Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Effect of conducting composite polypyrrole/polyaniline coatings on the corrosion resistance of type 304 stainless steel for bipolar plates of proton-exchange membrane fuel cells

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ARTICLE INFO

Article history: Received 4 April 2008 Received in revised form 22 April 2008 Accepted 22 April 2008 Available online 2 May 2008

Keywords: PEMFC Stainless steel bipolar plates Bilayer conducting polypyrrole/polyaniline coatings HCl solution Corrosion Electrical contact resistance

ABSTRACT

A bilayer conducting polymer coating composed of an inner layer of polypyrrole (Ppy) with large dodecylsulfate ionic groups obtained by galvanostatic deposition, and an external polyaniline (Pani) layer with small SO_4^{2-} groups obtained by cyclic voltammetric deposition was prepared to protect type 304 stainless steel used for bipolar plates of a proton-exchange membrane fuel cell. The corrosion performance of the bare and coated steel in 0.3 M HCl was examined by electrochemical impedance spectroscopy, polarization and open-circuit potential measurements. The experimental results indicated that both the composite Ppy/Pani coatings and the single Ppy coatings increased the corrosion potential of the bare steel by more than 400 mV (saturated calomel electrode), and increased the pitting corrosion potential by more than 500 mV (saturated calomel electrode). The bilayer coatings could reduce the corrosion of the alloy much more effectively than the single Ppy coatings, serving as a physical barrier and providing passivity protection, with acceptable contact resistance.

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1. Introduction

The proton-exchange membrane fuel cell (PEMFC) is a promising power generation system that converts the energy of the reaction of hydrogen with oxygen (or air) to electricity, with water as the only byproduct due to its reduced emissions, high power density and low operating temperatures. Although great progress has been made in reducing the manufacturing cost of PEMFC, materials cost is still a great challenge to their commercial application. Among the PEMFC components, the bipolar plates account for about 80% of the total weight and 45% of the stack cost [1]. The bipolar plate is a multifunctional component that conducts current between cells, facilitates water and thermal management through the cell, and distributes and separates the cathodic and anodic reactant gases. The development of low cost, light, thin bipolar plates is of great significance to the commercial applications of PEMFC. The main materials studied to date for bipolar plates include graphite, metal and graphite polymer composites. The most commonly used bipolar plate material is graphite or its composites with low surface contact resistance and high chemical stability. Unfortunately, graphite is too brittle

to be machined to form thin plates with gas channels on each side, and it has relatively high gas permeability, which lowers the power density of the fuel cell stack. Moreover, the machining of flow fields on graphite plates is expensive, hindering the widescale commercial use of graphite. Metallic bipolar plates exhibit great competitiveness with respect to graphite bipolar plates due to their high electrical conductivity, acceptable material cost, high strength, low gas permeability, and applicability to mass production. Moreover, metallic materials can be machined to thin plates with flow channels, which can reduce significantly the volume and weight of a PEMFC. The metals investigated so far include stainless steel, aluminum, titanium and nickel. The main problem associated with metallic materials is their lack of ability to resist corrosion in a weakly acidic medium usually containing SO₄²⁻, Cl⁻, F⁻ ions, etc., and reactant gases inside the PEMFC without forming passive films and metal ions. The formation of passive films increases the contact resistance, while the dissolution of metals contaminates the membrane electrodes. The passivation and dissolution of metals during operation undoubtedly cause considerable power loss. Therefore, some coatings, including carbon-based and metalbased, have been proposed to protect the metallic bipolar plates [2-6], aiming at achieving high corrosion resistance and low contact resistance. Recently, Tawfik et al. [7] presented an overview of metal bipolar plates for use in PEMFC.





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^{0378-7753/\$ -} see front matter © 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.jpowsour.2008.04.056

Electrically conducting polymers have been candidates for corrosion protection of metals such as stainless steel, carbon steel, copper and aluminum [8–16] since DeBerry [8] found that an electrochemically deposited polyaniline film decreased the corrosion rate of a pre-passivated steel. Biallozor and Kupniewska have recently reviewed the study of electrodeposition of conducting polymers on active metals and their properties [16]. It is possible to protect metallic bipolar plates with conducting polymer films while keeping low contact resistance, especially in the cathode side of a PEMFC, where these polymer films are expected to be more conductive by doping in an acidic solution, because the electrical conductivity of the polymer films is related to their degree of oxidation. To date, there are few reports of the application of conducting polymer coatings to a PEMFC [17–19]. One of the authors of this work tried to apply conductive polypyrrole (Ppy) coatings for the protection of stainless steel bipolar plates of a PEMFC, and observed a significantly improved corrosion resistance of the Ppycoated stainless steel during exposure to HCl for 50 day [17]. Joseph et al. [18] investigated polyaniline and polypyrrole conducting polymers electrodeposited on stainless steel bipolar plates, confirming an improved corrosion resistance of the coated plates with acceptable contact resistance.

The presence of micropores within electrically synthesized conductive polymers allows the inward diffusion of electrolytes, probably giving rise to the delamination of the films and corrosion of the substrate alloy. Thus, it is of great importance to reduce the porosity of the conductive coatings for their corrosion resistance. The deposition of multilayered conducting polymer coatings or composites may be an effective way to improve the corrosion resistance of electrodes [20-22]. Tan and Blackwood [20] investigated the corrosion protection offered by multilayered conducting polymer coatings and observed that the degree of protection was a function of the deposition order of the copolymer, with the best performance for films consisting of a Pani layer on top of a Ppy layer on stainless steel. Tuken et al. [21] reported that the multilayered Ppv/Pphe coatings provided much better corrosion protection to mild steel in an acidic solution than the single coatings by decreasing the porosity and the mobility of the electrolyte solution within the pores of the coatings.

In this study, bilayer Ppy/Pani coatings were electrodeposited on type 304 stainless steel (304SS), and the corrosion behavior in HCl solution was examined to explore the potential of composite polymer coatings for the protection of metallic bipolar plates of a PEMFC.

2. Experimental procedures

2.1. Electrodeposition of polymer coatings

The present study used 304SS as the base material. The sheetshaped specimens with an exposed surface area of 1 cm² were coated with epoxy resin, followed by grinding with 240[#]grit emery paper, and cleaning with distilled water and acetone. Electropolymerization was carried out in a glass cell with a stainless steel plate as the counter electrode. For comparison, a single Ppy film doped with dodecylsulfate (DS⁻) was deposited galvanostatically on the steel at a current density of 3 mA cm⁻² for 15 min in aqueous 0.4 M pyrrole containing 0.15 M supporting electrolyte sodium dodecylsulfate (SDS) at 5 °C under a nitrogen atmosphere. For the preparation of bilayer coatings, a Ppy layer doped with DS⁻ was first galvanostatically deposited on the steel in 0.4 M pyrrole-0.15 M SDS for 12 min, followed by the electrodeposition of a Pani layer with the small counterion SO₄^{2–} over the Ppy layer from aqueous solutions of 0.5 M aniline and 1 M H₂SO₄ at 5 °C using a cyclic voltammetry technique. The total charge for the deposition of the bilayer coatings with a thickness of around 15 μ m was controlled to be the same as that for the single Ppy coatings.

2.2. Contact resistance measurements

The contact resistance of the coatings was measured as shown in Fig. 1. A graphite plate was placed between the two-coated metallic plates, and the electrical resistance was measured as a function of the compaction pressure.

2.3. Electrochemical measurements

A conventional three-electrode system was used for the electrochemical measurements, with a platinum sheet as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. In order to evaluate the protection of the coatings rapidly, an accelerated test was conducted at room temperature in highly corrosive 0.3 M HCl relative to the solution used for a real PEMFC.

All electrochemical measurements were conducted at room temperature with a Princeton Applied Research PAR2273 Potentiostat/Galvanostat. Potentiodynamic polarization was undertaken with a potential scan rate of 20 mV min⁻¹ after 1 h immersion in 0.3 M HCl. Potentiostatic polarization was conducted at 600 mV (SCE) which is close to the operation potential of the cathode for a PEMFC [23]. Electrochemical impedance measurements were carried out between 0.01 Hz and 100 kHz at open-circuit potential. The amplitude of input sine-wave voltage was 5 mV.

3. Results and discussion

3.1. Electropolymerization of polymer films

Fig. 2 shows the potential versus time curve for the electropolymerization of Ppy film at a current density of 3 mA cm^{-2} . The potential decreased sharply in the very initial stage, followed by slow decrease. The instantaneous decrease of the initial potential is related to the nucleation overpotential of the Ppy film on the steel. Once the Ppy film started to grow, the potential decreased slowly. In addition, the growth of Ppy films can be associated with an oxygen evolution reaction accounting for one fraction of the current, since Ppy is known as a catalyst for the O₂ evolution reaction [24].

Fig. 3 shows three cyclic voltammograms for the electrodeposition of Pani on the Ppy-coated steel in $1 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M}$ aniline. In the first positive cycle, the onset of electropolymerization was observed at around 0.75 V (SCE), which shifted negatively with an



Fig. 1. Schematic diagram for contact resistance measurements.



Fig. 2. Potential versus time curve for the galvanostatic synthesis of polypyrrole films on 304 stainless steel.

increase in the cycling number. Two reduction peaks were observed at around 0.4V (SCE) and 0V (SCE), respectively, which shifted towards more negative values with increasing the number of cycles. From the second cycle, two new oxidation peaks were observed at 0.2 V (SCE) and 0.5 V (SCE), respectively, which shifted to a more positive potential with an increase in the number of cycles. Pani has two oxidation and one reduction states, i.e. completely oxidized pernigraniline (PE), partially oxidized emeraldine (EM) and fully reduced leucoemeraldine (LE) forms. The doped EM state is the conductive form. The oxidation peaks at 0.2 V (SCE) and 0.5 V (SCE) are attributed to the transformation of Pani from the LE state to the EM state, and from the EM state to the PE state, respectively, while the two reduction peaks at 0.4 V (SCE) and 0 V(SCE) correspond to the conversion of Pani from the PE state to the EM state, and from the EM state to the LE state, respectively. It is noted that the polymerization reaction of Pani occurs on the top of the Ppy layer, and inside it due to the presence of micropores across it, producing a composite coating more compact than the single Ppy layer, as confirmed by the following corrosion tests.

3.2. Electrochemical polarization measurements

Fig. 4 shows the potentiodynamic polarization curves for the steel with and without coatings after immersion in 0.3 M HCl for 1 h. The corrosion potential and corrosion current (determined by



Fig. 3. Cyclic voltammograms for the synthesis of polyaniline films on the Ppycoated 304SS.



Fig. 4. Potentiodynamic polarization curves of the bare and coated 304 stainless steel in 0.3 M HCl solution.

Tafel extrapolations) for the bare steel are -362 mV (SCE) and 44.2 μ A cm⁻², respectively, while those for the Ppy-coated steel are 61 mV (SCE) and 2.65 μ A cm⁻², and for the composite Ppy/Panicoated steel are 106 mV (SCE) and 48.7 μ A cm⁻², respectively. Thus, the polymer coatings caused a positive shift of more than 400 mV in the corrosion potential, relative to the bare steel. However, the corrosion current density for the Ppy/Pani-coated steel was close to that for the bare steel, but was significantly higher than that for the Ppy-coated steel, which is due to the oxidation of the bilayer coating rather than to the corrosion of the substrate alloy, as suggested by Santos et al. [25]. The polarization current for the conducting polymer-coated steel results from the oxidation of the substrate steel, and from the oxidation of the polymer or ion exchange between the solution and the polymer. The higher electrochemical activity of the bilayer coatings resulted in higher anodic current density than that of the single Ppy coating. Additionally, significant positive shifts in the pitting corrosion potential were observed with the Ppy and Ppy/Pani coatings, with values of more than 600 mV (SCE) as compared to 80 mV (SCE) for the bare steel. This suggests that the coatings are effective barriers to the inward diffusion of Cl⁻ ions, and thus inhibit the corrosion of the substrate alloy.

To compare the corrosion performances of the coatings, potentiostatic polarization was conducted at +600 mV (SCE), which is close to the cathode operation potential of PEMFC, as shown in Fig. 5. The polarization current density for the Ppy-coated steel increased clearly after polarization for \sim 2 h, indicating that the corrosive species has penetrated through the coating to cause a pitting corrosion of the substrate alloy, whereas the Ppy/Pani coating still protected the steel from pitting corrosion after 6 h polarization, suggesting that the bilayer coatings can inhibit the inward penetration of Cl⁻ more effectively than the single Ppy coatings, and thus offer better protection to the alloy.

3.3. Open-circuit potential measurements

Fig. 6 shows the open-circuit potential (E_{ocp}) versus time curves for the bare and coated steel in 0.3 M HCl. E_{ocp} for the bare steel increased with exposure time in the very initial stage, and then decreased to around -310 mV (SCE). The initial value of E_{ocp} for the Ppy coating was higher than that for the bare steel by more than 450 mV (SCE). This value started to increase with time during the initial 25 h immersion, probably related to the passivation of the substrate alloy or the anionic interchanges of DS⁻ and chloride, and solvent exchange between the film and the solution. With extended exposure, however, E_{ocp} decreased



Fig. 5. Polarization current versus time curves for the steel covered with the single Ppy coating and the composite Ppy/Pani coating, respectively, in 0.3 M HCl solution during galvanostatic polarization at +600 mV(SCE).



Fig. 6. Open-circuit potential versus time curves for the bare and coated steel in 0.3 M HCl solution.

significantly, reaching a value of -264 mV(SCE) after immersion for 16 days, close to that typical of the bare steel, suggesting that a sufficient amount of the electrolyte solution has penetrated through the coating to cause severe corrosion of the substrate alloy. It is evident that in this stage the efficiency of the coating as an effective physical barrier and anodic protection have decreased.



Fig. 8. Equivalent circuits for fitting the impedance diagram: (a) the bare steel; (b) the Ppy-coated steel; (c) the Ppy/Pani-coated steel.

Unlike the single Ppy coating, E_{ocp} for the Ppy/Pani-coated steel was kept at around 250 mV (SCE) with a small fluctuation during immersion in 0.3 M HCl for 36 days. Although this potential was higher than the pitting corrosion potential of the bare steel, the alloy did not suffer from pitting corrosion. It is evident that the bilayer coating can inhibit the inward penetration of corrosive species more effectively than the single Ppy coating, and thus exhibits excellent corrosion resistance. The fact that the initial potential of the bilayer coating was higher than that of the single Ppy coating is probably related to its higher redox potential.

3.4. Electrochemical impedance measurements

Fig. 7 shows the typical Nyquist and Bode plots for the corrosion of 304SS in 0.3 M HCl after immersion for various lengths of time. The Nyquist plots were composed of a capacitive loop that expanded with increasing time of immersion, related to the passivation process of the alloy. The impedance behavior of the bare steel can be represented by the equivalent circuit shown in Fig. 8a, where R_s is the solution resistance, C_{dl} is the double-layer capacitance and R_t is the charge transfer resistance. The non-ideal capacitive response of the corrosion system was taken into account by using a constant phase element (CPE) instead of a pure capacitance in the fitting procedures. The impedance of CPE is written as

$$Z_{\rm CPE} = Y_0^{-1} (j\omega)^{-n} \tag{1}$$

where Y_0 is the admittance magnitude of CPE and n is an exponential term. Pure capacitance behavior is represented by n = 1, while in practice n often ranges from zero to 1.

Fig. 9 shows the typical Nyquist and Bode plots of the Ppycoated steel after immersion in 0.3 M HCl for various lengths of



Fig. 7. Nyquist and Bode plots for the bare steel after various exposure times in 0.3 M HCl solution.



Fig. 9. Nyquist and Bode plots for the Ppy-coated steel after various exposure times in 0.3 M HCl solution.

time. Unlike the bare steel, the impedance diagrams of the Ppycoated steel exhibited clearly at least two time constants, with much larger impedance. The capacitive loop expanded with the immersion time during the initial stage, and then contracted. The high-frequency section reflects the responses from the films, and the low-frequency part reflects the responses from the electrochemical reaction occurring at the film/substrate alloy interface. After exposure for 384 h, the impedance values decreased significantly, suggesting that the coating has lost its protection. Thus, the impedance spectra can be fit by using the parallel circuit shown in Fig. 8b, where $C_{\rm f}$ represents the film capacitance, $R_{\rm f}$ is the resistance of micropores through the polymer, and $C_{\rm dl}$ and $R_{\rm t}$ are the double-layer capacitance and the charge transfer resistance along the film/alloy interface, respectively.

Fig. 10 shows the Nyquist and Bode diagrams for the composite Ppy/Pani coatings after immersion in 0.3 M HCl for various lengths of time. All the Nyquist plots were clearly composed of a small capacitive loop at the high-frequency region and a line almost per-

pendicular to the real axis at low frequency during exposure for 30 days, indicating an effective barrier behavior. The high-frequency loop represents the impedance responses of the polymer film, while the low-frequency line is related to the doping/undoping processes controlled by the diffusion in the polymer film. The impedance diagrams can be fit by the equivalent circuit shown in Fig. 8c, where Z_d represents the diffusion impedance.

Figs. 7, 9 and 10 indicate clearly that the fitting results for the electrochemical impedance spectra of the bare steel and the coated steel in 0.3 M HCl are rather good: some electrochemical parameters are given in Tables 1–3.

Table 2 indicates that R_f and R_t increased with the progress of corrosion, followed by a dramatic decrease after exposure for 384 h. R_f is the sum of the electronic resistance R_e describing the movement of the electrons in the Ppy chains and the ionic resistance R_i of electrolyte within the pores of Ppy. The increase of R_f is related to the reduction of the Ppy films during exposure, which increased R_e , and to the increase of R_i due to the accumulation of the corrosion



Fig. 10. Nyquist and Bode plots for the Ppy/Pani-coated steel after various exposure times in 0.3 M HCl solution.

Table 1

| 1 1 1 1 1 1 1 1 1 1 |
|---------------------------------------|
|---------------------------------------|

| Time (h) | $R_{\rm s} \left(\Omega {\rm cm}^2\right)$ | $Y_{\rm dl} (\Omega^{-1} { m cm}^{-2} { m S}^{-n})$ | n | $R_t \left(\Omega \mathrm{cm}^2 \right)$ |
|----------|---|--|--------|---|
| 1 | 3.159 | 4.268E-4 | 0.7728 | 660.3 |
| 18 | 3.610 | 7.748E-4 | 0.7690 | 812.1 |
| 60 | 3.919 | 1.050E-3 | 0.7139 | 1022 |
| 100 | 3.667 | 1.121E-3 | 0.7522 | 1247 |

Table 2

Fitting results of impedance spectra at open-circuit potential for the corrosion of the Ppy-coated 304SS after various exposure times in 0.3 M HCl solution

| Time (h) | $R_{\rm s}$ (Ω cm ²) | $Y_{\rm f} (\Omega^{-1} { m cm}^{-2} { m S}^{-n})$ | n _f | $R_{\rm f} (\Omega {\rm cm}^2)$ | $Y_{\rm dl} (\Omega^{-1} { m cm}^{-2} { m S}^{-n})$ | n _{dl} | $R_t (\Omega \mathrm{cm}^2)$ |
|----------|--|---|----------------|---------------------------------|--|-----------------|-------------------------------|
| 2 | 1.108 | 5.492E-4 | 0.826 | 49.5 | 1.250E-3 | 0.616 | 4288 |
| 24 | 1.051 | 4.262E-4 | 0.760 | 189.6 | 8.571E-4 | 0.680 | 2.670E4 |
| 96 | 1.503 | 8.228E-4 | 0.664 | 429.1 | 6.096E-4 | 0.763 | 2.369E4 |
| 144 | 2.179 | 6.952E-4 | 0.614 | 1672 | 1.254E-4 | 0.865 | 5.450E4 |
| 336 | 1.580 | 6.715E-4 | 0.543 | 3360 | 1.156E-4 | 0.952 | 7.53E4 |
| 384 | 1.784 | 1.274E-3 | 0.652 | 11.85 | 1.88E-3 | 0.697 | 235.1 |

Table 3

Fitting results of impedance spectra at open-circuit potential for the corrosion of the Ppy/Pani-coated 304SS after various exposure times in 0.3 M HCl solution

| Time (h) | $R_{\rm s} \left(\Omega {\rm cm}^2\right)$ | $Y_{\rm f} (\Omega^{-1}{ m cm}^{-2}{ m S}^{-n})$ | n _f | $R_{\rm f} \left(\Omega {\rm cm}^2\right)$ | $Y_{\rm d} \; (\Omega^{-1} { m cm}^{-2} { m S}^{-n})$ | n _d |
|----------|---|--|----------------|---|---|----------------|
| 2 | 4.731 | 1.939E-3 | 0.8235 | 0.1582 | 0.2686 | 0.9581 |
| 23 | 4.624 | 1.470E-3 | 0.7579 | 0.2573 | 0.2616 | 0.9599 |
| 150 | 3.838 | 2.629E-3 | 0.6443 | 0.5157 | 0.2548 | 0.9582 |
| 480 | 2.435 | 1.586E-4 | 0.8279 | 0.5611 | 0.2617 | 0.9592 |
| 720 | 3.040 | 1.475E-4 | 0.8318 | 0.7238 | 0.2533 | 0.9629 |

products within the pores of the coatings. The increase in the values of R_t is ascribed to the formation of the corrosion products. The significant decrease of R_f and R_t indicated that the coating has lost its protection, and the substrate alloy suffered rapid corrosion (active dissolution). In this stage, the corrosion potential of the coated steel decreased noticeably towards that of the bare steel.

Table 3 shows that R_f for the composite coatings changed little with exposure time up to 30 days, and was significantly smaller than that for the single Ppy coatings, suggesting a much lower electrical resistance. The composite coatings could protect the alloy more effectively than the single Ppy coatings both as a physical barrier and as an effective oxidizer.

Aggressive species are transported towards the substrate alloy by ion exchange and by inward penetration of the electrolyte along pinholes or defects in the coatings. As a barrier, conductive films should be as compact as possible. The combination of two different ions-permselective films is expected to reduce significantly the ingress of corrosive species, as observed in the present study, because Pani could be electropolymerized on the surface of the Ppy layer to form a top layer, and within the network of the Ppy layer to produce a complex structure that reduces the porosity of the inner Ppy film.

It is accepted that the conductive polymers could provide protection to the metal due to their barrier effect and their anodic protection effect. To maintain the alloy in the passivity domain, the polymer is reduced slowly and the corrosion potential decreases slowly to that of the bare alloy. If the conducting polymer coating has been reduced to an insulating form, it operates just as a barrier layer. Therefore, good adhesion of the coatings to the alloy surface and the inhibition of reduction of the polymer coatings are very important factors. Ppy film doped with large anions repels anions due to its cation permselectivity, and thus is effective against metal corrosion. The dissolution or passivation of metals and cations in solution can cause a reduction of the Ppy film, which, however, can be inhibited to a certain extent if a Pani layer is deposited on the Ppy film. The reduction of the inner Ppy film requires cation flow, which is hindered due to the anion permselectivity of the external Pani, and thus is effectively suppressed. For the bilayer Ppy/Pani coatings, even if the internal Ppy is reduced, the external Pani could oxidize it *in situ* as follows:

$$Ppy + EM^{2+} + A^{-} \rightarrow Ppy^{+}A^{-} + LE$$
(2)

The reduced Pani could also be oxidized again in solutions:

$$O_2 + LE + H_2O \rightarrow EM^{2+} + 2OH^-$$
 (3)

In this way, the external Pani acts as an anion reservoir to maintain a good conductivity of the coatings. It can be concluded that the composite coatings exhibit much better corrosion resistance than the single Ppy coating.



Fig. 11. Contact resistance of the polymer-coated and -uncoated 304 stainless steel plates compared with the graphite plates.

3.5. Contact resistance

Fig. 11 shows the contact resistance versus compaction force curves of the coated and bare steel and for graphite plates. The contact resistance for the uncoated steel decreased significantly with increasing compaction pressure, followed by a slow decrease to very low values close to those of graphite plates. Compared to the uncoated steel, the contact resistance for the Ppy-coated steel under low compaction forces was significantly low, and decreased instantly to stable values. Unlike the bare and Ppy-coated steel, the contact resistance of the Ppy/Pani-coated steel plates and the graphite plates changed little with increasing compaction pressure, with values of 0.30 and $0.06\,\Omega\,cm^2$, respectively. Above 1.5 MPa pressure the contact resistance of the polymer-coated steel plates, which is the sum of bulk polymer resistance, interfacial resistance and the resistance of the oxide film formed during electrodeposition, was larger than those of the bare steel and graphite plates. The contact resistance for the Ppy/Pani-coated steel was slightly smaller than that for the Ppy-coated steel, suggesting that the composite coating is more conductive than the single Ppy coating.

4. Conclusions

Bilayer coatings, consisting of the inner conducting Ppy doped with large DS⁻ ions and the outer conducting Pani doped with small SO₄²⁻ ions, have been prepared successfully on 304SS for the bipolar plates of a PEMFC by galvanostatic and cyclic voltammetric deposition, respectively. Electrochemical measurements in 0.3 M HCl indicated that the composite coatings inhibited the corrosion of the alloy significantly better than the single Ppy coating. The coating increased the corrosion potential of the alloy by more than 400 mV (SCE), with a more positive shift for the composite coatings. Moreover, significant positive shifts in the pitting corrosion potential were observed with the Ppy and Ppy/Pani coatings, with values of more than 600 mV (SCE) as compared to the value of 80 mV (SCE) for the bare steel. However, the free corrosion current density for the composite coatings was close to that for the bare steel, but significantly higher than the single Ppy coatings, probably related to a contribution from the oxidation/reduction reaction of the polymer coatings, rather than to the corrosion of the substrate alloy. The composite coatings exhibited greater chemical stability than the single Ppy coating, with a corrosion potential of around 250 mV (SCE) during exposure for up to 36 days. This may be due to the bilayer coating acting as better barriers to trap chloride and more efficient oxidizers to maintain the metal in the passivity domain. The different ions permselectivity of the Ppy underlayer and the Pani top layer increases the barrier effects of the composite coating. Meanwhile, the external Pani with higher redox potential could oxidize the internal Ppy layer in situ, thus maintaining the anodic protection effect of the composite coating.

Conductive polymers have high levels of electron conductivity in their oxidized state and provide a high level of corrosion protection to metals such as stainless steel. These polymers should not be faced with "the formation of passive oxide films", as observed on some metal-based coatings, and should be more conductive in acidic environments, especially in the cathode side of a PEMFC. Electrodeposition of conductive polymer coatings has the advantage of being a highly controllable, relatively low cost process. Though our primary results confirmed the better performance of the composite conducting Ppy/Pani coating than the single Ppy coating, extensive studies are still needed to characterize the corrosion behavior and contact resistance of these coatings in real PEMFC environments. We believe that if an effective corrosion-resistant and conductive coating can be developed, cheaper metal bipolar plates will have wide application potential.

Acknowledgements

This project was supported by the National Natural Science Foundation of China. The authors thank Professor F. Gesmundo from DICheP, Universita di Genova, Italy, for helpful corrections in reviewing this manuscript.

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