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Electrochemical synthesis of polypyrrole/polyhedral oligomeric silsesquioxane nanocomposite on copper for corrosion protection

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ABSTRACT

Electrochemical synthesis of polypyrrole (PPy)/polyhedral oligomeric silsesquioxane (POSS) nanocomposite on copper is studied using cyclic voltammetry technique in aqueous sodium benzoate solution. The resulting PPy/Cu and PPy/POSS/Cu films were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analysis. The performance of PPy and PPy/POSS nanocomposite as protective coatings against corrosion of Cu in 3.5% NaCl solution is assessed by potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). The corrosion potential for PPy/POSS/Cu is positively shifts by 0.071 V in comparison with uncoated copper. The corrosion current density is found to be 24.08, 7.23, and 2.101 μA/cm^2 for uncoated Cu, PPy coated Cu and PPy/POSS coated Cu, respectively. The results showed that by adding the POSS nanostructures within PPy matrix, the current density of the monomer oxidation decreased, significantly. The EIS studies indicated that the charge transfer resistance increases with the presence of PPy/POSS and accordingly, protection of copper improved against corrosion action.

1. Introduction

Copper is one of the most important nonferrous metals that has been used in different industries and water distribution networks [1]. The protection of copper against corrosion has received reliable attention, recently. To date, many materials have been examined as potential candidate of anti-corrosion like inorganic inhibitors [2], heterocyclic organic compounds containing nitrogen, sulfur or oxygen atoms such as azoles [3–6], amines [7–10], amino acids [11,12], etc. In recent years, there has been much interest in the study of conducting polymers on metals because of their corrosion-inhibiting action and reduced corrosion rate [13,14]. Among all conducting polymers, polyaniline (PANI) and polypyrrole (PPy) take special focus because of their good stability and applications in supercapacitors [15], cell growth [16], solar cells [17,18], corrosion protection [19,20] and sensing [21]. Polyaniline is less attractive than PPy due to the possible presence of benzidine moieties in the polyaniline backbone, which may yield carcinogenic products upon degradation [22]. Many researches have been conducted on PPy as coating for copper protection. Fenelon and Breslin have electropolymerized pyrrole on Cu to generate a homogeneous and adherent PPy films. These films exhibited significant corrosion protection properties in acidified and neutral 0.1 M NaCl solutions even on polarization to high anodic potentials [23]. Pyrrole was electropolymerized on copper from a salicylate solution by Annibaldi et al. The positive potential shift of the corrosion potential observed for PPy coated copper confirmed that this polymer has significant role on corrosion protection [24]. Lei et al. electrosynthesized PPy films on copper from phytic acid (IP_6) solution by constant current oxidation. Obtained results showed that the protective and oxidative properties of the PPy-IP_6 film. The film is degraded during the long time immersion in NaCl solution and finally potential decreased to −0.05 V indicating protection of the PPy-IP6 layer against copper corrosion [25]. In other study, the corrosion protective properties of highly adherent polypyrrole films were studied using dihydrogen phosphate solution. The electrochemical techniques revealed that the polypyrrole coating effectively protects the copper substrate from corrosion in a chloride solution [26]. Herrasti et al. have successfully electropolymerized pyrrole on Cu to generate a homogeneous and adherent film. It was observed that this film presents excellent corrosion behavior in highly aggressive media such as 3% NaCl [27]. Tuken and co-workers reported the formation of polypyrrole/polythiophene (PPy/PTh) coated copper for corrosion protection in 3.5% NaCl solution. It was shown that the PPy/PTh coating could provide effective protection against copper corrosion for considerable immersion periods [28].

Recently, investigations have been shown that the synthesis of polymers in the presence of nanoparticles (NPs) can increase their

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ability to interact with the ions liberated during the corrosion in the presence of NaCl [29]. For example, it is reported that the incorporation of TiO_2 nanoparticles within PPy matrix improved the corrosion protection, biocompatibility and barrier effect of PPy on 316L stainless steel substrate [30]. Tallman et al. has synthesized PPy/Al_2O_3 nanocomposites as coating for corrosion protection of aluminum alloy. The presence of alumina NPs improved the coating behavior upon exposure to aggressive solution due to swelling of dedoped PPy and absorbed moisture penetration inside the coating [31].

Polyhedral oligomeric silsesquioxane (POSS) are well known as novel building blocks for inorganic–organic hybrid materials unlike traditional organic compounds. POSS derivatives are nonvolatile, odorless and environmentally friendly materials [32]. The incorporation of POSS NPs into a polymeric material can dramatically improve its mechanical properties and reduce its flammability, heat evolution, and viscosity during processing. In the present study the PPy/POSS nanocomposites electrosynthesized on copper surface in sodium benzoate solution. The corrosion protection properties of this layer were investigated using various electrochemical techniques. To the best of our knowledge, there are no reports in the literature about the electropolymerization of pyrrole in the presence POSS nanostructures on copper for corrosion protection properties.

2. Experimental

2.1. Materials

Pyrrole (99%) is purchased from Fluka. The POSS derivative of octa methyl POSS was obtained from Hybrid Plastics Co. Sodium benzoate (99%) and all other chemicals used in this study were purchased from Merck Chemical Co. Pure water with an 18 MΩ-cm resistivity was produced using a Millipore water purifier (MilliQ, Millipore, 18.2 MΩ-cm, USA).

The pyrrole monomer was distilled while the other analytical grade chemicals were used without any further purification. The electrosyntheses were performed in an aqueous solution of 0.5 M pyrrole in 0.25 M sodium benzoate in the presence of POSS nanostructure prepared using ultrapure water. All the experiments were carried out at room temperature and in atmospheric pressure. To produce a stable and homogenous dispersion of POSS, the test solutions were treated by ultrasonication for 15 min at 25 °C.

2.2. Electrochemical measurements

Electropolymerization and the electrochemical studies were carried out in a conventional three electrode system with a copper sheet (area 1 cm^2) as working electrode, platinum wire as counter electrode, and Ag/AgCl (KCl 3 M) as reference electrode. Prior to each electrochemical test, the working electrode was mechanically polished with abrasive paper (1500 grade) and rinsed by distilled water and acetone and then dried in air. Polymerization was achieved by cyclic voltammetry by sweeping the potential in the region between −1.0 and 1.5 V during 20 cycles using a Potentiostat/Galvanostat EG&G Model 263 A; USA with a PC and electrochemical set up that controlled with M 270 software. Continuous stirring of the electrolyte was performed using a magnetic stirrer and sonication was conducted in order to prevent agglomeration of POSS additives in the electrolyte suspension. Corrosion performance of the PPy/POSS coated copper was investigated using electrochemical impedance spectroscopy (frequency range from 10^5 to 10^{-2} Hz and amplitude of 10 mV) using a Frequency Response Detector EG&G Model 1025; USA with a PC and electrochemical set up that is controlled with M398 software. Potentiodynamic polarization measurements were performed at 1 mV s^{-1} in 3.5% NaCl solution at room temperature. EIS measurements were conducted at open circuit potential.

2.3. Characterization of PPy and PPy/POSS films

The structures of PPy and PPy/POSS nanocomposites coated Cu were analyzed by FT-IR reflectance spectrophotometry (using a Bruker spectrometer model 22 Vector, Germany). Analysis of the spectra were done using the version 4 of Opus software. Scanning electron microscopy (SEM) images of the PPy film and PPy/POSS NC were taken with Vega 5135 (Tescan, Brno, Czech Republic) and HV (high voltage) 1500 V instrument.

3. Results and discussion

3.1. Cyclic voltammetry studies

Cyclic voltammetry was used for the electrochemical synthesis of PPy and PPy/POSS nanocomposites on the copper electrode. The CV curves recorded on copper, in the potential range required for the electropolymerization of pyrrole in sodium benzoate solution were presented in Fig. 1. A copper oxidation shoulder was observed at −0.2 V which attributed to the formation of Cu species on the electrode surface, as reported earlier [33]. During reverse scan, two main peaks were seen which expected to be ascribed to the reduction of cooper oxides formed in the corresponding anodic scan. The first peak at −0.48 V could be attributed to the partial reduction of Cu species. The second peak at −0.79 V is well defined peak with a relatively large area and might be assigned to the reduction of the remaining Cu species which was not reduced under the first peak. On the other hand, during reverse scan, Cu oxide is slowly destroyed and two oxidation processes occur in the potential range between −0.45 and −0.8 V resulting in precipitation of Cu(II) benzoate on the electrode surface. Fig. 2 shows the cyclic voltammograms of copper in solution containing 0.2 M pyrrole and 0.25 M sodium benzoate in the absence and the presence of POSS NPs. Fig. 2a shows the successive scans of the electropolymerization of PPy on Cu in 0.25 M sodium benzoate solution by sweeping the potential in the region between −1.0 and 1.5 V at a scan rate of 100 mV s^{-1} during 20 cycles. As can be seen in the first scan, an oxidation peak attributed to the oxidation of monomer appears at about 1.1 V with current density of 2.1 mA cm^{-2}. Then, the intensity of this oxidation peak gradually declines with further increasing of the scan number and in the 4th cycle reaches a stable trend that confirms the

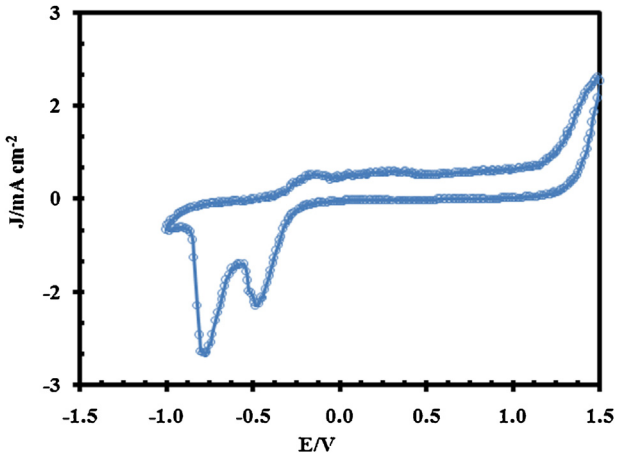

Fig. 1. Cyclic voltammograms on a copper electrode in an aqueous solution of 0.25 M sodium benzoate at 100 mV s^{-1}.