efficiency (PE) can be measured from EIS method. The EIS data obtained from both blank and coating with polypyrrole/CeO$_2$ nanocomposite samples were fitted with the equivalent circuit. According to the values of protection efficiency the coating with nanocomposite demonstrated higher resistance against corrosion compared to blank coating.

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