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Short Communication

Methanol as the Modifier of Nanostructured Pt Films for Enhenced Electrocatalytic Methanol Oxidation Reaction Electrocatalysis

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A rough Pt films (Pt_{meth}) were electrodeposited on a glassy carbon electrode (GCE) in a methanolcontaining aqueous bath for electrocatalytic oxidation of methanol. Scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD) and electrochemistry techniques were used to characterize the Pt films. Comparing to the conventional Pt films which electrodeposited in a methanol-free aqueous bath (Pt_{com}/GCE), the Pt_{meth}/GCE exhibits an improved electrocatalytic activity and poisoning-tolerance towards electrooxidation of methanol. The mechanism responsible for the improved performance has been discussed, and the principle can be extended for electrochemical preparation of other catalytic films in the energy and catalysis fields.

Keywords: Electrodeposition; Pt Films; Methanol-Containing Aqueous Bath; Electrocatalytic Methanol; Improved Electrocatalytic Activity.

1. INTRODUCTION

In order to meet the need for environmental protection and sustainable use of energy, new energy development and clean and efficient use of existing energy has become the key to the technological research. The electrocatalytic oxidation of methanol is the focus of attention for the application and development of direct methanol fuel cells (DMFCs) [1-3]. At present, anode catalyst poisoning and the slow methanol oxidation kinetics is the main factor to limit the practical application of DMFCs [4, 5]. Platinum is a noble metal catalyst commonly used for electrocatalytic oxidation of

methanol, but its catalytic activity will be notably decreased by the strong surface-adsorption of CO as a possible reaction intermediate during methanol oxidation [6, 7], which caused the poison of catalyst surface and prevent further oxidation of methanol [8, 9]. Hence, improving the performance and electrochemical availability of Pt material ectrocatalyst has been attracted great attention for years [10-16].

There are mainly three methods of preparation of porous platinum material such as template[16, 17], template-free and de-alloying methods[18]. Template method is based on the porous organic or inorganic materials as templates, and immersed in a metal salt solution or colloidal solution, loading the metal to the template, and then select a certain method remove the template, and finally get the desired porous metal catalyst. Wang proposed a new synthetic way for reducing the use of Pt in a catalytic system by increasing the surface area and modifying the Pt surface structure [19]. Mesoporous Pt films were electrodeposited from an aqueous solution including K₂PtCl₄ and three types of nonionic surfactant with different molecular weights. Jung demonstrated highly engineered nanoporous Pt films by the dealloying of a Pt-Si binary alloy system with a predetermined alloy composition [20]. Controlled pore dimensions and nanostructures were obtained by tailoring the Pt-Si alloy composition followed by selective Si etching. The formed nanoporous Pt films showed a 32times-higher catalytic activity than Pt/C catalysts, with a high current density and low charge-transfer resistance during methanol electro-oxidation. Raoof prepared Pt nanostructure on GCE by electrochemical deposition with the addition of white dextrin [21], the prepared nano-Pt results in an electrochemically active surface much larger than that of Pt microparticles prepared by the same procedure without dextrin. In addition, Xu fabricated a nanoporous PdPt alloy with uniform ligament size and controllable bimetallic ratio through the selective dealloying of Al from PdPtAl ternary alloys [22]. Compared with commercial Pd/C, Pd, Pt catalyst, the as-prepared PdPt exhibits greatly enhanced electrocatalytic activity. Sawy prepared a thin and porous Pt-Ir films with controlled compositions on Au and applied as methanol oxidation catalyst [23].

It is well known that methanol can penetrate into the cathode from the anode through the Nafion membrane[24]. The methanol permeation not only lead to waste of fuel, but also accumulate additional amount of water in the cathode, which affects the output voltage and the discharge performance of the DMFC[25-27]. The adsorption of methanol and its products negatively affects the electrocatalytic oxidation of methanol on platinum, however, it is thus anticipated that the dynamic adsorption-desorption of methanol added in the Pt-electroplating bath (and its electrooxidation products) on electroplating Pt films may efficiently alter the electrodeposits process and the electrocatalytic activity of the Pt deposits, as compared with the use of conventional methanol-free bath. Previously, we reported that an Au films electrocatalytic activity toward glucose oxidation in neutral aqueous solution [28]. Herein, we prepared a Pt_{meth} films on glassy carbon electrode (GCE) by the electrodeposition in methanol-containing aqueous bath comparing to platinum film (Pt_{com}) prepared with the conventional electrodeposition in methanol-free bath, the Pt_{meth} films showed high catalytic activity for methanol electrocatalytic oxidation, and have a greater oxidation current density.

2. EXPERIMENTAL

2.1 Apparatus

All electrochemical experiments were conducted on an CHI660C electrochemical workstation (CH Instrument Co.), and a conventional three-electrode electrolytic cell was used. A disk GCE of 3.0-mm diameter served as the working electrode, the KCl-saturated calomel electrode (SCE) as the reference electrode, and a carbon rod as the counter electrode. All potentials here were cited versus SCE. A field emission scanning electron microscope (SEM, ZEISS-SIGMA HD) coupled with an energy dispersive X-ray spectrometer (EDS) unit was employed to evaluate the electrode morphology and composition. The X-ray powder diffraction (XRD, Rigaku Ultima IV, Cu K*a* radiation) was used to determine the phase purity and crystallization degree of Pt catalyst. Pt loadings on the GCE were dissolved by a solution containing concentrated HCl and HNO₃ (V / V = 3:1) and was measured by an ICP-AES (PS-6, American baird company).

2.2 Reagents

 $H_2PtCl_6 \cdot 6H_2O$ was obtained from Chemicals Company of Tianjin (Tianjin, China). Methanol was purchased from Shanghai Chemicals Factory (Shanghai, China). H_2SO_4 was purchased from Chemicals Company of Zhuzhou (Hunan, China). All other chemicals were of analytical grade or better quality and used as received. Milli-Q ultrapure water (Millipore, $\geq 18 \text{ M}\Omega$ cm) was used throughout. All experiments were carried out at room temperature ($25 \pm 2 \text{ °C}$).

2.3 Preparation of the modified electrode and catalytical procedures

The GCE was polished to a mirror using 0.3 and 0.05 μ m alumina slurry, and water-rinsed thoroughly. After successive sonication in ethanol and ultrapure water, the electrode was rinsed with water and dry with pure nitrogen. The Pt_{meth}/GCE was prepared by cyclic voltammetry (CV) at 50 mV s⁻¹ between -0.22 ~ 0.15 V (initial potential at 0.45 V) for 200 cycles in 1.5 mM H₂PtCl₆ + 1.0 M CH₃OH + 0.5 M H₂SO₄ solution. For comparison, the Pt_{com}/GCE was prepared similarly with the Pt_{meth}/GCE only in methanol-free bath. Pt_{meth}/GCE and Pt_{com}/GCE were characterized in 0.5 M H₂SO₄ solution by CV method firstly. Then the property of electrocatalytic oxidation CH₃OH was studied by Was studied by linear sweep voltammetry in 0.5 M H₂SO₄ + 0.5 M CH₃OH solution for 2000 s at 0.6 V. At beginning of electrocatalytic oxidation of methanol, the prepared electrodes were immersed in 0.5 M H₂SO₄ solution and cycled between -0.22 and 1.2 V at 0.5 Vs⁻¹ until repeatable cyclic voltammograms were attained.

3. RESUITS AND DISCUSSION

3.1 Optimization of the conditions of the prepared electrodes

Firstly, we optimized CH₃OH and H₂PtCl₆ concentrations in plating solution by taking the catalytic activity as indication signal in 0.5 M CH₃OH + 0.5 M H₂SO₄ solution, as shown in Figure. 1A. It can be seen the optimum conditions of CH₃OH and H₂PtCl₆ concentrations of Pt_{meth}/GCE are 1.0 mM and 1.5 mM, respectively. The affection of the CH₃OH molecules on the electrodepositions of Pt films was studied, as shown in Figure. 1B. In the absent of CH₃OH, there have two pairs of redox peaks of hydrogen adsorption/desorption at near -0.07/-0.08 V and -0.15/-0.16 V (curve a), while in the present of CH₃OH, the two pairs of redox peaks of hydrogen adsorption/desorption at near -0.07/-0.08 V and -0.15/-0.16 V (curve a), while in the present of CH₃OH, the two pairs of redox peaks of hydrogen adsorption/desorption disappeared (curve b), and the background current was dramatically reduced. The results showed that the present of CH₃OH in the solution may be result in the eliminate adsorption of the H⁺ from the GCE surface. In order to illustrate the phenomenon, the CV of the prepared Pt_{meth}/GCE was conducted from -0.2~0.1 V in the 0.5 M H₂SO₄ with (curve a') or without (curve b') 0.5 M CH₃OH, as showing in insert in Fig. 1B. The results have confirmed the conclusions drawn from the above CV experiments of the electrodeposition. So, we have reasonably concluded that the CH₃OH play important role in the electrodeposition of Pt films.



Figure 1. (A) Effects of several experimental parameters for fabricating Pt_{meth}/GCE on catalytic activity toward 0.5 M CH₃OH by CV in 0.5 M H₂SO₄. (B) CV of the deposition of Pt films in 1.5 mM H₂PtCl₆ + 0.5 M H₂SO₄ electrolyte without (a) or with (b) 1.0 M CH₃OH and Pt_{meth}/GCE in 0.5 M H₂SO₄ electrolyte without (a') or with (b') 1.0 M CH₃OH insert at the scan rate of 50 mV s⁻¹.

3.2 Characterization of the prepared electrodes

Figure 2 shows the morphology of the Pt_{com}/GCE and Pt_{meth}/GCE . As can be seen, the large spherical aggregates formed through the settlement of several small Pt nanoparticles. In the absent of 0.5 M CH₃OH, the deposited nanostructured particles were loosely packed with low coverage of particles over GCE with average particle size ~200 nm (Figure 2A). However, in the present of 0.5 M CH₃OH, the Pt_{meth} particles are closely packed (higher particle density) with average particles size is also ~150 nm over Pt_{meth}/GCE (Figure 2B). The Pt nanoparticles were probably covered with CH₃OH

adsorbed on the electrode surface and consequently they were stabilized. At first, $H_2PtCl_6\cdot 6H_2O$ was electro-reduced, and then Pt nuclei were formed. With increasing of electrodeposition time, the isolated and randomly nanoparticles aggregated driven by the minimization of interfacial energy. It seems that when CH₃OH was added into the electrolyte solution, a large number of nuclei were formed simultaneously. In the absent of CH₃OH, the surface of GCE offered a small number of active sites, the deposited Pt nanoparticles on the GCE were loosely packed with lower coverage with larger size. When CH₃OH was added into the electrolyte solution, the adsorption of the CH₃OH on the surface of GCE offered many active sites which will results in fast growth nuclei. Based on the studies, we strongly believe that CH₃OH can control the growth of the Pt films. The catalyst composition was determined by EDS spectra. From the EDS results, Pt was the major elements, the mass ratio of Pt on the Pt_{com}/GCE and Pt_{meth}/GCE was 57.96% and 64.05% respectively. On the Pt_{com}/GCE, the mass ratio of oxygen and carbon was 1.26% and 40.78% respectively, which may be come from working electrolyte solution. While on the Pt_{meth}/GCE, the mass ratio of Oxygen and carbon was 1.78% and 34.17% respectively, which may be come from both working electrolyte solution and CH₃OH.



Figure 2. SEM images and EDS spectrum (below) of Pt_{com}/GCE (A) and Pt_{meth}/GCE (B).

The crystal structures of the prepared catalysts have been characterized by XRD, the results were shown in Figure 3. The reflection peaks of Pt_{meth}/ITO (indium tin oxide) and Pt_{com}/ITO composites located at 39.9, 46.1, 67.4 and 79.2 were attributed to the (111), (200) and (220) planes of Pt, respectively, which was consistent with a face-centered cubic crystalline (fcc) structure. The XRD pattern of ITO substrate was also displayed insert in Figure 3. (curve c), it can be observed that the peaks at 21.2, 30.2, 35.2, 50.4 and 60.1 were related to the diffraction peak of ITO glass. These results demonstrate the existence of Pt_{com} and the Pt_{meth} have an fcc structure. Compared with Pt_{com}/ITO films, the diffraction peaks of Pt (111) and Pt (200) on Pt_{meth}/ITO were enhenced and the diffraction peaks of Pt (311) appeared on the curves.



Figure 3. X-ray diffraction pattern for Pt_{com}/ITO (a), Pt_{meth}/ITO (b) and ITO (c) substrates.

 Pt_{com}/GCE and Pt_{meth}/GCE were also characterized in 0.5 M H₂SO₄ solution by CV method, as shown in Figure 4. Two pairs of redox peaks of hydrogen adsorption/desorption were found near -0.1 V, and the formation and reduction peak of platinum oxides (including the reduction of dissolved oxygen) were found at about 0.78/0.46 V, which are similar to the CV curves reported at polycrystalline Pt electrodes in 0.5 M H₂SO₄. Interestingly, we obtained notably higher redox peaks for hydrogen adsorption/desorption and formation/reduction of platinum oxides on Pt_{meth}/GCE than on Pt_{com}/GCE , indicating that electrodeposition of Pt films have an increased roughness.



Figure 4. The CV at Pt_{com}/GCE (a) and Pt_{meth}/GCE (b) in 0.5 M aqueous H_2SO_4 at the scan rate of 50 mV s⁻¹.

The electrochemical surface areas (ECSA) can be calculated using the hydrogen adsorption peaks by the following equation [29, 30]:

$$\text{ESCA} = \frac{\text{Q}_{\text{H}}}{0.21 \times \text{L}_{\text{Pt}}}$$

Where Q_H is the integrated hydrogen adsorption or desorption, L_{Pt} is the Pt loading (mg), and the value of 0.21 represents the charge of hydrogen for adsorption or desorption on a monolayer of hydrogen (mC cm⁻²). The ECSA of Pt_{com}/GCE and Pt_{meth}GCE are 0.42 and 0.71 cm² mg⁻¹, respectively. A larger ECSA was obtained for Pt_{meth}GCE than Pt_{com}/GCE.

3.3 Electrochemical behavior of CH₃OH on different electrode

Figure 5 shows the CVs of Pt_{com}/GCE and Pt_{meth}/GCE under acidic conditions (0.5 M H₂SO₄ + 0.5 M CH₃OH) from -0.22 to 1.2 V. For forward sweep, the potential of the oxidation on Pt_{com}/GCE and Pt_{meth}/GCE were both at 0.65 V. However, the peak current density of methanol oxidation reaction on Pt_{meth}/GCE (377.8 mA mg⁻¹, curve b) was about two times of that on Pt_{com}/GCE (190.8 mA mg⁻¹, curve a). The results showed that the Pt_{meth}/GCE exhibits superior electrocatalytic activity for the methanol electro-oxidation than Pt_{com}/GCE . In addition, the peak current ratio I_f/I_b of the forward (I_f) to the reverse (I_b) can be used to describe the catalyst tolerance to carbonaceous species accumulation. A higher ratio indicates more effective removal of the poisoning species on the catalyst surface and little accumulation of carbonaceous residues on the modified electrode surface [31, 32]. The I_f/I_b ratio for Pt_{meth}/GCE catalyst was 1.31, which is higher than that of Pt_{com}/GCE ($I_f/I_b=1.08$), indicating more intermediate carbonaceous species were oxidized to carbon dioxide in the forward scan on Ptmeth/GCE than on Pt_{com}/GCE, and superior to the other types Pt electrodes as reported in literature, such as the Pt/CCG hybrid (0.83) [33], three-dimensional Pt on Pd bimetallic nanodentrites supported on graphene nanosheets (1.25)[34], the Pt-CNT catalysts (1.4)[35], and the commercial E-TEK catalyst (0.74), the comparison as shown in table 1. The experimental results demonstrate that more effective methanol oxidation reaction occured on Ptmeth/GCE in the forward potential scan because of the forming less poisoning species.

Electrode	$I_{\rm f}/I_{\rm b}$	Reference
Pt/CCG/GCE	0.83	[33]
TP-BNGN/GCE	1.25	[34]
Pt-CNT/GCE	1.4	[35]
Pt/RGO/GCE	1.33	[36]
Pt/CeO ₂ /RGO/GCE	1.3	[37]
Pt _{meth} /GCE	1.31	This work

Table 1. Comparison of I_f/I_b values of methanol oxidation reaction at different Pt electrodes in acid solution.

CCG: chemically converted graphene; TP-BNGN: Pt on Pd bimetallic nanodentrites supported on graphene, RGO: reduced graphene oxide.



Figure 5. Electrochemical responses of the Pt_{com}/GCE (a) and Pt_{meth}/GCE (b) in 0.50 M H₂SO₄ + 0.5 M CH₃OH at the scan rate of 50 mV s⁻¹.

3.3 The catalytic activity and poisoning-endurance of the prepared electrode

In order to evaluate the catalytic activity and poisoning-endurance of Pt_{meth} , the Pt_{com}/GCE and Pt_{meth}/GCE were examined using *i-t* methods. Figure 6 shows the current density-change curve of Pt_{meth}/GCE and Pt_{com}/GCE at 0.6 V in 0.5 M H₂SO₄ + 0.5 M CH₃OH in 2000 s. High current density at beginning due to rich active site with methanol activation and double battery. Then, it was rapidly declined with the active sites occupied by CO substances generated in methanol oxidization leading to a rapid deactivated of Pt catalyst, and reached a plateau after about 400 s. The current density of the two electrodes both decreased throughout the process, but the current density of Pt_{meth}/GCE was always higher than that of the Pt_{com}/GCE , showed that Pt_{meth}/GCE had higher anti-drug capabilities compared with Pt_{com}/GCE , and more conducive to the building and practical application of DMFCs.



Figure 6. Chronoamperograms of the Pt_{meth}/GCE (a) and Pt_{com}/GCE (b) in 0.5 M H₂SO₄ + 0.5 M CH₃OH at 0.6 V.

4. CONCLUSIONS

A simple and quick electrochemical route was used to synthesize Pt_{meth} film in a methanolcontaining Pt plating solution. The comparison of the SEM images showed that methanol has played a critical role in controlling the size of the Pt nanoparticles and the density of the nanoparticles. The methanol prevents the Pt nanoparticles agglomerating during the electrodeposition and also stabilizes them on the electrode surface. This study confirms that when the catalytic target molecules coexist in the solution of catalytic materials can actively adjust the performance of prepared catalytic materials. The present method may be provided a new strategy towards the synthesis of other noble metals nanostructures with extensive applications.

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ALL THE AUTHORS ARE NO CONFLICTS OF INTEREST

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