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Sonoelectrochemical synthesis, optimized by Taguchi method, and corrosion behavior of polypyrrole-silicon nitride nanocomposite on St-12 steel

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ABSTRACT

This work describes a new sonoelectrochemical synthesis method of novel composite materials based on silicon nitride (SiN) nanoparticles and intrinsically conducting polypyrrole (PPy). The sonoelectrochemical synthesis of polypyrrole coating and polypyrrole-silicon nitride (PPy-SiN) nanocomposite performed and corrosion behavior of these coatings on St-12 steel was studied by electrochemical methods. A design of experiment (DOE) technique using the Taguchi method has been applied to optimize the affecting factors on the sonoelectrochemical synthesis of PPy-SiN nanocomposite such as current density, synthesis time and amount of nanoparticles.

The corrosion protection of St-12 steel by polypyrrole and polypyrrole-SiN nanocomposite coatings were investigated by open circuit potential (OCP) time trends, potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS) in NaCl 3.5% solution. The Kramers–Kronig transformation (KK) was applied to evaluate the validity of the experimental impedance data. The results prove that the addition of nanoparticles increased corrosion resistance of coatings and improved the surface morphology. Scanning electron microscopy (SEM) images reveal that the nanocomposite coatings form compact, homogenous and dense films on the St-12 steel surfaces.

1. Introduction

In recent years, there has been considerable interest in the use of ultrasonic irradiation for the electrochemical reactions by the chemists and electrochemists. The ultrasound irradiations in electrochemical reactions have significant effects on the reaction yield, the selectivity and the film appearance [1]. Sonoelectrochemistry can offer several benefits in the processes including the electrosynthesis of chemical compounds, electroanalysis, electroplating, preparation of nanomaterials and electrocatalysis [2,3]. Also conductive polymers have been widely studied over the last years for corrosion protection of metals [4–7]. Due to some excellent electrical and electronic properties, they have been proposed for applications such as corrosion protection, electrochromic displays, sensors, light-emitting organic diodes (O-LEDs), super capacitors, light-weight batteries and gas permeation and separation membranes and etc. [8–13]. In addition to advantages of these coatings, there are some limitations such as irreversible depletion of charges stored in the polymer layer during the system's redox reactions and losing the quality of polymer coatings with time. Therefore, the efforts have been focused on the use of nanoparticles as the second constituent to improve these disadvantages [14–19]. Because of their unique properties, nanostructured materials in nano scale have received enormous interests. Polypyrrole (PPy), a conducting conjugated polymer, has attracted much interest due to its low cost, easy synthesis, good stability, and environmentally safe performance [16]. Nanocomposites are the new class of materials which exhibit superior properties such as high strength, and excellent anti-corrosive properties with respect to conventional materials.

There are several works dealing with the sonoelectrochemical methods for synthesis of some conducting polymers and studying the effects of ultrasonication on synthesized polymers [20–25].

The aim of this study is to introduce a new sonoelectrochemical synthesis method for application of polypyrrole (PPy) and polypyrrole-silicon nitride (PPy-SiN) nanocomposite on St-12 steel. In addition, the effect of some important parameters such as applied current density, synthesis time and amount of nanoparticles on

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Table 1
The main composition parameters of the St-12 steel.

Fe	C	Mn	P	S	Cr	Mo	Ni
99.6	0.046	0.215	0.006	0.006	0.013	0.002	0.038
Al	Co	Cu	Nb	Ti	V	W	Sn
0.040	0.008	0.022	0.002	0.003	0.003	0.007	0.010
Mg	Zn	Pb	As	Zr	Ce	Sb	Ta
0.003	0.015	0.001	0.001	0.001	0.001	0.001	0.002

the corrosion protection performance of the coatings have been investigated. Moreover, the Taguchi method was applied to find the optimum conditions for the synthesis. The advantage of using this method during electrosynthesis of polymer films is to justify the experimental conditions regarding the corrosion resistance as the main response.

The experiments were performed at optimum conditions predicted by Taguchi method and the corrosion behavior was studied by electrochemical methods, and surface morphology was investigated by scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

The chemicals such as pyrrole monomer, oxalic acid and silicon nitride nanoparticles were purchased from Merck (Germany) and dodecylbenzene sulfonic acid (DBSA) as an acid dopant was supplied by Fluka. Pyrrole was distilled at reduced pressure prior to use.

Sonoelectrochemical deposition of coatings was performed in a solution containing 0.1 M oxalic acid, 0.1 M pyrrole monomer and DBSA by galvanostatic deposition at different constant current densities. The chemical composition of the St-12 steel alloy is given in Table 1.

2.2. Instruments

An Autolab PGSTAT 30 advanced Potentiostat/Galvanostat system was used for synthesis and electrochemical studies.

Ultrasound generating device (Dr. Hielscher S400UP model) was employed and the frequency of ultrasonic wave irradiated through a titanium transducer (dipped in solution) was 25 kHz. The surface morphology of the films was characterized by an scanning electron microscopy (Philips, XL30 model).

2.3. Sonoelectrodeposition of coatings

Electrochemical deposition of the PPy and PPy-SiN films was performed using a constant current density in the presence of the sono-irradiation power.

The synthesis process was carried out in a three-electrode cell configuration with a saturated calomel reference electrode (SCE), a platinum plate as the counter electrode and a St-12 steel sample as working electrode. The St-12 steel alloy samples were mounted in a polyster resin, and exposed electrode was ground with emery paper (400–2500 grit), rinsed with distilled water, and then degreased. The tip of the horn that was attached to the power supply of the sonication device was inserted into the solution.

2.4. FT-IR studies

The Fourier transform infrared (FT-IR) spectra of PPy-SiN nanocomposite, pure PPy and SiN nanoparticles were also recorded by Bruker, Tensor 27 spectrophotometer in the wave number range of 4000–500 cm^{-1}. After preparation of the films (PPy and PPy-SiN nanocomposite) on St-12 steel, the film was scrabbed and mixed with KBr to make the FT-IR spectra.

2.5. Corrosion measurements

The Polarization and EIS techniques were used for corrosion measurements of the prepared films in a NaCl 3.5% solution at room temperature. The exposed sample area was 1 cm^2. All impedance measurements were recorded at open circuit potential in the frequency range of 100 kHz to 10 mHz with a wave amplitude of 10 mV. The real and imaginary parts of the impedance data in the complex plane were analyzed using the ZView® (II) software to determine the parameters of the proposed equivalent electrical circuit models.

The corrosion behavior of the coatings was assessed by potentiodynamic polarization tests which carried out at room temperature. The polarization measurements were carried out in the range of ±250 mV versus OCP at scan rate of 5 $mV\,s^{-1}$. From the anodic and cathodic polarization curves, the Tafel regions were identified and extrapolated to corrosion potential (E_{corr}) to get corrosion current density (i_{corr}). The corrosion potential (E_{corr}), corrosion current density (i_{corr}) and polarization resistance (R_p) were deduced from the Tafel plots. To calculate polarization parameters, NOVA 1.8.14 software (Metrohm, Autolab B.V. Company) was used.

2.6. Experimental design

At the present work, Taguchi design of experiment (DOE) technique has been applied to optimize the three electrochemical parameters. The nine Taguchi experiments were performed to synthesize the coatings and the corrosion resistance of coatings was obtained as main responses. The Minitab software was used and the signal-to-noise (S/N) ratio at each levels for various factors was plotted. Depending on the types of the characteristics, there are several S/N ratio: lower is best (LB), nominal is best (NB) and higher is best (HB) [26]. In the present study, corrosion resistance of coatings intended to be maximized, so the HB characterization was adopted.

3. Results and discussion

3.1. Electrodeposition

In the case of electropolymerzation on oxidizable metals, the choice of supporting electrolyte is very important because of competition between monomer and metal substrate oxidation. In the presence of oxalic acid, as used in this work, a pseudo-passive layer develops on steel surface that prevents base metal dissolution while allowing polymer growth on the surface [27].

The potential–time curves for the galvanostatic electrodeposition of polypyrrole (PPy) and polypyrrole-silicon nitride (PPy-SiN) on St-12 steel from aqueous solutions containing pyrrole 0.1 M, $H_2C_2O_4$ (0.1 M) and (350 mg/L) SiN in nanocomposite deposition at a current density of 4 mA/cm^2 are shown in Fig. 1. The curves consist of three regions (a–c in Fig. 1) corresponding to the active dissolution of the substrate, creation of pseudo-passive layer and electropolymerisation of pyrrole, respectively. The coating thickness examined by ElektroPhysik (eXacto) was 3.4 ± 0.9 μm.

3.2. Taguchi method

In this work, we studied the effect of three factors each at three levels with an aim to obtain the conditions for the nanocomposite coatings with the highest corrosion resistance. The factors and levels that are used to design an L9 orthogonal array have been summarized in Table 2. The corrosion resistance of the coatings was