



Corrosion protection of type 304 stainless steel bipolar plates of proton-exchange membrane fuel cells by doped polyaniline coating

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ABSTRACT

Polyaniline coating doped with dodecylbenzenesulfonate anions is electrodeposited galvanostatically on type 304 stainless steel used as bipolar plates of proton-exchange membrane fuel cell from a basic solution of 0.3 M aniline monomer solution containing sodium dodecylbenzenesulfonate as a supporting electrolyte. Electrochemical measurements in 1 M H₂SO₄ and in 0.3 M HCl show that the polyaniline coating increases the free corrosion potential of the steel by more than 300 mV and 450 mV, respectively, with a corrosion rate more than two orders of magnitude lower than that of the uncoated steel. Long-term exposure studies show that the coating is highly stable and inhibits the corrosion of the steel effectively.

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1. Introduction

The proton-exchange membrane fuel cell (PEMFC) is a promising power generation system that converts the chemical energy of hydrogen and oxygen (or air) to electricity, with water as the only byproduct and with the advantages of reduced emissions, high power density and low operating temperature. At present, however, the high cost of materials is limiting the commercial application of PEMFCs. As 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, bipolar plates of PEMFC account for about 80% of the total weight and 45% of the stack cost [1]. The development of inexpensive, thin and light bipolar metallic plates is needed to meet the requirements for commercial applications of PEMFC. The materials investigated for the construction of bipolar plates have included graphite, metal and graphite-polymer composites, among which graphite is the most commonly used due to its low surface contact resistance and high corrosion resistance. However, graphite and graphite composites are brittle and permeable to gases, and cannot be machined to form thin plates with gas channels on each side. Metallic bipolar plates have received considerable attention due to their high electrical conductivity, acceptable material cost, relatively high strength, low gas permeability, and

applicability to mass production. Moreover, metallic materials can be used to manufacture thin plates with flow channels, thus significantly reducing the volume and the weight of PEMFC. The main problems associated with the use of metallic materials, however, are corrosion or dissolution, because PEMFC environments are weakly acidic media containing SO₄²⁻, Cl⁻, F⁻ etc. The dissolved metal ions may contaminate the membrane electrodes, while the formation of a passive film on the bipolar plate surface increases the contact resistance. Coating processes using mainly carbon-based and metal-based materials, have been proposed to protect metallic bipolar plates by providing high corrosion resistance and low contact resistance [2–6]. Recently, Tawfik et al. [7] presented an overview of metallic bipolar plates for PEMFC.

Conductive polymers, such as polyaniline (Pani), polythiophene and polypyrrole (PPy) have been studied extensively with respect to their potential applications, such as electrochemical sensors, capacitors etc. Conductive polymers have been candidates for metal protection against corrosion [8–16], since DeBerry [8] reported that an electrochemically deposited Pani film could provide anodic protection for stainless steel. Conducting polymer coatings have the potential to protect metallic bipolar plates against corrosion, with acceptable contact resistance due to their high level of electrical conductivity. There are a few reports of studies on the corrosion protection of metallic bipolar plates by polymer coating [17–21]. One of the authors of this paper applied a conductive PPy coating for protection of the metallic bipolar plates of PEMFC and observed improved corrosion resistance during exposure to HCl for 50 days [17]. Joseph et al. [18] reported the electrodeposition of conduct-

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ing polymers Pani and PPy on stainless steel bipolar plates, and confirmed the improved corrosion resistance of the coated plates with acceptable contact resistance.

Pani is promising for the protection of metals due to its good chemical stability, high level of electrical conductivity, processability, easy polymerisation and low cost of the monomer. The characteristics of Pani coatings, such as electrical conductivity and thermal stability, depend on the oxidation state of the polymer and on the nature of the counter anion. Surfactant agents composed of a polar or hydrophilic region with positive or negative charge and a non-polar hydrophobic region, respectively, are responsible for phenomena such as surface activity and micellization [22]. Cai et al. observed that Pani synthesized in H_2SO_4 with the addition of surfactant anions sodium dodecylbenzenesulfonate (SDBS) or SDS showed a more ordered arrangement of the chain [23]. de Albuquerque Maranhão [22] reported that when surfactant agents were added, the surfactant anions could interact with the polymer and affect its macroscopic and microscopic properties. The use of Pani coatings doped with surfactant anions was examined in this study.

The electrodeposition of Pani is commonly done in acidic aqueous solutions, in which oxidizable metals are usually highly corroded [24]. The competition between electrodeposition and metal corrosion hinders the effective formation of an adhesive Pani coating. In this study, Pani was electrodeposited onto type 304 stainless steel from a basic solution, with SDBS as a supporting electrolyte. The corrosion performance of the coated steel in H_2SO_4 and in HCl was investigated to determine its potential application as an electrically conducting and corrosion-resistant coating for the metallic plates of PEMFC.

2. Experimental procedures

Type 304 stainless steel (304SS) was used as the base material. Sheet-shaped specimens were cut from the bulk, and then ground with 240#grit SiC paper, followed by cleaning with distilled water and then acetone. Pani coatings of $\sim 15 \mu\text{m}$ thickness were electrodeposited galvanostatically onto 304SS at a current density of 2.5 mA cm^{-2} at 25°C from a basic (pH 9–10) aqueous solution of 0.3 M aniline monomer and 0.15 M SDBS in a single compartment with a stainless steel plate as the counter-electrode.

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. The corrosion tests of the coated samples with a working surface area of 1 cm^2 were conducted with a Princeton Applied Research PAR 2273 Potentiostat/Galvanostat in 1 M H_2SO_4 and in 0.3 M HCl at room temperature. Potentiodynamic polarization was undertaken with a potential scanning rate of 20 mV min^{-1} . Potentiostatic polarization at 450 mV (SCE) close to the operating potential of cathode for PEMFC was conducted in H_2SO_4 solution. Electrochemical impedance measurements were made in the range 0.01 Hz–100 kHz, with an amplitude of 5 mV for the input sine-wave voltage. Infrared spectroscopy (IR) was used to characterize the Pani coatings.

3. Results and discussion

3.1. Electrodeposition of Pani coatings

Fig. 1 shows the potential versus time curve for the galvanostatic electrodeposition of Pani coatings onto 304SS. There is an obvious potential peak relating to the nucleation over-potential. The gradual decrease of potential with time in the later stage was attributed to growth of the Pani film on the alloy surface.

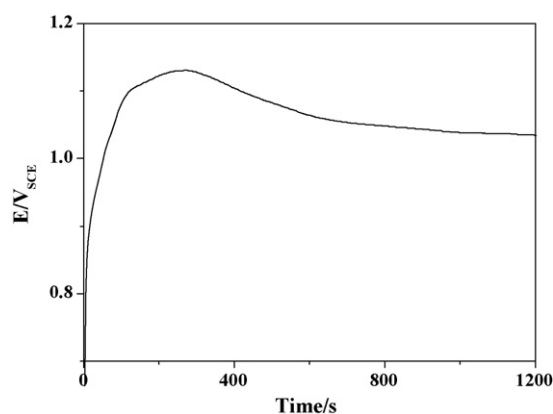


Fig. 1. Potential versus time curve for the galvanostatic electrodeposition of Pani coating on type 304 stainless steel.

3.2. Infrared spectroscopic analysis

The structural characteristics of the Pani coatings were analysed by IR in the range $3000\text{--}750 \text{ cm}^{-1}$, as shown in Fig. 2. The peak at 1493 cm^{-1} represents the vibration of a C–C bond. The peak at 1305 cm^{-1} is due to the vibration of a C–N bond. The peaks at 1124 cm^{-1} and 831 cm^{-1} represent the vibrations of C–H bonds in and out of plane, respectively. These peaks are in accordance with the characteristic peaks of Pani reported in the literature [25]. The peak observed at 1040 cm^{-1} was attributed to S=O, relating to the doped anions DBS^- . It was concluded that the electrochemical polymerisation of aniline had occurred, resulting in the deposition of a Pani coating doped with DBS^- onto 304SS.

3.3. Corrosion behaviour in 1 M H_2SO_4

3.3.1. Electrochemical polarization measurements

Fig. 3 shows the potentiodynamic polarization curves for uncoated and for Pani-coated steel after immersion in 1 M H_2SO_4 for 1 h. 304SS was in the active state at free corrosion potential (E_{corr}). With increasing potential, the corrosion of the uncoated steel changed from an active state to a passive state with a wide passive region. However, the coated steel was in the passive state at E_{corr} , and the polarization current increased with increasing potential, but with a smaller polarization current than that of 304SS at potentials below 830 mV (SCE). The free corrosion potential and the free corrosion current density of 304SS were determined to be

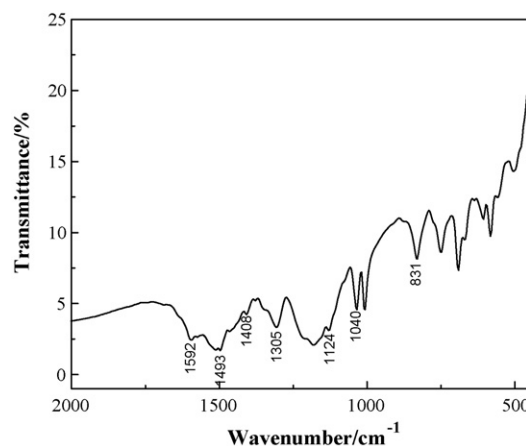


Fig. 2. FTIR spectrum of Pani coating doped with dodecylbenzenesulfonate anions deposited on type 304 stainless steel.

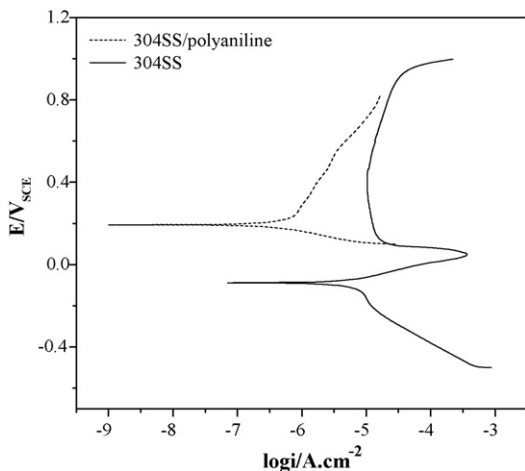


Fig. 3. Potentiodynamic polarization curves of the uncoated and Pani-coated type 304 stainless steel in 1 M H₂SO₄.

–89 mV (SCE) and 8.3 $\mu\text{A cm}^{-2}$, respectively, while those for the Pani-coated steel were 211 mV (SCE) and 0.05 $\mu\text{A cm}^{-2}$, respectively. It is clear that the Pani coating shifted anodically the E_{corr} of 304SS by 300 mV, with a corrosion rate two orders of magnitude lower than that of the uncoated steel. The slow increase in the polarization current of the coated steel with the polarization potential is related, in part, to the contribution of the polymer oxidation, because the anodic polarization current of the Pani-coated steel results from oxidation of the substrate alloy, and from the oxidation of the polymer.

Fig. 4 shows the potentiostatic polarization curve of the coated steel in 1 M H₂SO₄ solution at 450 mV. The polarization current decreased instantly with time to the level of 10^{-7} A cm⁻², significantly lower than the passive current for the uncoated steel with a level of 10^{-5} A cm⁻². It is clear that the Pani coating inhibits effectively the corrosion of the substrate steel.

3.3.2. Free corrosion potential

The good corrosion protection of the Pani coating was confirmed by the E_{corr} versus time curves for the uncoated and the Pani-coated steel, as shown in Fig. 5. For 304SS, E_{corr} increased with time in the initial stage, and then decreased to a relatively stable value of –130 mV (SCE) during exposure for 100 h, while that for the coated steel decreased slowly with time from the initial value of 325 mV (SCE) to 165 mV (SCE) after exposure for 1200 h. It is clear that the Pani coating increased E_{corr} of 304SS significantly. Fig. 5b shows that E_{corr} for the coated steel fluctuated with time, probably because of the inward penetration of corrosive species. The inward permeation of solution to the coating/substrate interface caused the

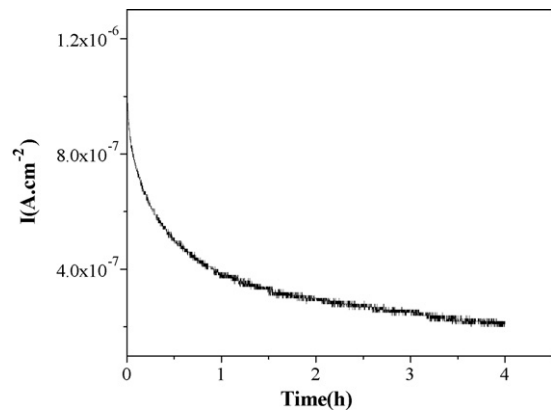


Fig. 4. Potentiostatic polarization curve of the Pani-coated 304 stainless steel at 450 mV (SCE) in 1 M H₂SO₄.

corrosion of the substrate alloy, resulting in the decrease of E_{corr} . It is notable that the above process could also induce the reduction of Pani, with electron transfer between the substrate and the coating. Electrically conductive Pani can act as an effective catalytic oxidizer, which could passivate 304SS and give rise to the increase of E_{corr} . As a result, the fluctuation of E_{corr} with exposure time for the coated steel was observed during immersion in H₂SO₄.

Besides a catalytic oxidizer, Pani coating can act as a barrier, and the effectiveness can be affected by the doping anions. It has been reported that electrodeposited Pani coating with small counter ions such as Cl⁻ or SO₄²⁻ were highly porous and solution-accessible, and thus were not an effective barrier [26]. For the Pani films doped with the large DBS⁻, however, the hydrophilic region of the surfactant neutralizes the positive charges of Pani, and the hydrophobic region intertwists the polymer chain, which minimizes the surface area of the coating in contact with corrosive species. In addition, synthesis in a basic solution can avoid the competition between Pani polymerisation and metal oxidation or dissolution, thus producing a more compact Pani coating. Pani coatings doped with DBS⁻ inhibit the inward penetration of corrosive species more effectively than the smaller Cl⁻ or SO₄²⁻. Taken together, the results described above confirm that Pani coatings offer good protection of 304SS against corrosion.

3.3.3. Electrochemical impedance spectroscopy

Fig. 6 shows typical Nyquist and Bode plots for 304SS after immersion for various lengths of time in 1 M H₂SO₄. The Nyquist plots consist of two capacitive loops, which can be represented by the equivalent circuit shown in Fig. 5, where R_s is electrolyte resistance, R_f and C_f are the resistance and capacitance, respectively, of the porous corrosion products formed on the alloy surface, and R_t

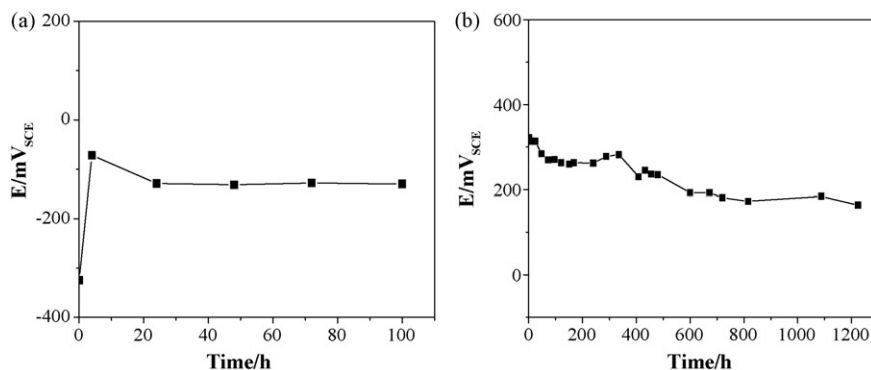


Fig. 5. Open-circuit potential versus time curves for the uncoated steel (a) and the Pani-coated type 304 steel (b) immersed in 1 M H₂SO₄.

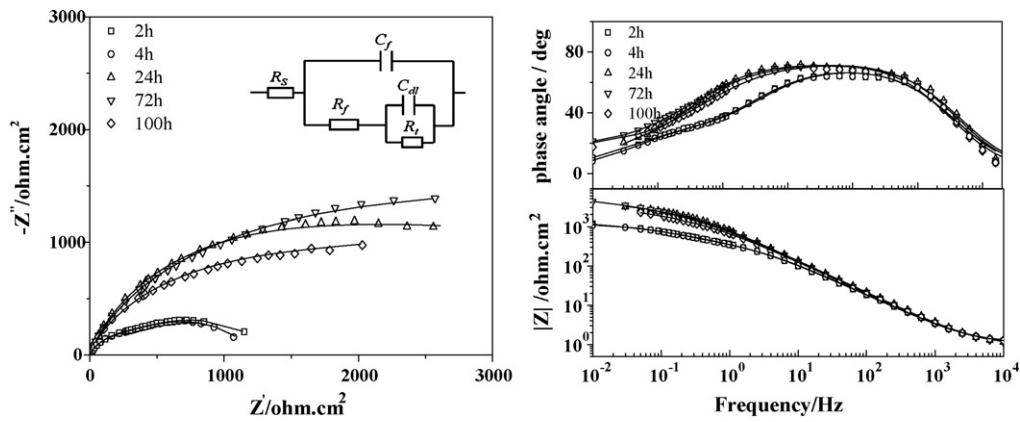


Fig. 6. Nyquist and Bode plots for the uncoated steel after immersion in 1 M H₂SO₄ for various lengths of time.

Table 1

Fitted results of impedance spectra for the corrosion of 304SS after exposure for various lengths of time in 1 M H₂SO₄ at open-circuit potential.

Time (h)	R _s (Ω cm ²)	Y _f (S ^{-α} Ω ⁻¹ cm ⁻²)	n _f	R _t (Ω cm ²)	Y _{dl} (S ^{-α} Ω ⁻¹ cm ⁻²)	n _{dl}	R _t (Ω cm ²)
2	1.037	3.224E-4	0.797	403.1	1.775E-3	0.586	969
4	1.051	3.131E-4	0.798	386.8	1.673E-3	0.621	846
24	0.943	2.058E-4	0.813	2692	1.882E-3	0.598	2744
72	0.971	2.556E-4	0.816	2171	8.784E-4	0.640	3354
100	1.144	2.667E-4	0.816	1530	1.163E-3	0.554	3094

and C_{dl} are the charge transfer resistance and double-layer capacitance, respectively. A constant phase element (CPE) was used in the fitting procedures; the electrochemical impedance plots shown in Fig. 6 were fit on the basis of the equivalent circuit and the results are given in Table 1. The value of R_t tends to increase with exposure time, suggesting the decreased corrosion rate is due to the formation of porous film on the alloy surface.

Unlike the Nyquist plots for the uncoated steel, those for the coated steel showed a depressed semicircle at high frequencies and a straight line at low frequencies, as shown in Fig. 7. The high-frequency loop, representing the impedance response of the polymer film, decreased with time, while the low-frequency linear portion indicated that the corrosion process was controlled by the diffusion of corrosive species through the Pani coating. The impedance features did not change with time during exposure for 50 days, suggesting the Pani coating was an effective barrier against the inward penetration of corrosive species. The impedance plots of the coated steel can be represented by the equivalent circuit shown in Fig. 7, where Z_d is the diffusion impedance. Fig. 7 shows that the fitting results are rather good, and some fitted parameters are given in Table 2. R_f decreased with time, due to the inward per-

meation of electrolyte, which is in accordance with the decrease of E_{corr} (Fig. 5b).

3.4. Corrosion performance in 0.3 M HCl

The results presented above confirmed that the Pani coating doped with DBS⁻ could improve the corrosion resistance of 304SS significantly. Taking into account the presence of Cl⁻, mainly from the preparation of the catalytic platinum layer in the real PEMFC environments [27], the corrosion behaviour of uncoated and Pani-coated 304SS was also examined in highly corrosive 0.3 M HCl solution relative to the real PEMFC environment, aiming to evaluate quickly the corrosion protection of the coatings. Fig. 8 shows the potentiodynamic polarization curves of the Pani-coated and the uncoated steel in 0.3 M HCl. 304SS was in the active state at E_{corr}, and its free corrosion potential and corrosion current density were -373 mV (SCE) and 77 μA cm⁻², respectively. Moreover, 304SS suffered from pitting corrosion at potentials higher than 80 mV (SCE). It is obvious that 304SS underwent more severe corrosion in 0.3 M HCl than it did in 1 M H₂SO₄. Unlike the uncoated steel, the Pani-coated steel was in the passive state at E_{corr}, and the

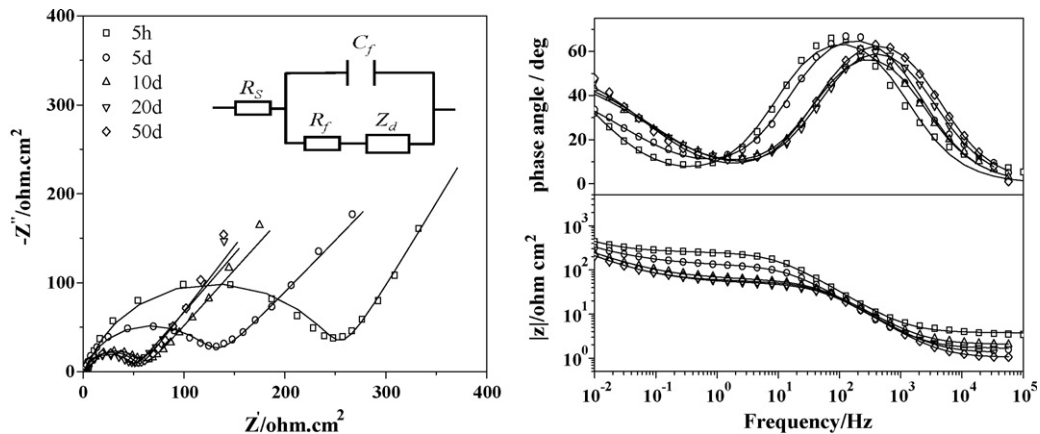
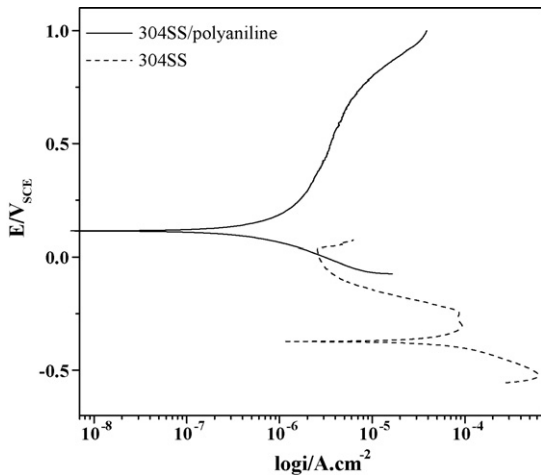
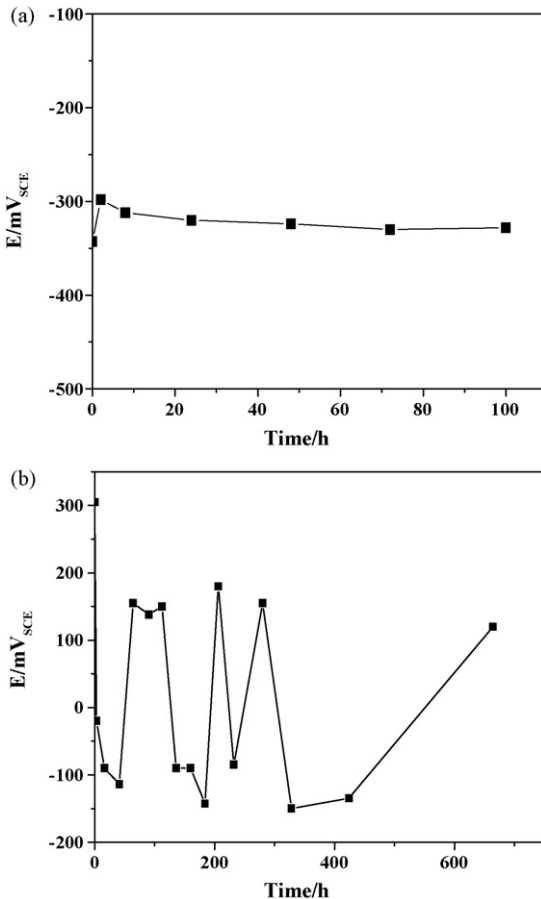


Fig. 7. Nyquist and Bode plots for the Pani-coated steel after immersion in 1 M H₂SO₄ for various lengths of time.

Table 2Fitted results of impedance spectra for the corrosion of Ppy-coated 304SS after immersion for various lengths of time in 1 M H₂SO₄ at open-circuit potential.

Time	R_s (Ω cm ²)	Y_f ($S^{-\alpha} \Omega^{-1} \text{cm}^{-2}$)	n_f	R_f (Ω cm ²)	Y_{dl} ($S^{-\alpha} \Omega^{-1} \text{cm}^{-2}$)	n_{dl}
5 h	3.755	1.310E-4	0.848	248.9	2.537E-2	0.690
8 h	3.761	1.349E-4	0.846	189.0	2.777E-2	0.683
5 d	1.671	1.653E-4	0.857	125.1	1.959E-2	0.552
10 d	2.057	1.618E-4	0.842	58.3	2.417E-2	0.573
20 d	1.311	1.630E-4	0.847	48.5	2.904E-2	0.585
34 d	1.418	1.644E-4	0.846	61.8	3.163E-2	0.598
47 d	1.075	1.608E-4	0.852	55.2	3.170E-2	0.621
50 d	1.043	1.540E-4	0.858	53.8	3.170 E-2	0.620

**Fig. 8.** Potentiodynamic polarization curves of uncoated and Pani-coated type 304 stainless steel immersed in 0.3 M HCl.**Fig. 9.** Open-circuit potential versus time curves for uncoated (a) and Pani-coated (b) type 304 steel immersed in 0.3 M HCl.

free corrosion potential and corrosion current density were 114 mV (SCE) and $0.35 \mu\text{A cm}^{-2}$, respectively. Significant positive shift in the pitting corrosion potential was observed with the Pani coating, with a value of more than 700 mV (SCE) as compared to 80 mV (SCE) for the bare steel, suggesting that the coating is an effective barrier to the inward diffusion of Cl⁻ ions, and thus inhibits the corrosion of the substrate steel.

E_{corr} for the uncoated steel in 0.3 M HCl increased with time in the initial stage, and then decreased to around -310 mV (SCE), while that for the Pani-coated steel decreased with time from the initial value of 150 mV (SCE) to -120 mV (SCE), and then returned to around 150 mV (SCE), as shown in Fig. 9. During exposure for 665 h, E_{corr} maintained this kind of fluctuation, but with a short fluctuation interval in the initial 325 h of exposure. The fluctuation of E_{corr} for the coated steel is due to the inward penetration of corrosive species to the coating/substrate interface, giving rise to the corrosion and subsequent passivation of the substrate, as discussed above. This result confirmed the effectiveness of the Pani coating in protecting the substrate alloy as both a catalytic oxidizer and a barrier. Additionally, the potential fluctuation in 0.3 M HCl is more evident than that in 1 M H₂SO₄.

4. Conclusions

A Pani coating doped with the large anionic surfactant DBS⁻ was electrodeposited galvanostatically onto type 304 stainless steel from a basic solution instead of an acidic solution. The Pani coating increased the free corrosion potential of 304SS by more than 300 mV (SCE) in 1 M H₂SO₄ and by 450 mV in 0.3 M HCl, and decreased the free corrosion current density significantly. Potentiostatic polarization at 450 mV close to the working potential of cathode for PEMFC and long-term exposure test for 50 days confirmed the high stability of the Pani coating in 1 M H₂SO₄. Fluctuation of the free corrosion potential was observed for the Pani-coated steel in 0.3 M HCl, and there was a small fluctuation in 1 M H₂SO₄. As a barrier to the inward permeation of corrosive species, and as an effective catalytic oxidizer maintaining the passive state of the substrate alloy, the Pani coating doped with DBS⁻ offers excellent corrosion protection for 304SS in acidic solutions containing either Cl⁻ or SO₄²⁻.

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