Electrocatalytic Performance of Pt Supported on Polyaniline-Poly(styrene sulfonate) Hydrogel

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ABSTRACT: A new type of polyaniline-poly (styrene sulfonate) (PAn-PSS) hydrogel was fabricated with high concentrations of aniline (An) and PSS via supramolecular self-assembly. Then 30 segments of cyclic voltammograms from -0.2 to 0.8 V were conducted to deposit the Pt particles on the surface of the hydrogel. For comparison, PAn-PSS colloid was synthesized with the ordinary method. The morphology and composition of the PAn-PSS hydrogel–Pt and PAn-PSS colloid–Pt were investigated by the TEM and EDX measurements. Furthermore, the shift of the feature bands in FTIR and UV–vis spectra confirms that the PAn-PSS hydrogel has interactions with Pt. So the Pt particles are dispersed and the electrons are shuttled more freely, which is beneficial for the electrochemical performance. The cyclic voltammograms and chronoamperometric measurements show that Pt supported on the PAn-PSS hydrogel has preferable electrocatalytic performance toward the oxidation of methanol than the one on PAn-PSS colloid. Hence, PAn-PSS hydrogel–Pt can be a promising catalyst for methanol in fuel cells. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: hydrogels; electrochemistry; synthesis

INTRODUCTION

Nowadays, direct methanol fuel cell (DMFC) is developing quickly.[1–5] High-energy conversion efficiency, convenient transportation, and low pollutant emission of DMFC attract the attention of the whole world.[6,7] As the major subject of DMFC, the proper catalyst for methanol oxidation in anode has been studied for a long time. Because of the excellent catalytic activity, Pt is regarded as a suitable catalyst for the oxidation of methanol.[8–10] However, the high price and heavy load of Pt hinder its applications. Scientists have found that some support materials can disperse Pt, increase the specific surface area, improve the catalytic activity, and decrease the load of Pt.[11–13] The conducting polymers have been employed to be the support because of the obvious characteristics, such as high electrical conductivity as well as remarkable optical activity.[14] It is considered that the conducting polymers or conducting polymer–carbon composites can stabilize Pt or Pt compounds and help the Pt particles to be highly dispersed.[15–18] Polyaniline (PAn) is one of the most popular conducting polymers that have been investigated. The merits of PAn include the high conductivity, fast charge and discharge, easy preparation, and low price.[19–22] When doped with poly (styrene sulfonate) PSS, PAn has improved stability, conductivity, miscibility, and electroactivity.[21,23] Therefore, PAn-PSS has been chosen to be the support of Pt and other metallic catalysts.[24,25]

Hydrogel, which is a special form of conducting polymers, has developed quickly in recent years.[14,26] Our research group has invented a new type of PAn-PSS hydrogel.[27] The synthesis of the hydrogel involves high concentrations of An and PSS. The PAn chains with positive charges and PSS chains with negative charges react via supramolecular self-assembly. The new concentrated PAn-PSS hydrogel has better capacitance performance, including higher energy density, higher power density, and improved electrochemical stability. In the present article, we deposit Pt on the surface of the PAn-PSS hydrogel as well as the traditional PAn-PSS colloid through cyclic voltammograms. It is reported for the first time that the PAn-PSS hydrogel–Pt possesses a better electrocatalytic activity for the oxidation of methanol than the PAn-PSS colloid–Pt. The reason is that higher concentrations of PAn and PSS result to more electrostatic forces as well as stronger interactions with Pt particles. Hence, the PAn-PSS hydrogel has better interactions with Pt than PAn-PSS colloid, which benefits the catalytic ability of Pt particles.

EXPERIMENTAL

Preparation of PAn-PSS hydrogel and PAn-PSS colloid

In the preparation of the polyaniline-poly (styrene sulfonate) (PAn-PSS) hydrogel, the concentrations of

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aniline (An) and poly (sodium 4-styrenesulfonate) (NaPSS) were both 0.5 mol/L. In the preparation of PAn-PSS colloid, the concentrations were both 0.1 mol/L. The preparation method of the hydrogel is as follows: (1) 10 mL of 1 mol/L HCl and 10 mL of NaPSS solution were mixed. (2) 900 µL of An monomers were added into the as-prepared mixture, then stirred with glass rod uniformly to get a solution. (3) 2.28 g of ammonium peroxysulfate (APS) as the oxidant was added into the solution resulting from the last step. (4) The resulting mixture was stirred with glass rod for 1 min at room temperature and placed without agitation for 12 h to form PAn-PSS hydrogel. (5) Hydrogel products were purified by dialysis against a large amount of distilled water for 1 week to wash out low molecular weight components. (6) The obtained hydrogels were freeze-dried and ground to powders for the deposition of Pt.

The preparation method of PAn-PSS colloid is similar to the PAn-PSS hydrogel. The amount of NaPSS, H_2O, Pan, and APS was 2 mL, 8 mL, 180 µL, and 0.456 g, respectively.

Preparation of PAn-PSS hydrogel–Pt and PAn-PSS colloid–Pt

Preparation of PAn-PSS hydrogel and PAn-PSS colloid electrode

(1) 2 mg of PAn-PSS hydrogel was ultrasonically dispersed in 2 mL of H_2O. (2) Then 10 µL of obtained solution was dropped on the surface of the glassy carbon electrode. The glassy carbon electrode was covered by PAn-PSS hydrogel film uniformly. (3) After that, 1.5 µL of Nafion was transferred onto the surface of the PAn-PSS hydrogel. The resulting electrode was denoted as PAn-PSS hydrogel electrode.

The PAn-PSS colloid electrode was prepared with the same operation method.

Electrochemical deposition of Pt on PAn-PSS hydrogel and PAn-PSS colloid

The electrochemical deposition and measurement were performed with a CHI600 electrochemical analyzer and a conventional three electrode electrochemical cell. A Pt plate was used as the auxiliary electrode. The saturated calomel electrode (SCE) electrode was used as the reference electrode. All the potentials were quoted with respect to SCE.

The electrochemical deposition steps were as follows: (1) The as-prepared PAn-PSS hydrogel was immersed into the electrolyte (mixture of 0.5 mL of 0.0193 mol/L H_2PtCl_6, 7 mL of H_2O, and 0.5 mL of saturated KCl solution). (2) 30 segments of cyclic voltammograms were conducted. Potential range was from -0.2 to 0.8 V. The sweeping scan rate was 50 mV/s. (3) Then, the electrode deposited with Pt

was washed with distilled water. This electrode was denoted as PAn-PSS hydrogel–Pt electrode.

Pt was electrodeposited on the PAn-PSS colloid electrode under the same condition to get the PAn-PSS colloid–Pt electrode.

As comparison, another PAn-PSS colloid electrode was synthesized with the method published in literatures.[25,28] Then the Pt particles were deposited on its surface. It was denoted as PAn-PSS colloid (l) –Pt electrode.

Characterization and operation conditions

When the electrochemical test was performed, the electrolyte was 0.5 mol/L H_2SO_4 with and without 1 mol/L CH_3OH.

Transmission electron microscope (TEM) spectra and energy dispersive X-ray spectroscopy (EDX) were obtained from TECNAI20 (FEI, Holland) instrument. Fourier-transform infrared spectra (FT-IR) of the samples were recorded on an IS100 spectrometer (Nicolet, USA). UV–vis absorption spectra were recorded on a UV-240 spectrometer (Shimadzu, Japan). Before the testing of UV–vis, the hydrogel or colloid was diluted to a proper concentration with distilled water.

RESULTS AND DISCUSSION

As shown in Figure 1, PAn-PSS hydrogel and colloid have different macroscopic appearances. The difference is due to the concentrations of the PAn and PSS. The interaction between PAn and PSS is due to the existence of the electrostatic force. So when the concentrations of PAn and PSS increase, the distance between the polymer chains is shortened and the electrostatic force increases.[27,29] The structure gets compact as can be seen in the picture.

Figure 2 demonstrates the FTIR spectra of (A) PAn-PSS hydrogel and (B) PAn-PSS hydrogel–Pt. As shown in the spectrum (A), the feature peaks at 1597 and 1496 cm^{-1} refer to the quinone and benzene ring deformation.[30] The C—N stretching of the secondary aromatic amine can be seen according to the peak at 1303 cm^{-1}.[24] The band at 1130 cm^{-1} can be explained to be the aromatic C—H in-plane bending modes. The characteristic peaks at 1070 and 1033 correspond to the symmetric stretching of SO_3^- and SO_2^-. Besides, the peak at 1007 cm^{-1} is assigned to in-plane bending of *para*-substituted phenyl ring, indicating that PSS was in existence in the samples.[31] Whereas, in spectrum (B), all these bands shift to the high-frequency direction, which results from the presence of Pt and the interactions between Pt and PAn-PSS hydrogel.[28]

UV–vis spectra of (a) PAn-PSS hydrogel and (b) PAn-PSS hydrogel–Pt are shown in Figure 3. Since PAn-PSS has two forms, one is the doped state and
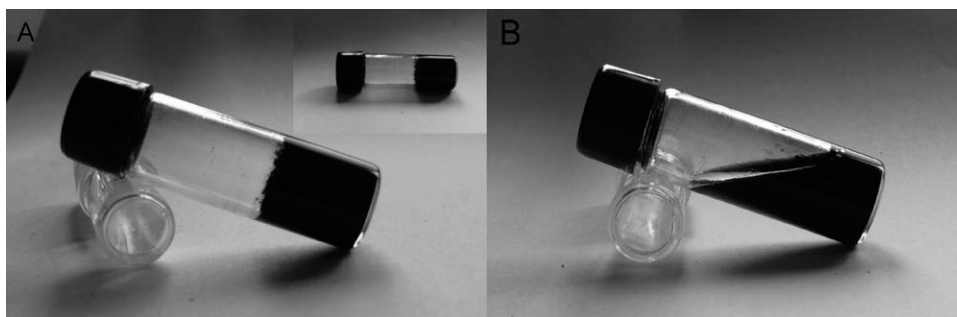
Figure 1 Macroscopic appearances of PAn-PSS hydrogel (A) and colloid (B).

the other is the dedoped state. As displayed in the plot (a), the feature bands of the PAn-PSS hydrogel are at 357, 430, 800 nm. These peaks correspond to the doped state PAn-PSS[25,27] indicating that the PAn-PSS hydrogel exists as doped state. While the third band of the PAn-PSS hydrogel–Pt in plot (b) appreciably shifts to 767 nm which is assigned to the dedoped PAn. This shift indicates that after depositing Pt, the PAn-PSS has slightly changed to the dedoped state. The doped PAn chains are positively charged and the dedoped PAn has no charge on its chains. When Pt particles are electrochemical deposited on PAn, a portion of doped PAn with positive charges is reduced to dedoped PAn at the same time. So in Figure 3, the absorption peak of PAn-PSS hydrogel–Pt in plot (b) negatively shifts, showing that the doped PAn has been slightly reduced to dedoped PAn. However, the amount of the reduced doped PAn is small, so the electrostatic forces and the property of hydrogel will not be affected. On the other hand, because the PAn and Pt are reduced simultaneously, the interaction between them is enhanced.

Figure 4 shows the TEM images of PAn-PSS (hydrogel and colloid)–Pt. Black Pt particles and gray PAn-PSS can be seen obviously. In picture (A), Pt particles are distributed relatively separately on the PAn-PSS hydrogel, and the size of the particles is 200 nm in average (at the same time, a black area (a) and a gray area (b) are analyzed by EDX.) However, Pt particles locate apart from the PAn-PSS matrix in picture (B). So the Pt particles and the PAn-PSS colloid have no interactions with each
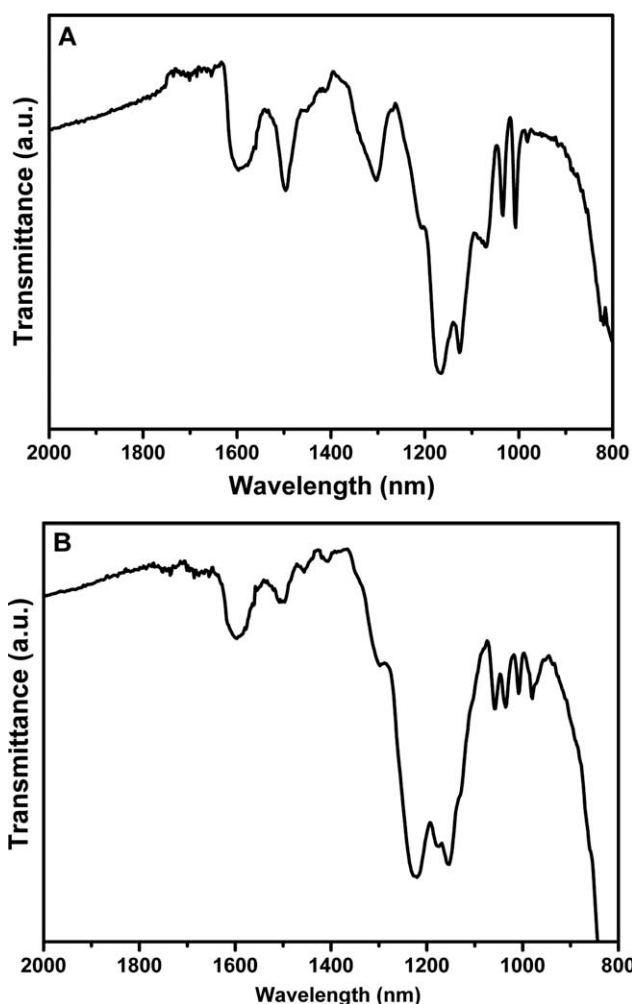

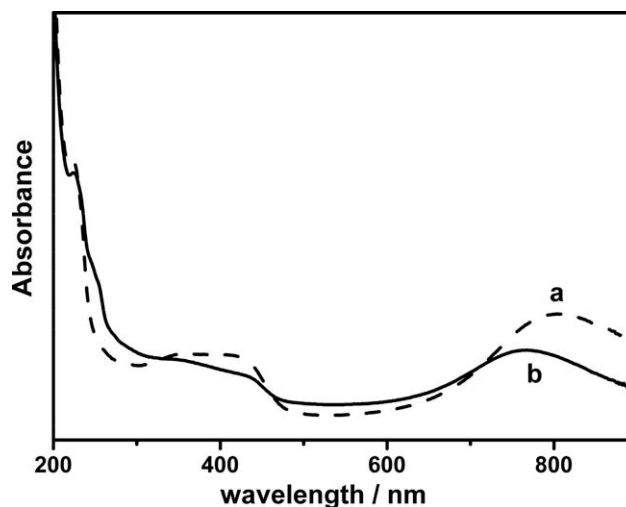**Figure 2** FTIR spectra of (A) PAn-PSS hydrogel and (B) PAn-PSS hydrogel–Pt.

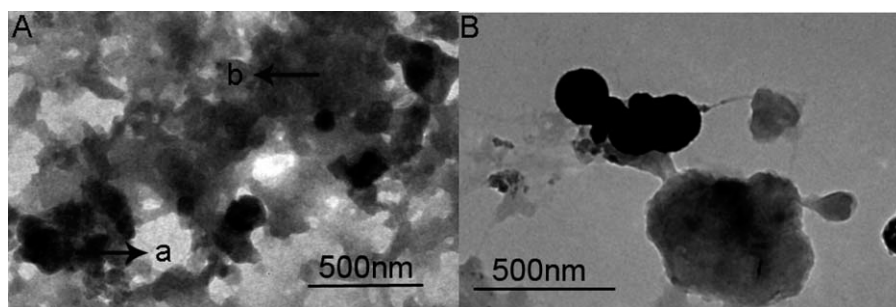**Figure 3** UV–vis spectra of (a) PAn-PSS hydrogel and (b) PAn-PSS hydrogel–Pt.

Figure 4 TEM images of (A) PAn-PSS hydrogel–Pt and (B) PAn-PSS colloid–Pt.

other. The Pt particles are aggregated, which is disadvantageous for electrocatalytic performance.[29,32]

Figure 5 displays the EDX spectra of the black area (a) and the gray area (b) in the first TEM image. For area (a), the peaks of Pt were observed, implying that the black spots were Pt particles. Cu peak existed due to the Cu plate. In spectrum (B), which shows the area (b) in the first TEM image, we can see that the Pt peaks disappeared and C peaks were dominant. The EDX spectra indicate the existence of Pt and PAn. The content of Pt in spectrum A is 36.4 atom%, the average particle size is about 100 nm.

Figure 6 displays the cyclic voltammograms of the 0.5 mol/L H_2SO_4 solution using different electrodes. First, the comparison of the areas of the two peaks of the adsorption/desorption of hydrogen (between −0.2 and 0 V) in the two plots shows that the PAn-PSS hydrogel–Pt catalyst has more active sites than the PAn-PSS colloid–Pt catalyst. Because in the PAn-PSS hydrogel–Pt catalyst, Pt particles have not aggregated as the PAn-PSS colloid–Pt, the former catalyst has larger specific surface area. Thereby, it provides more active sites to catalyze the reaction. Second, two sets of redox peaks are obviously. The peaks located at about 0.3 and 0.5 V correspond to the redox between leucoemeraldine and emeraldine, the redox between emeraldine and pernigraniline of polyaniline, respectively.[33]

It has been found that the PAn-PSS hydrogel has better electrocatalytic performance than PAn-PSS colloid.[27] Then the electrocatalytic ability of PAn-PSS hydrogel–Pt toward methanol oxidation is studied here. Figure 7 shows the linear sweeping voltammograms of 1 mol/L CH_3OH in 0.5 mol/L H_2SO_4 solution at the different catalyst electrodes. They are (curve a) PAn-PSS hydrogel–Pt, (curve b) PAn-PSS colloid –Pt, (curve c) PAn-PSS colloid (l)–Pt and (curve d) PAn-PSS hydrogel catalyst electrodes, respectively. The oxidation peaks of methanol with the PAn-PSS hydrogel–Pt electrode (curve a) and PAn-PSS colloid–Pt electrode (curve b) are both at 0.65 V. The oxidation peaks of methanol with the PAn-PSS colloid (l) (curve c) electrode and PAn-PSS hydrogel electrode (curve d) locate at 0.66 and 0.70 V. The current densities of the oxidation peak in these four plots are 2.86, 2.39, 1.15 and 0.68 mA/cm^2, respectively. The PAn-PSS hydrogel–Pt electrode has 19% more current density than the PAn-PSS colloid–Pt electrode, indicating that the PAn-PSS hydrogel–Pt electrode has better electrocatalytic ability for the oxidation of methanol. Because the PAn-PSS hydrogel has stronger interactions with Pt than PAn-PSS colloid, the electrons transfer more quickly in the network of PAn-PSS hydrogel, which benefits the oxidation of methanol. Furthermore, the Pt particles on the PAn-PSS hydrogel–Pt are
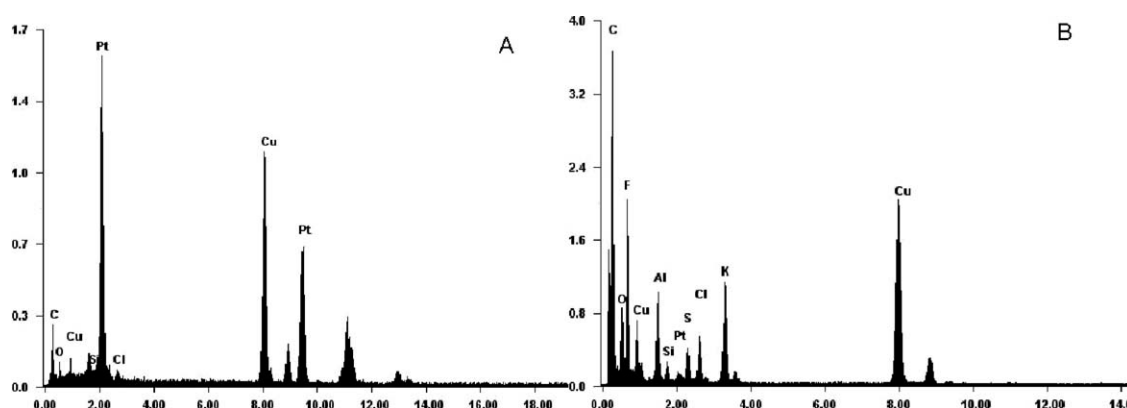

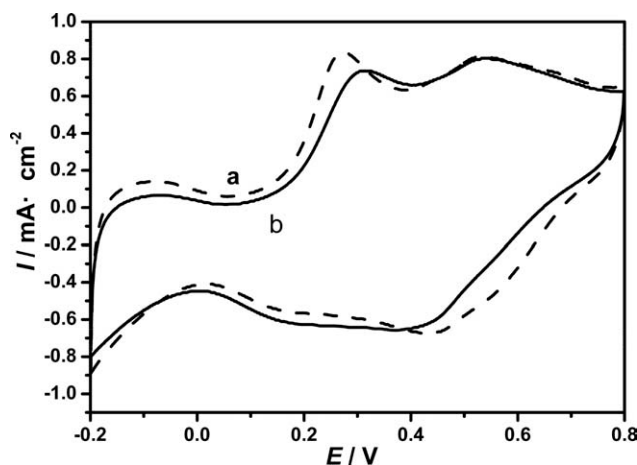**Figure 5** EDX spectra of two different areas of the PAn-PSS hydrogel–Pt.

Figure 6 Cyclic voltammograms of 0.5 mol/L H_2SO_4 solution at (a) PAn-PSS hydrogel–Pt and (b) PAn-PSS colloid–Pt catalyst electrodes.

dispersed instead of aggregating, so the sufficient active sites are available.

Figure 8 shows the current–time curves of methanol oxidation in 0.5 mol/L H_2SO_4 and 1 mol/L CH_3OH solution on different electrodes at 0.65 V. The chronoamperometric tests were conducted for 2500 s under 0.65 V. Obviously, the current density at 2500 s of PAn-PSS hydrogel–Pt catalyst electrode (b) 0.2543 mA/cm^2 is larger than that of PAn-PSS colloid–Pt catalyst electrode (a) 0.1486 mA/cm^2. Based on the Cottrell equation $i_i = \frac{nFAD^{1/2}c_0}{(\pi t)^{1/2}}$, where n represents the number of electrons transferred/molecular, F for the Faraday's constant, A for the electrode area. c_0 for the concentration, the ratio of the co-efficient on the PAn-PSS hydrogel–Pt is PAn-PSS colloid–Pt electrode D_h/D_c can be calculated to be 3.001, suggesting that the PAn-PSS hydrogel–Pt catalyst has better electrocatalytic stability.
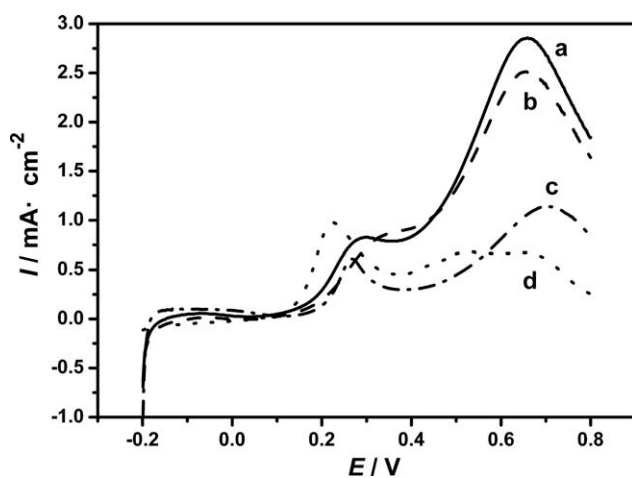

Figure 7 The linear sweeping voltammograms of 1 mol/L CH_3OH in 0.5 mol/L H_2SO_4 solution at (a) PAn-PSS hydrogel–Pt, (b) PAn-PSS colloid–Pt, (c) PAn-PSS colloid (l)–Pt, and (d) PAn-PSS hydrogel catalyst electrodes.
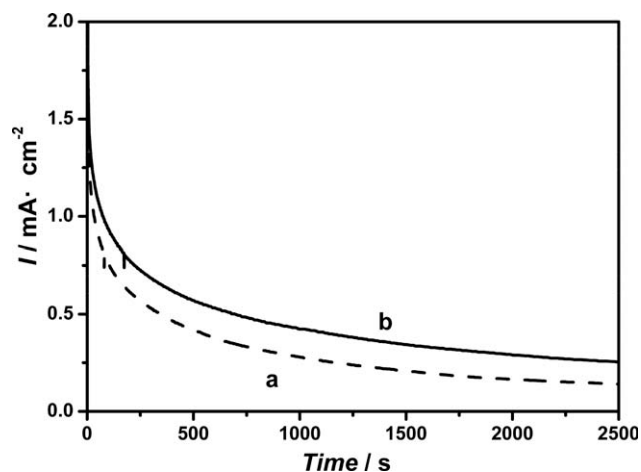

Figure 8 Chronoamperometric curves of 1 mol/L CH_3OH in 0.5 mol/L H_2SO_4 solution at (a) PAn-PSS colloid–Pt and (b) PAn-PSS hydrogel–Pt catalyst electrodes at 0.65 V.

CONCLUSION

In conclusion, when the PAn-PSS hydrogel prepared via supramolecular self-assembly was applied in electrocatalysis, the material shows better performance than the traditional PAn-PSS colloid. We have fabricated the PAn-PSS hydrogel–Pt catalyst by the means of electrochemical deposition. The macroscopic appearances of the PAn-PSS hydrogel and PAn-PSS colloid show the different mechanical structure. Then the spectral properties of the PAn-PSS hydrogel and PAn-PSS hydrogel–Pt have been investigated. The results show that the concentrated PAn-PSS hydrogel has much stronger interactions with Pt particles, comparing with the PAn-PSS colloid. Hence, the PAn-PSS hydrogel–Pt has more excellent electrocatalytic ability toward the oxidation of methanol as well as electrocatalytic stability, and the PAn-PSS hydrogel–Pt can be an eligible catalyst of the oxidation of methanol in DMFC.

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