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Corrosion protection of aluminum by electrochemically synthesized composite organic coating

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ABSTRACT

The corrosion performance of TiO_2 doped polypyrrole coated (PPy-TiO_2) aluminum and application as anode material for direct methanol fuel cell were investigated. The surface morphology was analyzed by scanning electron microscopy, atomic force microscopy, energy-dispersive X-ray spectroscopy and X-ray diffraction technique. The conductivity values of coatings were measured with four probe technique. The electrochemical impedance spectroscopy and anodic polarization obtained at periodic intervals for 168 h. The corrosion resistance of Al/PPy-TiO_2 is almost 5 times higher than Al for 168 h immersion. PPy-TiO_2 coating has better electrocatalytic activity than PPy for methanol oxidation reaction.

1. Introduction

Nano composite organic coatings have been extensively preferred in photovoltaic applications, energy saving systems, etc [1,2]. Aluminum is regarded as a good substrate for this purpose because of its low density, strength, electrical and thermal conductivity [2]. For instance, the micro direct methanol fuel cell was fabricated by adopting aluminum alloys as a substrate for the first time by Deng et al. [3]. Yuan et al. [4] developed the air-breathing aluminum current collectors for powering portable applications. To obtain strong anti-corrosion resistance, 3 μm Au layer was deposited on the current collectors using chemical plating. It was compared with the graphite and stainless steel. The Au coated Al current collector exhibited superior characteristics in electric conductivity measurements. Pournaghi-Azar and Habibi [5] used palladized aluminum as a substrate for electrosynthesis of poly(phenylenediamines) (PPDA) and they modified with Pt micro-particles. Coating has electrocatalytic activity for the electrooxidation of methanol, but covering the surface of Al/Pd/Pt electrode by PPDA film, enhances slightly the electrocatalytic oxidation peak current of methanol. Although aluminum has several advantages in many applications, corrosion is an important problem for aluminum and its alloys. There are countless studies that have been examined against corrosion, but combining polymer films with inorganic materials such as TiO_2 has many advantages [1]. The composite organic coatings have shown significant corrosion resistance. Zubillaga et al. [6] investigated corrosion protection of AA3105 aluminium alloy via supporting an anodic film with incorporated polyaniline (PANI) and TiO_2 nanoparticles. The polymeriztion mechanism was offered as, TiO_2 has the point of zero charge at pH 5.9, it may be positively charged in the acidic polymerization H_3PO_4 bath. Due to the positive charge on TiO_2, the $H_2PO_4^-$ ions adsorb on TiO_2. These specifically adsorbed anions would work as a charge compensator for positively charged PANI chain in the formation of polyaniline–TiO_2 composites. Similar reaction mechanism has been put forward for PANI–MnO_2 composite [6]. The study showed that corrosion resistance of AA3105 was enhanced by the TiO_2 nanoparticles containing PANI coating. It is attributed to the TiO_2 particle rich thin film layer formed on the outer part of the coating [6]. The similar coating was produced by Radhakrishnan et al. [7] for protection of steel. PANI-TiO_2 coatings was synthesized by in situ polymerization with different TiO_2 ratio. The corrosion performance of coatings was associated with enhanced diffusion barrier properties of coatings and prevention of charge transport by TiO_2 [7]. Mahmoudian et al. synthesized polypyrrole-TiO_2 containing polyvinyl butyral coatings via chemical oxidative polymerization for preventing the corrosion of mild steel [8]. This composite organic coating decreased the corrosion rate of mild steel. Findings clearly indicates that the effect of the TiO_2 particles is similar to previous studies [6–8]. The studies [8–11] showed that combining polymer coatings with TiO_2 is beneficial in the corrosion researches. Although several polymer have been studied for

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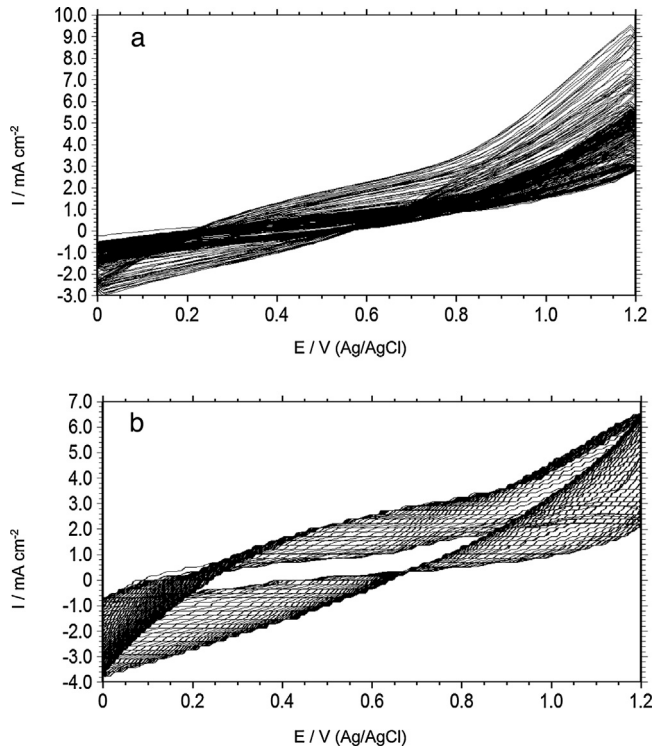

Fig. 1. The cyclic voltammograms of Al in 0.4 M oxalic acid in the presence of 0.1 M pyrrole (a) and 1 g L^{-1} TiO_2 + 0.1 M pyrrole (b) solutions (the scan rate: 50 mV s^{-1}).

this purpose [11–19], polypyrrole (PPy) has significant advantages such as high conductivity, availability, electrochemical and optical properties also effortless synthesis by chemical and electrochemical techniques [11–16].

In this study, PPy-TiO_2 composite coatings were electrochemically synthesized on Al 7075 electrode, the corrosion behavior and electrocatalytic activity on methanol oxidation reaction were investigated. TiO_2 were prepared via sol–gel method, composite coating was synthesized by cyclic voltammetry, characterized with scanning electron microscopy (SEM), atomic force microscopy (AFM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) techniques. The corrosion performance was determined by open circuit potential (E_{ocp})–time curves, electrochemical impedance spectroscopy (EIS) and anodic polarization curves. The electrocatalytic activity of Al/PPy and Al/PPy-TiO_2 were investigated for methanol electro-oxidation reaction by electrochemical measurements.

2. Experimental

TiO_2 particles were prepared via sol–gel method [20] by hydrolysis of titanium butyrate ($Ti(OC_4H_9)_4$). 1 mL of titanium butyrate and 0.8 mL of acrylic acid were mixed with 8.2 mL of ethanol. 1 mL of nitric acid and 39 mL of distilled water added the mixture at 343 K. It was kept for 3 h at 343 K. The gel was calcined at 773 K for 5 h. Other chemicals were purchased from Sigma–Aldrich (Adana, Turkey) products. The electrochemical synthesis of polypyrrole (PPy) was achieved by cyclic voltammetry in 0.1 M pyrrole and 1 g L^{-1} TiO_2 containing 0.4 M oxalic acid solutions. Prior to each experiment, the Al electrode (with 0.196 cm^2 surface area) was mechanically abraded with abrasive paper (1200 grade) and cleaned in a 1:1 acetone: ethanol mixture then rinsed with water. The CHI 604D electrochemical analyzer (serial number R0633) was used for all electrochemical experiments. The counter electrode was a platinum sheet (with 2 cm^2 surface area), and the reference electrode

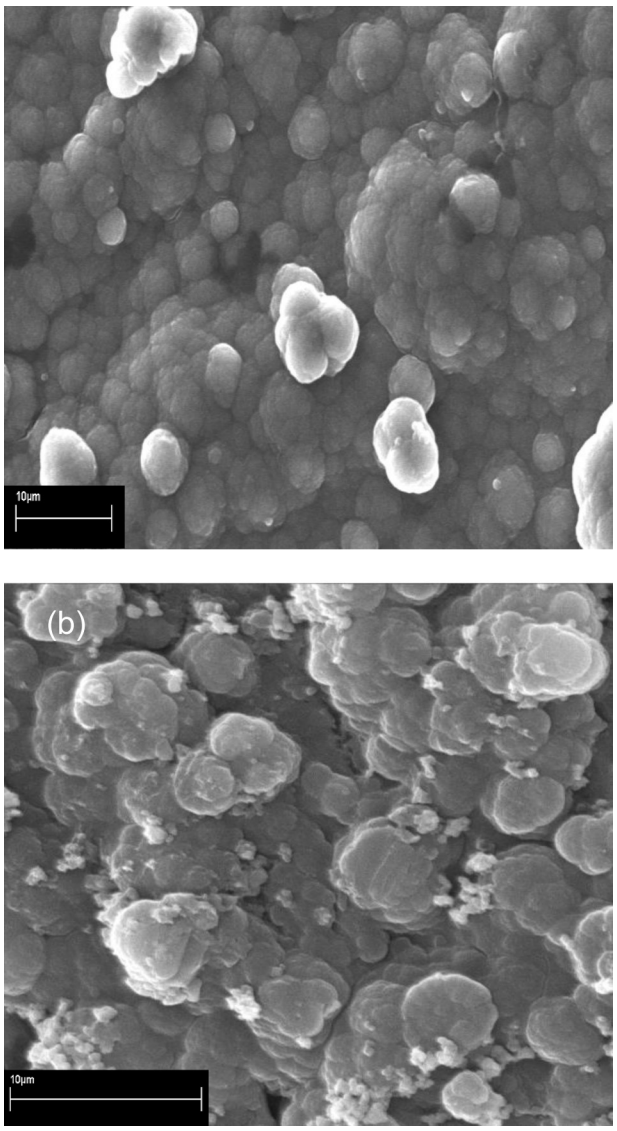

Fig. 2. SEM micrographs of Al/PPy (a) and Al/PPy-TiO_2 (b) surfaces.

was Ag/AgCl (3 M KCl). The cyclic scans were recorded between 0.0 and 1.2 V (Ag/AgCl), the scan rate was 50 mV s^{-1}. For each experiment, a freshly prepared 50 mL solution was used. The test solutions were opened to the atmosphere, and the temperature was controlled with thermostat (Nuve BS 302 serial number 03–0033). The surface of electrodes was examined by SEM and AFM. The SEM images were taken using a Carl Ziess Evo 40 SEM instrument. The chemical composition of the electrode surfaces was determined by energy-dispersive X-ray spectrometer (EDX) which is part of SEM device. Thermal analyses data were obtained under nitrogen atmosphere using Pyriss Diamond TG/DTA PerkinElmer thermal analysis and Pyriss 7.0 data-processing system at a heating rate of 10 °C/min. The AFM images were taken using with Park Systems instrument (scan size: 10 μm × 10 μm, scan rate: 1.001 Hz). The X-ray diffraction (XRD) patterns of electrodes were recorded on a Bruker AXS D8 with CuKα radiation (λ = 0.15406 nm). The conductivity values of coatings was determined using the four terminal DC method. For this purpose, the polymer films were peeled off the electrodes' surfaces mechanically and their pellets were prepared then Four Point Probe (serial number FPP 470) was used. The conductivity measurements were obtained at 20 °C. The EIS experiments were employed between 100 kHz–0.006 Hz at open circuit

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