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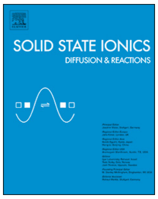

Potentiodynamic and electrochemical impedance spectroscopy study of anticorrosive properties of p-type conductive polymer/TiO_2 nanoparticles

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A B S T R A C T

We introduce a simple and facile strategy for dispersing of nanoparticles within a p-type conducting polymer matrix by in situ electropolymerization using oxalic acid as the supporting electrolyte. Coatings prepared from polypyrrole–nano-metal oxide particles synthesized by in situ polymerization were found to exhibit excellent corrosion resistance much superior to polypyrrole (PPy) in an aggressive environment. The anti-corrosion behavior of polypyrrole films in different states and the presence of TiO_2 nanoparticles synthesized by electropolymerization on copper electrodes have been investigated in a corrosive solution using potentiodynamic polarization and electrochemical impedance spectroscopy. The electrochemical response of the coated electrodes in polymer and nanocomposite state was compared with bare electrodes. The use of TiO_2 nanoparticles has proved to be a great improvement in the performances of polypyrrole films for corrosion protection of copper samples. The polypyrrole synthesized in the presence of TiO_2 nanoparticles coated electrodes offered a noticeable enhancement of protection against corrosion processes. The exceptional improvement of performance of these coatings has been associated with the increase in barrier to diffusion, prevention of charge transport by the nanosize TiO_2, redox properties of polypyrrole as well as very large surface area available for the liberation of dopant due to nano-size additive.

1. Introduction

In recent years the development and use of organic compounds and conducting polymers as protective coatings against the corrosion of metals and alloys have become one of the most exciting new research fields due to their oxidation and reduction properties [1, 2]. Although the traditional anticorrosion materials provide excellent corrosion protection coatings, their usage is limited in practice due to their toxicity. So, alternative approaches are needed in order to eliminate hazardous effects from the environment and to protect human health. While corrosion control via conductive polymer can be attributed to the ability of the polymer to form a physical barrier against corrosive agents and maintains the metal in a passive state, in some cases the rate of the cathodic reaction, such as oxygen reduction, can be minimized [3].

Polypyrrole (PPy) is one of the most promising conductive polymers due to its high conductivity, stability and ease of synthesis [4, 5] Physical and structural properties of conductive polymers could affect the degree of corrosion protection of coatings. There is a significant interest in developing electrochemical methods to deposit the homogeneous and adherent polymer since these methods provide better control on morphology, thickness, and conductivity of coatings [6]. Although it is very easy to electropolymerize pyrrole to generate the conducting polymer on inert substrates, including gold or platinum, there are major limitations in the case of oxidisable metal substrates, such as copper [7]. The dissolution of the working electrode is reached before the monomer oxidation due to its low corrosion potential in aqueous media and consequently the electropolymerization reaction is impeded. In order to overcome this difficulty, one approach is the use of an electrolyte including an appropriate anion that deposits the complex compound with the dissolved copper and induces copper passivity, so electropolymerization of the monomer can begin on the passivated copper [8, 9].

Copper and copper-based alloys have been one of the most common materials used in a great variety of applications due to its excellent electrical and thermal conductivity, mechanical workability, and other relatively noble properties [10]. Although, copper and its alloys are generally known to be relatively noble materials, their corrosion take place at a significant rate depending on the service environment which limits greatly their application in practice. In order to control and

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reduce corrosion of copper and its alloys in corrosive media, several techniques have been applied. For example, Li et al. [11] have reported that 4-amino-antipyrine exhibits good inhibiting properties for copper corrosion in 3.0 wt% NaCl solution and the inhibition efficiency decreases with increasing the temperature. In similar work, Li's group [12] have investigated the inhibition effect of 5-Mercapto-3-phenyl-1,3,4-thiadiazole-2-thione potassium (MPTT) self-assembled monolayer (SAM) on copper surface. They have reported that the MPTT SAM inhibits both anodic and cathodic reactions with an anodic predominance. Quraishi's team [13] have studied the inhibition effect of three triazole derivatives namely 4-amino-4H-1,2,4-triazole-3thiol (ATT), 4-amino-5-methyl-4H-1,2,4-triazole-3thiol (AMTT) and 4-amino-5-ethyl-4H-1,2,4-triazole-3thiol (AETT) against the corrosion of copper in 0.5 M HCl solution and have indicated that all three examined compounds are cathodic type inhibitors. El-Haddad [14] has introduced chitosan as a green inhibitor for copper corrosion in 0.5 M HCl solution and showed that inhibition efficiency increased with increasing the concentration of inhibitor. Tansug et al. [15] have synthesized a new corrosion inhibitor namely methyl 3-((2-mercaptophenyl)imino)butanoate (MMPB) for copper protection and evaluated its inhibition efficiency in acidic media. Recently, Mallaiya et al. [16] have reported that ciprofloxacin can act as a good inhibitor for the corrosion of copper in both in 1.0 M HNO_3 and 0.5 M H_2SO_4 solutions.

In present work, polypyrrole nanocomposite in absence and presence of TiO_2 has been deposited by electrochemical method on copper using an oxalate electrolyte. The nanocomposite films have been synthesized by cyclic voltammetry (CV) method and characterized by scanning electron microscope (SEM) and EDS. The protective effect of nanocomposites films have been investigated by potentiodynamic and electrochemical impedance spectroscopy (EIS) techniques.

2. Experimental

All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. Electrochemical measurements were recorded using Zahner Zennium and a conventional three-electrode system was used throughout this work. Copper rods embedded in a Teflon holder were used as working electrodes. Before each experiment, the electrode was polished successively with 500 and 1000 emery paper, cleaned in distilled water and degreased in acetone. Following this pretreatment, the electrode was immediately transferred to the electrochemical cell. Saturated Ag/AgCl electrode and a Pt wire were employed as the reference and counter, respectively.

PPy and its composites were formed on the copper surface using pyrrole monomer solutions (5 mL 0.1 M pyrrole in 0.3 M oxalic acid and 5 mL 0.3 M pyrrole in 0.3 M oxalic acid) and pyrrole monomer and TiO_2 suspension (5 mL 0.3 M pyrrole in 0.3 M oxalic acid, and 0.001 g TiO_2 nanoparticles) under ultrasonic irradiation, respectively. The electropolymerization was carried out by potential cycling (5 cycles at a scan rate of 10 mV s^{-1} between 0.5 and 1.3 V vs. Ag/AgCl). The EIS measurements were carried out at the open circuit potential with amplitude of 5 mV ac potential in the frequency range of 100 kHz to 100 mHz. All capacitance values used in this paper were normalized by fitting on Z-view program. The potentiodynamic current-potential curves were recorded by sweeping the electrode potential automatically from −0.4 to 0.6 V vs. Ag/AgCl with scanning rate of 1 mV s^{-1}. Morphology and particle dispersion were investigated by scanning electron microscopy (SEM, Mira 3-XMU). All studies were carried out at 298 ± 2 K.

3. Results and discussion

3.1. Electrosynthesis of PPy composite film

In this section, in order to investigate the effect of electrolyte type, the electrochemical synthesis of polypyrrole was carried out in different electrolytes such as HNO_3, H_2SO_4 and $NaNO_3$ by cyclic voltammetry method in the potential range from −0.4 to +1.8 V. In the presence of these electrolytes, polypyrrole coating does not form on the surface of the copper. Subsequently, by studying previous works on the synthesis of polypyrrole on copper [17], the electropolymerization of pyrrole must be carried out in electrolytes that can form a sticky film of polypyrrole on the surface of copper. In the inorganic acids used in the process of electropolymerization, copper is oxidized and this prevents the formation of adhesive and uniform film. One way to avoid this problem is to passivate the electrode before the electrogeneration of the polymer in oxalic acid medium [17]. Oxalate anions are known due to the formation of stable complexes with copper cations. In particular, oxalate anions (OX^{2-}) with Cu^{2+} could produce copper oxalate complexes with stoichiometric 1: 1 and 1: 2 as follows [17]:

$$Cu^{2+} + Ox^{2-} \leftrightarrow Cu(Ox) \tag{1}$$

$$Cu^{2+} + 2Ox^{2-} \leftrightarrow [Cu(Ox)_2]^{2-} \tag{2}$$

In addition, due to the acidity of the environment, the 1: 1 complex can be protonated as follows [17]:

$$Cu(Ox) + H^{+} \leftrightarrow [HCu(Ox)]^{+} \tag{3}$$

$[Cu\ (Ox)_2]^{2-}$ complex in the range of pH 3 to 11 is more stable than the other species. It has also been reported that the presence of dissolved Cu^{2+} species increases the efficiency of the synthesis of conducting polymers such as polypyrrole [17]. The stability of polypyrrole layers on the surface of copper electrode may be attributed to complex formation between copper cation and polymer due to the electron transfer between copper and polypyrrole, which prevents the attack of nuclear-like species such as water molecules [17]. In order to investigate the electrochemical behavior of copper in an oxalic acid solution, the surface of the electrode was scanned over 3 consecutive cycles in the potential range of −0.3 to +1.2 V at a scan rate of 10 mV s^{-1}. The cyclic voltammograms recorded in 0.3 M oxalic acid solution are shown in Fig. 1. In the first cycle at a potential of about 95 mV vs. Ag/AgCl an increase in the amount of anodic current was observed which demonstrates that copper dissolution has started. With further extension of potential in anode direction, a peak is observed at a potential of about 280 mV, which is attributed to an increase in the rate of copper dissolution. Then the current gradually decreases and remains approximately constant. The inactivation of the electrode surface during subsequent cycles results in a decrease in oxidation peak height. The percentage of current loss in the copper oxidation process in sequential cycles is given in Table 1. As seen from the values obtained for the anodic potential in subsequent cycles, due to the formation of copper inactive layers, the potential moves to lower positive values, which indicates the hard oxidation of copper. The inactivation mechanism is based on the formation of insoluble oxide and copper oxalate compounds, such as Cu(Ox) and $[Cu(Ox)_2]^{2-}$, on the electrode surface. During the reverse sweep at a potential of about 300 mV, an increase in

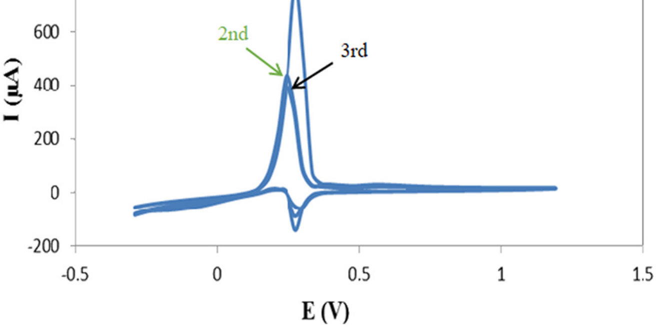

Fig. 1. Cyclic voltammograms of copper in 0.3 M oxalic acid.