

Comparison of the Electrocatalytic Performance of Pt and Pt-Ru for Oxidation of Methanol

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The electrocatalytic properties of platinum and platinum-ruthenium particles incorporated into polyaniline films are investigated for oxidation of methanol in sulphuric acid. It is observed that the electrocatalytic activity of the metal-modified polyaniline electrode depends greatly on the deposition condition of metal particles which can be optimized by the electrochemical formation conditions.

Key Words: Platinum-modified polyaniline film, Platinum/ruthenium-modified polyaniline film, Electrocatalytic activity, Methanol oxidation.

INTRODUCTION

Direct methanol fuel cells (DMFCs) are considered to be the most attractive power sources for the application in portable power sources, electric vehicle and transportation because it does not require any fuel processing equipment¹⁻³. Conducting polymers with porous structure and high surface area, such as polyaniline and polypyrrole, are usually used as matrix to incorporate noble metal catalysts in the application for electrooxidation of small molecules such as hydrogen, methanol and formic acid, *etc.* Such composite materials show the extraordinary electrocatalytic activity, which is comparable with or even exceeds that of bare platinum at relatively low platinum loadings⁴⁻⁹. However, a challenging problem in the development of a DMFC is to find an electrocatalyst that can effectively enhance the electrode kinetics of methanol oxidation^{10,11}. For several decades, platinum has been selected for use in the anode catalysts of commercial products^{12,13}. However, it is well known that some intermediate products of the reaction are strongly adsorbed at the electrode surface, acting as poisons (*e.g.*, CO_{ad}) and leading to a loss of the electrocatalytic activity of the electrode. The incorporation of transition metals (*e.g.*, Pt, Ru, Pd, *etc.*) particles into conducting polymer-coated electrodes can be used as one approach to promoting methanol oxidation⁴⁻⁸. The combination of Pt and Ru has long been recognized as having a synergistic enhancement for electrocatalytic oxidation of CO, H₂ + CO mixtures and organic molecules, which makes Pt-Ru surfaces attractive for fuel cell catalysis¹⁴.

Metal particles can be deposited by constant potential⁵⁻⁸ or cyclic potential mode^{15,16}. It is found that the electrocatalytic behaviour of the platinum particles deposited by different electrochemical methods was slightly different, perhaps reflecting a different distribution or state of the metal deposited¹⁶. At the same time, the deposition method of transition metal also influences the resulting surface structure, with consequences for electrocatalysis. Ruthenium can be deposited by many methods, such as spontaneous deposition, forced deposition, electrodeposition, physical vapour deposition, chemical vapour deposition and deposition in non-aqueous solvents¹⁷. Among the various methods, electrochemical method has attracted many interests in recent years because of its simplicity, convenience and wide range of applications¹⁶⁻²⁰. Habibi investigated the electrocatalytic oxidation of methanol on Pt and Pt-M (M = Ru, Ir and Sn) nanoparticles deposited by constant potential method¹⁹. Liu reported the effect of deposition sequence of platinum and ruthenium particles into nanofibrous network of polyaniline-poly(styrene sulphonic acid) on electrocatalytic oxidation of methanol, where, platinum and ruthenium were deposited by cycling the potential in the range of -0.25 to 0.80 V for 25 cycles with a scan rate²⁰ of 30 mV s⁻¹. To our best of knowledge, however, little work is done to study the influence of deposition parameters of metal particles, such as deposition mode (constant potential and cyclic voltammetry) and cycle numbers of cyclic voltammetry on the electrocatalytic activities of the electrode, which would allow this type of electrode to be optimized. Previous research has exhibited that the choice and preparation of the anode catalyst is the most important thing in the study of DMFC because the kinetics of methanol electro-oxidation are relatively slow, namely, about six orders of magnitude lower than those of hydrogen near room temperature²¹. Therefore, if the anode catalyst is of poor quality, a DMFC may not even operate.

In this work, Pt and Pt-Ru bimetallic catalysts supported on polyaniline films were prepared to study the effect of the formation conditions of Pt and Pt-Ru particles, such as deposition modes and cycle numbers on the oxidation of methanol and the electrocatalytic activities of the two electrodes under the same conditions are compared. It is desirable that the adjustment of the electrochemical parameters would allow the electrocatalytic nature of the composite electrode to be optimized.

EXPERIMENTAL

Aniline was purified by repeated distillation with zinc dust and stored under nitrogen gas. Other reagents were of analytical grade and were used as received. All the solutions were prepared with double distilled water. All electrochemical experiments were performed with a CHI650A Potentiostat/Galvanostat by using a double-compartment glass cell with 3-electrode configuration. The working electrode was a platinum disk (1.5 mm in diameter) encapsulated in epoxy resin (substrate electrode geometric area: 0.0177 cm²), a platinum sheet and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. All potentials in present studies were presented in the SCE scale. The working

electrode was polished mechanically using emery paper (grade 1200) to a mirror surface and then cleaned by potential cycling between -0.2 and 1.2 V at 50 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ until a stable voltammogram was obtained.

The polyaniline films were formed on the platinum working electrode by cyclic voltammetry at 50 mV s^{-1} between -0.2 and 0.9 V *versus* SCE in solutions of 0.1 M aniline + $0.5 \text{ M H}_2\text{SO}_4$ for 15 cycles. After preparation, the polyaniline film was modified with Pt (or Pt-Ru) particles in $3 \text{ mM H}_2\text{PtCl}_6 + 0.5 \text{ M H}_2\text{SO}_4$ solution (or $3 \text{ mM K}_2\text{PtCl}_6 + 1.3 \text{ mM NH}_4\text{RuCl}_5 + 0.5 \text{ M H}_2\text{SO}_4$ solution) by cyclic potential polarization (-0.1 to 0.8 V or -0.25 to 0.65 V) at 50 mV s^{-1} or by constant potential polarization (-0.1 or -0.25 V). The amount of platinum deposited into the polyaniline film can be estimated from measurements of the charge involved during the reduction of Pt^{4+} - Pt^0 ¹⁶. Electrocatalytic oxidation of methanol at platinum-modified polyaniline electrodes (Pt/PAni-Pt) or Pt-Ru-modified polyaniline electrodes (Pt/PAni-(Pt-Ru)) was examined in $0.5 \text{ M CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$ solution by cyclic voltammetry between 0 and 0.7 V at a sweep rate of 5 mV s^{-1} .

RESULTS AND DISCUSSION

Electrochemical preparation and morphology of polyaniline film: Polyaniline film can be deposited by electropolymerization. Fig. 1A shows the cyclic voltammograms during the electropolymerization of aniline on platinum disk from a solution containing 0.1 M aniline and 0.5 M sulphuric acid for 15 cycles in the potential limits from -0.2 to 0.9 V at a sweep rate of 50 mV s^{-1} . As can be seen, the electrooxidation of aniline starts at 0.85 V in the first cycle and produces the first layer of polyaniline. Subsequent cycles indicate a successive growth of the polyaniline film as evidenced by the increase in the redox currents and the thickness of obtained polyaniline film is $0.86 \mu\text{m}$, as determined by the height of the first peak in the redox process of polyaniline¹⁶.

As a powerful surface physical technique, SEM is used to provide morphological information of the polyaniline matrix. Fig. 1B shows SEM micrograph of the surface of the polyaniline film. As can be seen, similarly to the earlier reports⁵, the polyaniline film shows a porous and fibrillar structure and provides a high surface, indicating that polyaniline films can be used as matrix to incorporate noble metal catalysts in the application for electrooxidation of small molecule methanol.

Electrocatalytic activity of platinum modified polyaniline film electrode: In the procedures to prepare platinum-modified polyaniline film electrode, the platinum particles can be electrodeposited into polyaniline films by constant potential or cyclic potential and the catalytic activity of the electrodes are evaluated by their performance in electrooxidation of methanol. Fig. 2 shows the cyclic voltammetry of electrocatalytic oxidation of methanol with the electrocatalytic electrodes obtained by different deposition modes of platinum particles under the same deposition time. It is seen that 4 platinum-modified polyaniline film electrodes all exhibit electrocatalytic

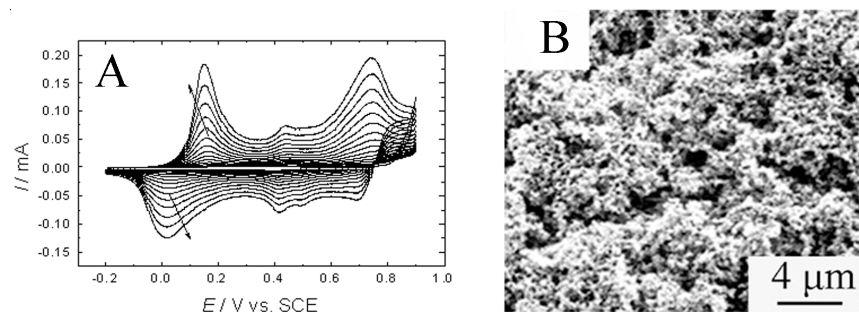


Fig. 1. (A) Cyclic voltammograms during the electropolymerization of aniline in 0.1 M aniline + 0.5 M H_2SO_4 solution ($v = 50 \text{ mV s}^{-1}$), (B) SEM micrographs of the surface of pure polyaniline

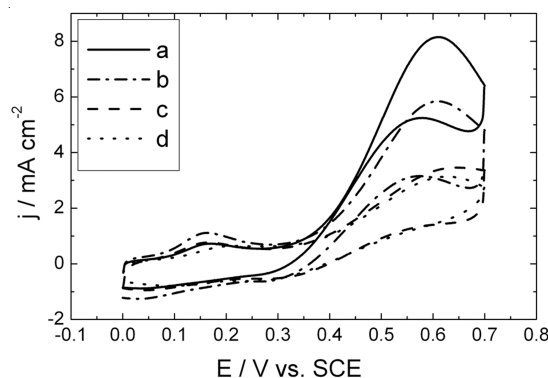


Fig. 2. Cyclic voltammograms of electrocatalytic oxidation of methanol with platinum-modified polyaniline film in 0.5 M CH_3OH + 0.5 M H_2SO_4 solution ($v = 5 \text{ mV s}^{-1}$). Platinum electrodeposition modes: constant potential (a. -0.25 V, c. -0.1 V) for 900 s and cycling potential (b. -0.25~0.65 V, d. -0.1~0.8 V) for 25 CVs

activity for the methanol oxidation, while the anodic peak current height of methanol oxidation, which appears in the positive going sweeps, changes greatly when the deposition mode changes. As can be seen, when the anodic potential is the same (-0.25 V), the electrocatalytic activity of electrodes obtained by constant potential deposition of platinum particles are better than that of electrodes obtained by cyclic potential. Moreover, even if the deposition time and deposition mode are the same, the electrodes obtained by constant potential -0.25 and -0.1 V also show different electrocatalytic behaviour. The platinum particles electrodeposited in the potential of -0.25 V exhibit the highest electrocatalytic activity for the oxidation of methanol, in comparison with the results obtained with other three deposition conditions (-0.1 V, -0.25~0.65 V -0.1~0.8 V, respectively), which probably reflects a different loading and dispersion (*i.e.*, surface area of active sites) of the platinum particles obtained by different electrodeposited modes. The dependence of peak current density of methanol oxidation on platinum loading corresponding to the 4 platinum-modified

polyaniline film electrodes formed by different electrodeposition mode of platinum particles is shown in Fig. 3. It can be seen that the oxidation peak current density is proportional to the platinum loading, which is similar to the earlier reports for methanol oxidation⁵. In other words, larger loading and higher dispersion of the deposited platinum particles will be of benefit to the adsorption and oxidation reaction of methanol, corresponding to higher oxidation current density in Fig. 3. Therefore, the deposition mode of constant potential -0.25 V was chosen for the electrodeposition of platinum particles within polyaniline matrix in this work.

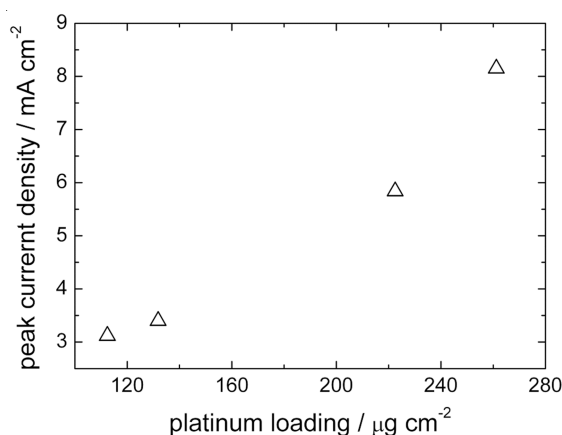
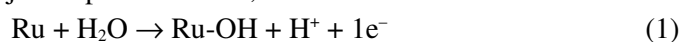


Fig. 3. Dependence of the peak current density on platinum loading for the oxidation peak at 0.62 V in the cyclic voltammetry of methanol oxidation on Pt/PAni-Pt electrode (PAni = polyanilines)

Electrocatalytic activity of Pt-Ru modified polyaniline film electrode: Co-deposition of Pt and Ru modifies the electronic structure of nearby platinum atoms, blocks the position that poisoning species are formed. Moreover, CO adsorption on Pt sites near Ru is weakened as compared with pure platinum, which may decrease the uptake of CO and may also facilitate oxidative removal of CO²². Compared with platinum, the polyaniline electrode modified by Pt-Ru bimetal shows better electrocatalytic activity and the anodic peak potential for methanol oxidation shift negative 50 mV under the same deposition condition (Fig. 4), which is in accordance with the report that methanol dehydrogenation on platinum sites (before oxidation to CO₂) has been shown to occur at lower potential on Pt-Ru surfaces^{23,24}. These changes have a number of implications for electrocatalysis.

The bifunctional mechanism of Pt promotion by Ru for methanol oxidation was first proposed by Watanabe and Motoo²⁵, in which the role of Ru is to supply activated water species (*i.e.*, adsorbed OH), which in turn oxidize adsorbed carbon containing species on adjacent platinum sites, as shown for the case of CO:



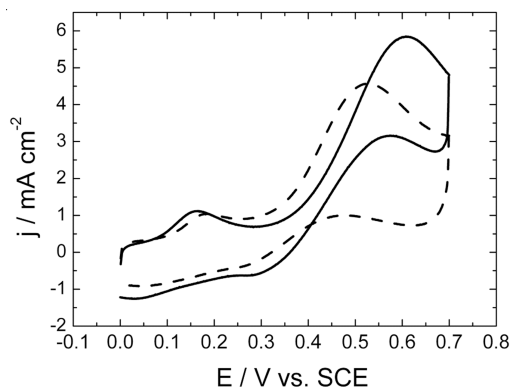


Fig. 4. Cyclic voltammograms of electrocatalytic oxidation of methanol on Pt/ PAni-Pt (solid) and Pt/PAni-(Pt-Ru) (dash) electrode in 0.5 M CH_3OH + 0.5 M H_2SO_4 solution ($\nu = 5 \text{ mV s}^{-1}$). Pt and Pt-Ru deposition mode: cyclic potential -0.25 to 0.65 V for 25 cycles (PAni = polyanilines)

Herein, CO may be either adsorbed directly onto platinum sites or formed from the decomposition of methanol or other organic molecules. In this way, the poisoned platinum is regenerated and can be reused as catalysts for direct methanol fuel cells.

Electrochemical deposition mode of Pt-Ru particles: In the process of depositing Pt-Ru particles into the polyaniline films, the deposited mode should also be studied to choose the optimal mode for the electrochemical deposition of metal particles which will be employed subsequently as active electrocatalysts for the oxidation of methanol. Like the deposition of Pt particles, the Pt-Ru particles are electrodeposited into the polyaniline films ($0.86 \mu\text{m}$) with the same deposition time, but the different deposition mode changes. Fig. 5 shows the effect of electrodeposition mode of Pt-Ru particles on the oxidation of methanol. As can be seen, the

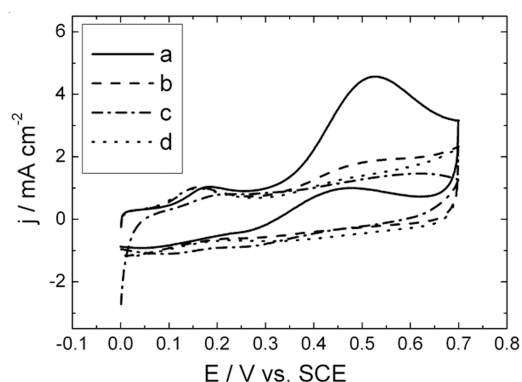


Fig. 5. Cyclic voltammograms of electrocatalytic oxidation of methanol on Pt/PAni-(Pt-Ru) electrode in 0.5 M CH_3OH + 0.5 M H_2SO_4 solution ($\nu = 5 \text{ mV s}^{-1}$). Pt-Ru deposition modes: cycling potential (a. -0.25~0.65 V, c. -0.1~0.8 V) for 25 CVs, constant potential (b. -0.25 V, d. -0.1 V) for 900s (PAni = polyanilines)

current peak of methanol oxidation is different when deposition mode changes. The Pt-Ru particles electrodeposited by cyclic voltammetry $-0.25\sim 0.65$ V exhibit the highest electrocatalytic activity for the oxidation of methanol and the electrode prepared by constant potential -0.1 V shows the lowest electrocatalytic activity, which is different from the sequence of platinum modified polyaniline electrode obtained by the four deposition modes (Fig. 2). The reason may be that for bimetal deposition, cyclic voltammetry mode can make Ru particle disperse around platinum particles better, which will be benefit to the adsorption of reactive oxygen species, enhance the oxidation reaction of reactive species and intermediate products and improve the electrocatalytic activity of electrode¹³. From the point of view of electrocatalytic activities of platinum particles, the deposition mode of cyclic potential $-0.25\sim 0.65$ V is selected to deposit platinum and ruthenium particles within the polymer matrix.

Conclusion

The oxidation of methanol on Pt and Pt-Ru catalysts supported by polyaniline films was investigated in sulphuric acid solution. Electrocatalytic activity of Pt and Pt-Ru catalysts prepared by different deposition mode show different electrocatalytic activities, which may be related to the distribution and state of metal particles incorporated in polyaniline film matrix. Results obtained from cyclic voltammetry of methanol oxidation reveal that constant potential -0.25 V was the best deposition mode for the deposition of platinum particles and bimetal deposited by cyclic potential $-0.25\sim 0.65$ V shows the best activity. Moreover, compared with platinum-modified polyaniline electrode, the anode peak potential of methanol oxidation of the Pt-Ru-modified electrode shifts negative 50 mV. The metal-modified polyaniline films formed by the optimization conditions exhibit great electrocatalytic effect on the oxidation of methanol.

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(Received: 25 March 2010; Accepted: 31 July 2010) AJC-8936