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Electrochemical corrosion characteristics of conducting polypyrrole/polyaniline coatings in simulated environments of a proton exchange membrane fuel cell

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ABSTRACT

A bilayer conducting polymer coating consisting of an inner layer of polypyrrole (Ppy) with large dodecylsulfate ionic groups and an external polyaniline (Pani) layer with small SO_4^{2-} groups was electrodeposited on type 304 stainless steel bipolar plates of a proton-exchange membrane fuel cell (PEMFC). The corrosion performance of conducting Ppy/Pani bilayer coatings on 304SS in simulated cathode and anode environments (0.1 M H_2SO_4 solution bubbled with air or H_2 at 80 °C) of a PEMFC was investigated by electrochemical impedance spectroscopy, polarization and open circuit potential measurements. The experimental results showed that the Ppy/Pani bilayer increased the free corrosion potential of the steel by about 310 mV (SCE) and 270 mV (SCE) in simulated cathodic and anodic environments of the PEMFC, respectively. Long-term exposure studies showed that the bilayer was highly stable and inhibited the corrosion of the steel effectively in simulated cathodic and anodic environments, which was attributed to its “self-healing” effect.

Introduction

The proton-exchange membrane fuel cell (PEMFC) is a clean and highly efficient power generation technology that converts hydrogen and oxygen gases into electricity and consists of a catalyst, a membrane electrode and bipolar plates. Of these components, the bipolar plates are the bulkiest component and also one of the most expensive parts to manufacture [1]. Until now, the main materials used for bipolar plates have been graphite and graphite composites. However, their low mechanical strength and high gas permeability inhibit their commercial application. In comparison, metallic bipolar plates possess excellent electrical conductivity, high strength, low gas permeability and can be manufactured at low cost and can also be processed into thin plates. Consequently, the volume and weight of a PEMFC are both decreased and the power density of the fuel cell stack is

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increased. However, in the weak acidic environment of a PEMFC (pH 2–4), which is correlated with the release of sulfonate groups and hydrogen ions from the proton-exchange membrane, metallic bipolar plates are usually attacked, with the formation of passive films and the dissolution of metallic ions [2]. In recent years, coatings with high corrosion resistance and electrical conductivity have been applied to protect metallic bipolar plates [3–7].

Conducting polymers have been proposed as candidates for corrosion protection of metallic bipolar plates [8–11]. Joseph et al. investigated Pani and Ppy conducting polymers electrodeposited on stainless steel bipolar plates and suggested that both coatings could improve the corrosion resistance of stainless steel bipolar plates with low contact resistance [8]. However, the stability of the coatings for extended immersion times was not investigated. Similarly, Gonzalez-Rodriguez found an increased corrosion resistance of polypyrrole coatings on 304 stainless steel (304SS) bipolar plates [9]. However, the coating degraded rapidly with prolonged immersion time. Thus, it is essential to boost the reliability of conductive polymers as a protective layer for metallic bipolar plates. Deyab proposed that a polyaniline coating mixed with carbon nanotubes (CNTs) could improve the corrosion resistance of aluminum bipolar plates effectively [12]. Rajkumar confirmed that the composite coatings improved the corrosion resistance of the single coating in acidic solution [13].

It is acknowledged that a conductive polymer could reoxidize the metal that is attacked, with the formation of a passive film, at the same time as the polymer is reduced, accompanied by the release of doped ions [14]. Once the polymer is completely reduced, it acts merely as a physical barrier [15]. In this study, a Ppy/Pani bilayer with a self-healing capacity was electropolymerized on type 304SS. To evaluate the stability of the bilayer credibly, the corrosion performance of the Ppy/Pani bilayer was investigated in simulated anodic and cathodic environments of a PEMFC.

Experimental procedures

Electrodeposition of Ppy/Pani coatings

Sheet-shaped sections of 304SS with an exposed surface area of 1 cm^2 were coated with epoxy resin, followed by grinding with 240# grit emery paper and cleaning with distilled water and acetone. Electrodeposition was carried out in a glass cell with a stainless steel plate as the counter electrode. For the preparation of the bilayer coatings, as described in Ref. [16], the inner Ppy layer doped with DS^- was galvanostatically electrodeposited on the stainless steel in aqueous 0.4 M pyrrole containing 0.15 M sodium dodecylsulfate (SDS) supporting electrolyte at 5 °C under a nitrogen atmosphere at a current density of 3 mA cm^{-2} for 12 min. The outer Pani layer with the small counter-ion SO_4^{2-} was electrodeposited over the Ppy layer from aqueous solutions of 0.5 M aniline and 1 M H_2SO_4 at 5 °C using a cyclic voltammetry technique. The thickness of the bilayer coatings was around 15 μm.

Electrochemical measurements

Electrochemical measurements in simulated cathodic and anodic environments (0.1 M H_2SO_4 bubbled with air or H_2 at 80 °C) were conducted in a three-electrode setup where a platinum sheet was selected as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. All tests were conducted with a Princeton Applied Research PAR2273 Potentiostat/Galvanostat under computer control. During the potentiodynamic polarization tests, the potential scan rate was 20 mV min^{-1} after 1 h immersion. In addition, potentiostatic polarization measurements were carried out at 600 mV (SCE) and −240 mV (SCE) to evaluate the stability of the polymer coating further in simulated anodic and cathodic environments, respectively. Electrochemical impedance measurements were carried out between 0.01 and 100 kHz at open circuit potential. The amplitude of the input sine-wave voltage was 5 mV.

Results and discussion

Electrochemical polarization measurements

Fig. 1 shows the potentiodynamic polarization curves for Ppy/Pani-coated 304SS and the bare steel after immersion for 1 h in the simulated anodic and cathodic environments. In the cathodic environment, 304SS was in the passive state at E_{corr} and the free corrosion potential and current density were −262 mV (SCE) and 0.197 mA cm^{-2}, respectively. For Ppy/Pani-coated steel the corrosion potential was 114 mV (SCE), improving by almost 380 mV (SCE) compared with the bare steel, and its corrosion current density was 0.161 mA cm^{-2}.

The corrosion current and the corrosion potential of 304SS in the anodic environment were 0.122 mA cm^{-2} and −341 mV (SCE), respectively, while those for the bilayer coated steel were 0.206 mA cm^{-2} and 64 mV (SCE), respectively. It can be seen that the corrosion current density for the Ppy/Pani-coated steel in the simulated anodic and cathodic environments is close to that of the 304SS, which is related to the oxidation of the bare steel and the polymer or the ion-exchange between the interface of the Pani/Ppy bilayer and the solution [17].

Fig. 2 shows the potentiostatic polarization at 600 mV (SCE) and −240 mV (SCE) for the Ppy/Pani coatings. The polarization current density of Ppy/Pani-coated steel decreased significantly to a steady value with increasing time at 600 mV (SCE). There was no obvious degradation after 4 h of polarization, indicating that the bilayer coating could prevent the inward diffusion of aggressive ions effectively. Similarly, the polarization current density of Ppy/Pani decreased significantly initially at −240 mV (SCE) and then remained stable with extended polarization time. After polarization for 4 h, it could be observed that the samples turned dark green, which was related to the reduction of the external polyaniline film.

Open circuit potential measurements

Fig. 3 shows the open circuit potential versus time curves for 304SS and the bilayer coating in simulated cathodic and

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