



## Effects of conductive polyaniline (PANI) preparation and platinum electrodeposition on electroactivity of methanol oxidation

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### Abstract

A modified galvanostatic method, termed the ‘pulse galvanostatic method’ (PGM) was used to synthesize nanofibular polyaniline (PANI). In contrast to granular PANI prepared by the conventional galvanostatic method (GM), nanofibular PANI has better conductivity and higher specific surface area. The nanofibular PANI electrode modified by Pt microparticles, at the same Pt loading, exhibits a considerably higher electrocatalytic activity on the methanol oxidation than that of the granular PANI electrode modified by Pt microparticles. Furthermore, the PGM method can be used as a good method for Pt microparticle electrodeposition. The composite electrode composed of PANI and Pt microparticles has the best electrocatalytic activity in the experimental range. The effects of Pt loading and methanol concentration, on the electrocatalytic activity for methanol oxidation have also been researched.

### 1. Introduction

Fuel cells are attractive sources of electrical power since they realize the direct conversion of chemical to electrical energy. Considerable interest has been directed to the use of fuel cells in electric vehicle technology. One promising system is the direct methanol fuel cell (DMFC). Since it requires little additional equipment compared to the extensive gas process technology for methanol reforming, the fuel is best transported and converted into energy from the liquid state [1–4]. Unfortunately, the expensive catalytic materials, such as platinum, and relatively low electrocatalytic efficiency for electrochemical reactions of the fuel are drawbacks. Anodic methanol oxidation at a platinum catalyst is a self-poisoning reaction which blocks the active electrocatalyst surface by strongly adsorbed reaction intermediates such as CO, the efficiency of the cell reduces due to poisoning of the catalyst and relatively poor mass-specific power densities are obtained [5, 6]. Therefore, it is necessary to place more emphasis on electrocatalyst research and to attain a significantly higher power density.

To improve both the oxidation rate and electrode stability, considerable efforts have been applied to the study of electrode materials for the direct electrochemical oxidation of methanol [7–16]. In these studies, some economical materials, including graphite, Nafion<sup>®</sup> film and glass carbon, and novel materials such as carbon nanotubes were used as substrate for dispersing plati-

num. Compared with pure platinum, the electrocatalytic activity of composite electrodes on methanol oxidation was improved to different extent. On the other hand, recent advances have shown that electronic conducting polymers such as polypyrrole [17, 18], polythiophene [19] and polyaniline [20–22] can serve as porous supports to disperse the platinum catalyst, due to their excellent properties. Among conducting polymers, polyaniline has been applied extensively to support platinum catalysts. Platinum dispersion inside such a support [20–22], which leads to a decrease in the amount of noble metal used, allows improvement of the catalytic activity for the oxidation of methanol via a better utilization of the platinum crystallites and, especially, in decreasing the poisoning effect [23].

Polyaniline has been mostly synthesized by a galvanostatic method (GM), a cyclic voltammetric method (CVM) or a potentiostatic method (PM). Polyaniline prepared by the above methods had a granular structure. The CVM method and PM method were commonly used as an electrodeposition method for platinum. Compared with CVM and PM methods, the pulse galvanostatic method (PGM) is a modified galvanostatic technology which may supply instantaneously high overpotential regardless of the relatively small mean current. The discontinuous current process reduces the concentration polarization of electrode/solution interface. In this work, the PGM method was used to synthesize polyaniline nanofiber directly onto stainless steel. Scanning electron microscopy (SEM) shows that

the nanofibular polyaniline film on stainless steel has a high specific surface area. The electrocatalytic properties of nanofibular polyaniline film, modified by the Pt microparticles, were investigated. In addition, platinum microparticles were electrodeposited by the PGM method. Compared with the conventional CVM method, the PGM method offers much higher deposition overpotential, to obtain finer platinum granule and produces a nanofibular polyaniline electrode modified by Pt nanoparticles.

## 2. Experimental details

### 2.1. Reagent and apparatus

Aniline was purified by repeated distillation and stored under nitrogen gas. All other reagents were of analytical grade. All solutions were prepared with twice distilled water.

The polyaniline films were synthesized by the pulse galvanostatic system (Handan Instrument Factory, China) or the galvanostatic system (Shenzhen Electronic Instrument Factory) using a two-electrode cell from 0.2 M aniline + 0.5 M sulfuric acid aqueous solutions kept at room temperature. The working electrode was a stainless steel disc with a surface area  $S = 0.95 \text{ cm}^2$ . The working electrode was polished mechanically using the emery paper (grade 1000) to a mirror finish and then cleaned in double distilled water in an ultrasonic bath. A platinum foil was used as counter electrode.

The electrochemical experiments were performed in a three-electrode cell, using a saturated calomel electrode (SCE) as reference electrode at room temperature.

### 2.2. Preparation of PANI-coated stainless steel (PANI/SS) electrode

PANI/SS electrodes were prepared by the PGM and GM methods. The parameters of the pulses used were as follows: the ratio of 'on' pulse period to 'off' pulse period ( $t_{\text{on}}:t_{\text{off}}$ ) = 50 ms:50 ms; mean current density  $1 \text{ mA cm}^{-2}$ . The PANI/SS electrode prepared by GM was performed in the conditions as constant current density =  $1 \text{ mA cm}^{-2}$ . The thickness of PANI films was estimated by the  $800 \text{ mC cm}^2$  reported in other literature [24].

### 2.3. The platinum modification on PANI/SS

Platinum microparticles were electrodeposited by CVM method and PGM method. Cyclic voltammetry was performed at  $100 \text{ mV s}^{-1}$  between 0.5 and  $-0.2 \text{ V}$  vs SCE in 0.5 M  $\text{H}_2\text{SO}_4$  containing 7 mM  $\text{H}_2\text{PtCl}_6$ . The PGM method was carried out at the following conditions:  $t_{\text{on}}:t_{\text{off}} = 0.1 \text{ ms}:9.9 \text{ ms}$ ; mean current density  $0.8 \text{ mA cm}^{-2}$ . The amount of loaded Pt microparticles was evaluated from the charge consumed during elec-

trodeposition, assuming that  $\text{Pt}^{4+}$  to  $\text{Pt}^0$  reduction is 100% efficient.

Electrocatalytic oxidation of methanol on PANI/SS electrodes containing dispersed Pt microparticles was examined in 2 M  $\text{CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$  solution by cyclic voltammetry at  $50 \text{ mV s}^{-1}$  between  $-0.2$  and  $0.9 \text{ V}$ .

Scanning electron microscopy (SEM) model (JEM-5600LV) was used to identify the morphology of PANI/SS electrodes loaded or unloaded by Pt microparticles.

## 3. Results and discussion

### 3.1. Morphology of PANI synthesized by PGM method and GM method

It has been reported that PANI films with dispersed Pt microparticles has a good electrocatalytic capacity [20–22]. PANI films with different microstructure can be obtained by different methods. In this section, the PANI films were synthesized by PGM method. Figure 1(a) shows the surface micrograph of the polyaniline films synthesized by PGM method. From Figure 1(a), polyaniline films with nanofibular structure can be observed. The fiber has a diameter of 70–100 nm and a length of

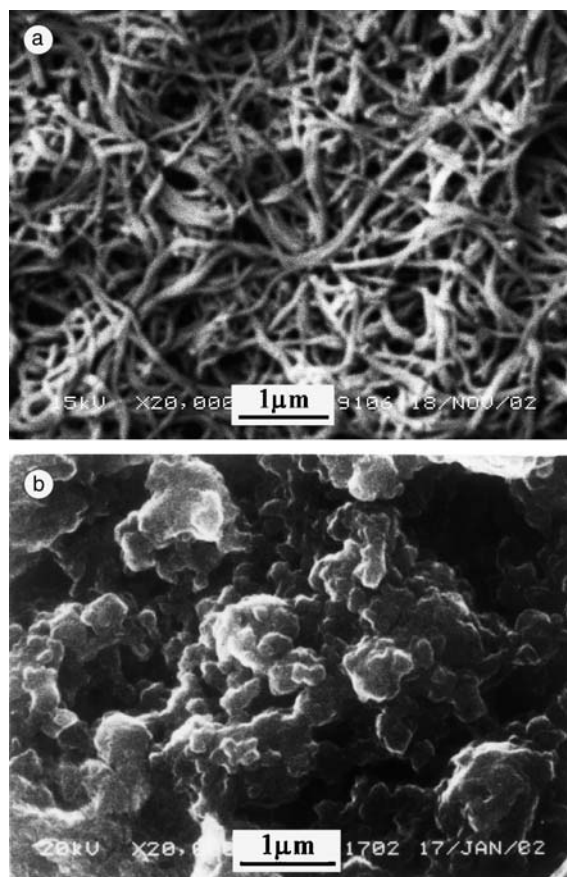


Fig. 1. Typical surface morphologies of PANI films prepared by PGM method (a) and GM method (b).

about  $10\ \mu\text{m}$ . For comparison, polyaniline films were synthesized by galvanostatic method (GM). The corresponding SEM result is shown in Figure 1(b). As reported in the other literature [25], a typical granular polyaniline structure with individual granules having different diameter is observed. Compared with granular PANI film, nanofibular PANI film has relatively higher specific surface area. The larger genuine area in the same geometric area is beneficial for Pt dispersion. Furthermore, the smaller transfer resistance of conductive particles in fibular PANI film decreases the catalyst poison [26]. This means that nanofibular PANI film can be used as a better catalyst support.

### 3.2. Different microstructure PANI supports for Pt catalyst

To investigate the influence of PANI microstructure on methanol oxidation, nanofibular PANI film prepared by PGM method and granular PANI film prepared by GM method were used as Pt catalyst support. Pt microparticles were electrodeposited by CVM method. Figure 2 exhibits cyclic voltammograms (CVs) of the electrocatalytic oxidation of methanol on different PANI/SS electrodes modified by Pt microparticles. It is clear that the Pt/nanofibular PANI/SS electrode has a higher oxidation peak current than that of the Pt/granular PANI/SS electrode. The corresponding micrographs are given in Figure 3. It can be seen that, for both the Pt/nanofibular PANI/SS electrode and Pt/granular PANI/SS electrode, the platinum microparticles are spread in a nonhomogeneous arrangement, of a size varying between 100 and 400 nm. However, the Pt/nanofibular PANI/SS electrode shows a loose and well-distributed structure, which exhibits superior electrocatalytic activity. This result may also be attributed to the larger specific surface area and faster charge transfer of nanofibular PANI film. In addition, the relationship between positive-going peak current of CVs in methanol solution and Pt loading is shown in Figure 4. It can be seen that, for both nanofibular PANI film and granular

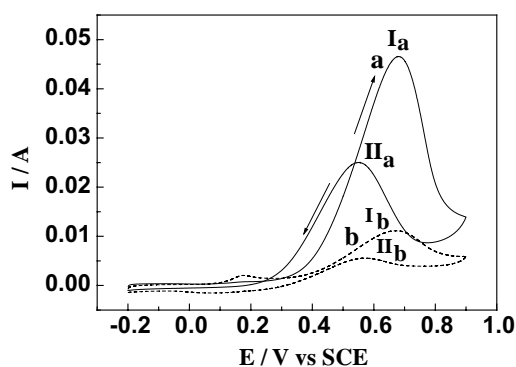


Fig. 2. CVs of  $\text{CH}_3\text{OH}$  oxidation on the Pt/nanofibular PANI/SS (a) and Pt/granular PANI/SS (b) (Pt loading is  $550\ \mu\text{g cm}^{-2}$  and Pt is electrodeposited by CVM method).

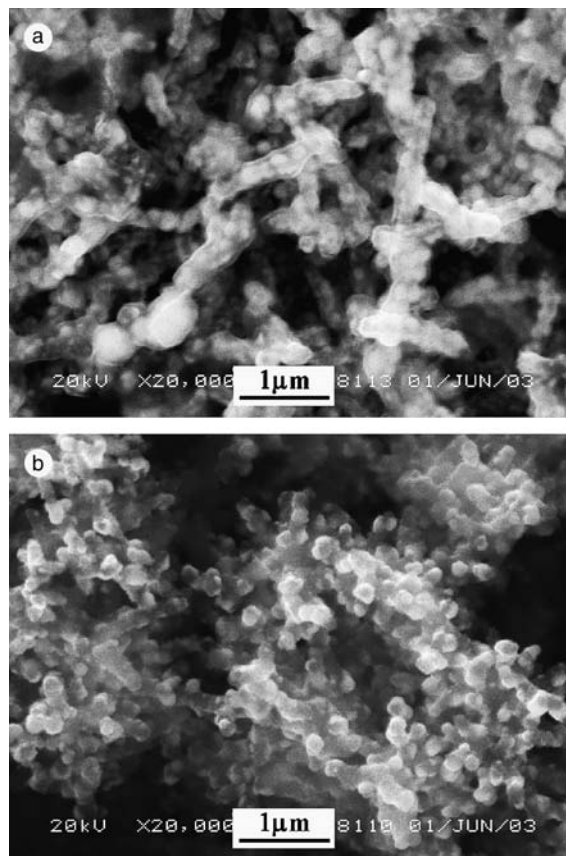


Fig. 3. SEM images of the Pt/nanofibular PANI/SS (a) and Pt/granular PANI/SS (b) (Pt loading is  $550\ \mu\text{g cm}^{-2}$  and Pt is electrodeposited by CVM method).

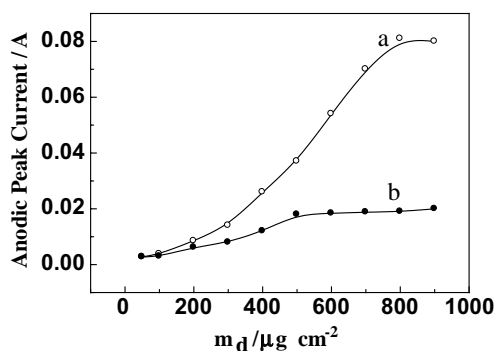


Fig. 4. The relationship between the peak current in the positive-going sweeping and the Pt loading. (Pt is deposited by CVM method) (a) Pt/nanofibular PANI/SS; (b) Pt/granular PANI/SS.

PANI film, the catalytic current is greatly increased with increase in the amount of Pt deposited. The catalytic current will keep as constant when the amount of deposited Pt increases to a certain value (i.e. for nanofibular PANI film,  $800\ \mu\text{g cm}^{-2}$ ; for granular PANI film,  $500\ \mu\text{g cm}^{-2}$ ). Nevertheless, it is observed that the catalytic activity of Pt/nanofibular PANI/SS electrode is much better than that of the Pt/granular

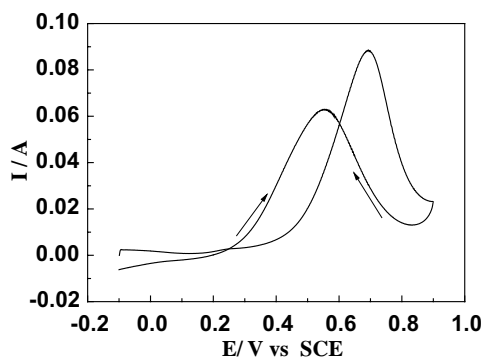


Fig. 5. Cyclic voltammogram of  $\text{CH}_3\text{OH}$  oxidation on the nanofibular PANI electrode modified by Pt microparticles. (Pt loading is  $550 \mu\text{g cm}^{-2}$  and PGM method is used to deposit Pt).

PANI/SS electrode. (i.e. the ratio of the anodic peak current densities is about 5 under the condition of Pt loading  $800 \mu\text{g cm}^{-2}$ ).

### 3.3. PGM electrodepositing Pt microparticles on the nanofibular PANI film

CVM method was extensively applied to electrodeposit Pt microparticles on different supports such as carbon foil [7], Nafion<sup>®</sup> film [11], carbon nanotube [8] and conductive polymer [17–22]. In Section 3.2. CVM method was used to deposit Pt microparticles into PANI film with different microstructure. According to typical electrodepositing theory, a high overpotential will lead to formation of fine crystals. Pulse galvanostatic deposition may offer considerable high peaks current resulting in the remarkable high overpotential between electrode and solution. In this section, PGM method was used to electrodeposit Pt microparticles into the nanofibular PANI film prepared by PGM method. The electrochemical form of the Pt/nanofibular PANI/SS electrode in methanol aqueous solution is given in Figure 5, which indicates a typical methanol oxidation process. From Figure 5, we can see that the Pt/nanofibular PANI/SS electrode obtained by PGM method has relatively better electrocatalytic activity than that of two kinds of electrodes shown in Figure 2 at the same platinum loading condition. The morphologies of composite electrodes are shown in Figure 6. It can be seen that the Pt microparticles with 50–100 nm diameter are homogeneously dispersed on PANI nanofiber, which exhibits considerably high specific surface area. These highly dispersed active centers enhance the electrocatalytic activity. Figure 7 shows the relationship between positive-going peak currents of CVs and the amount deposited Pt. The same rules as Figure 4 are observed. However, the anodic peak current is relatively higher than that of shown in Figure 4 at the same Pt loading condition (the height of the anodic peak current is two times than that of shown in Figure 4 when the Pt loading is  $800 \mu\text{g cm}^{-2}$ ).

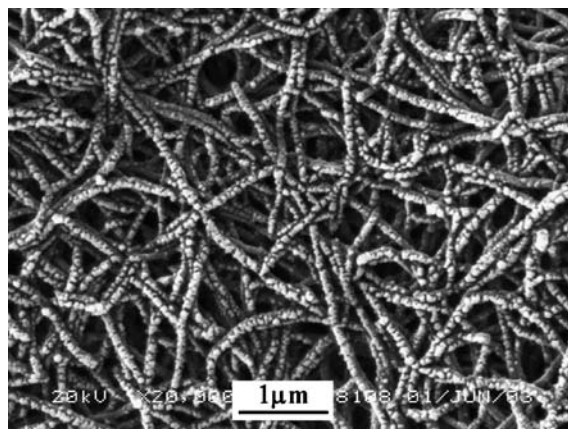


Fig. 6. SEM image of nanofibular PANI film modified by Pt microparticles (Pt loading is  $550 \mu\text{g cm}^{-2}$  and PGM method is used to deposit Pt).

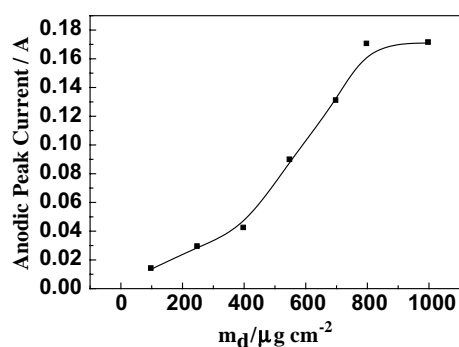


Fig. 7. Relationship between peak current in the positive-going sweeping and Pt loading (Pt is deposited by PGM method).

### 3.4. Effect of nanofibular PANI film thickness on electrocatalytic activity

PGM method is applied to synthesize nanofibular PANI and electrodeposit Pt microparticles. The composite electrode prepared by PGM method indicates considerably high electrocatalytic activity. For further interpretation, the influence of the thickness of nanofibular PANI film on electrocatalytic activity on methanol oxidation was investigated and the corresponding results are shown in Figure 8. Under the condition of constant Pt loading ( $500 \mu\text{g cm}^{-2}$ ), the anodic current rises dramatically at film thickness below  $1.25 \mu\text{m}$ , then the anodic current drops linearly.

### 3.5. Effect of methanol concentration on electrocatalytic activity of Pt/nanofibular PANI/SS electrode

The variation of the anodic current as a function of methanol concentration is given in Figure 9. As is shown, the anodic current increases significantly with increasing methanol concentration and changes a little at concentrations higher than 3 M. This is on account of the saturation of active sites at the electrode surface.

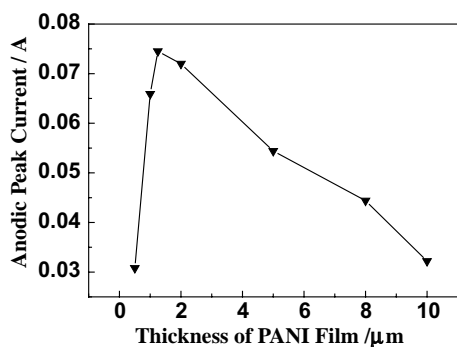


Fig. 8. Plot of peak current in positive-going sweeping as a function of nanofibular PANI film thickness. (Pt loading is  $500 \mu\text{g cm}^{-2}$  and PGM method is used to deposit Pt).

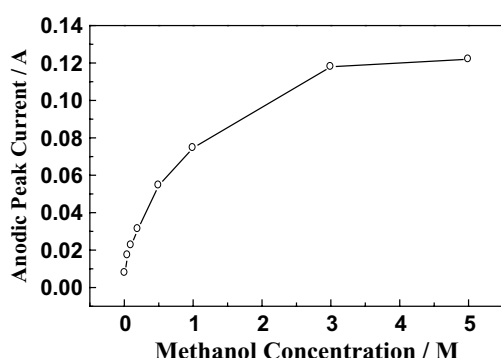


Fig. 9. Plot of anodic peak current in positive-going sweeping as a function of methanol concentration (Pt loading is  $500 \mu\text{g cm}^{-2}$  and PGM method is used to deposit Pt).

Therefore, the optimum concentration of methanol to obtain higher anodic current is about 2 M.

#### 4. Conclusion

The electrocatalytic oxidation of methanol on nanofibular polyaniline electrodes modified with Pt microparticles has been researched. The results show that modification of electrode surface by nanofibular PANI improves the electrocatalytic activity for methanol oxidation to a great extent. When the value of Pt loading is over  $200 \mu\text{g cm}^{-2}$ , the Pt/nanofibular PANI/SS electrode is greatly superior to the Pt/granular PANI/SS electrode in electrocatalytic activity. And the anodic peak current of methanol oxidation at Pt/nanofibular PANI/SS electrode is about 2–5 times bigger than that of Pt/granular PANI/SS electrode. The composite electrode of nanofibular PANI modified

by homogeneously platinum microparticles is prepared by PGM method, which has the best electrocatalytic activity on the methanol oxidation in the experimental range. Factors of methanol concentration, Pt loading, Pt microparticles support and Pt microparticles modification method all influence the anodic current for methanol oxidation significantly.

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