

Pt Supported on Ti for Methanol Electrooxidation by Magnetron Sputter Method

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Pt nanoparticles dispersed on Ti were successfully prepared by the magnetron sputtering method. The results show that the platinum loading is very low and the catalyst shows a very high activity for methanol oxidation in alkaline media. The electrochemical oxidation performance increases with the increasing platinum loading on Ti. The best platinum loading was found at 2.14 $\mu\text{g cm}^{-2}$. The anodic transfer coefficient (α) is 0.43. The diffusion coefficient (D) of methanol is calculated as $6.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (298 K) when the concentration of KOH and methanol is both 1.0 M.

Keywords: Fuel cells; Methanol electrooxidation; Magnetron sputtering; Ti

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) are recognised to be promising power sources for portable electronic devices and electric vehicles due to the much higher energy density than gaseous fuels such as hydrogen and natural gas [1-3]. Pt and Pt-based catalysts have been extensively investigated as the electrocatalysts for methanol electrooxidation [4-8]. However, the high price and limited supply of Pt constitute a major barrier to the development of DMFCs. One effective approach to the cost reduction is to reduce the usage of the Pt catalysts. Here, we fabricate titanium-supported Pt electrocatalysts by magnetron sputter method. The platinum loading is very low and the catalyst shows a very high activity for methanol oxidation in alkaline media. The titanium-supported catalysts present significant electrocatalytic activity towards the methanol oxidation [9-12]. Compared with the conventional structure of the anode, the Ti mesh anode has many advantages[13], e.g.: (i) simplicity; (ii) easily produced on a mass scale; (iii) low cost; (iv) allowing flexibility in terms of shape;(v) collects current

easily. Ti mesh anodes prepared by deposition of the platinum directly on the Ti mesh have been used in a DMFC and show a higher performance than platinum supported on carbon black [14-17]. Magnetron sputtering is a simple producer for the preparation of catalysts supported on carbon cloth to make membrane electrode assembly (MEA) [18-21]. Despite the magnetron sputtering is a simple producer for the preparation of catalysts, there is little information on the Pt supported on Ti by magnetron sputtering. Here, Pt nanoparticles with low platinum loading were prepared by magnetron sputtering and were used as catalysts for methanol electrooxidation in alkaline media.

2. EXPERIMENTAL PART

A Pt catalyst thin film was coated on the surface of Ti foil by magnetron sputtering. A sputtering system (HITACHI e1030) was employed to deposit Pt catalyst onto the Ti. The base vacuum pressure was set at 0.5 Pa in each sputtering operation. The investigated platinum thin films were deposited by DC mode of 12 mA magnetron sputtering in Ar plasma on Ti. The thickness of the films was varied in the range of 0.2–4 nm by precise control of the deposition time. The catalyst loading is proportional to the thickness of the sputtered films as for the thickest film of 1 nm the amount of Pt is $2.14 \mu\text{g cm}^{-2}$.

Electrochemical experiments were performed on a PARSTAT 2273 electrochemical workstation (Princeton, USA). A standard three-electrode cell was used and was controlled at 25°C using a water bath during the experiment. A platinum foil (3.0 cm^2) and saturated calomel electrode (SCE, 0.241 V versus SHE) were used as counter and reference electrodes, respectively. A salt bridge was used between the cell and the reference electrode. Scanning electron microscopic (SEM) analysis was performed with a Hitachi S-5200.

3. RESULTS AND DISCUSSION

Fig.1 shows the typical SEM images of the Pt/Ti with different platinum loading. Fig. 1a shows the SEM image of Pt/Ti with a platinum loading of $0.43 \mu\text{g cm}^{-2}$, indicating that the surface of titanium substrate is partly covered by platinum particles. The sizes of these particles are about 4 nm. Fig. 1b and Fig.1c show the SEM images of Pt/Ti with a platinum loading of $2.14 \mu\text{g cm}^{-2}$ and $4.29 \mu\text{g cm}^{-2}$, showing the sizes of these particles are more and more large and are 8 nm and 20 nm. Fig. 1d shows the SEM image of Pt/Ti with a platinum loading of $8.58 \mu\text{g cm}^{-2}$, indicating that the surface of titanium substrate is totally covered by platinum particles. Fig.2a is the energy dispersive X-ray analysis (EDXA) of Pt/Ti. The major peaks are corresponding to Ti, showing that the platinum loading is very low. The results indicate that the Pt nanoparticles on Ti were successfully prepared by the electrodeposition method used in this study.

Fig.3 shows the cyclic voltammograms of methanol oxidation in 1.0 M KOH solution containing 1.0 M methanol on Pt/Ti electrode with a platinum loading of $0 \mu\text{g cm}^{-2}$ (a), $0.43 \mu\text{g cm}^{-2}$ (b), $2.14 \mu\text{g cm}^{-2}$ (c) and $4.29 \mu\text{g cm}^{-2}$ 1.10 mg cm^{-2} . The scan rate is 50 mV s^{-1} in the potential range of -0.8 to 0.3 V. A methanol oxidation peak can be clearly observed. The methanol oxidation on Pt/Ti

electrode was characterized by two well-defined current peaks on the forward and reverse scans. In the forward scan, the oxidation peak is corresponding to the oxidation freshly chemisorbed species coming from methanol adsorption. The reverse scan peak is primarily associated with removal of carbonaceous species not completely oxidized in the forward scan than the oxidation of freshly chemisorbed species [22,23]. The magnitude of the peak current on the forward scan indicates the electrocatalytic activity of the Pt/Ti for the oxidation reaction of methanol. The onset potential of methanol oxidation is -0.62 V. The peak potential for methanol oxidation is -0.23 V. It can be seen that current increases with the increasing platinum loading. The best platinum loading was found on $2.14 \mu\text{g cm}^{-2}$ and the peak current density is 13 mA cm^{-2} . The results can be seen from the Fig.4.

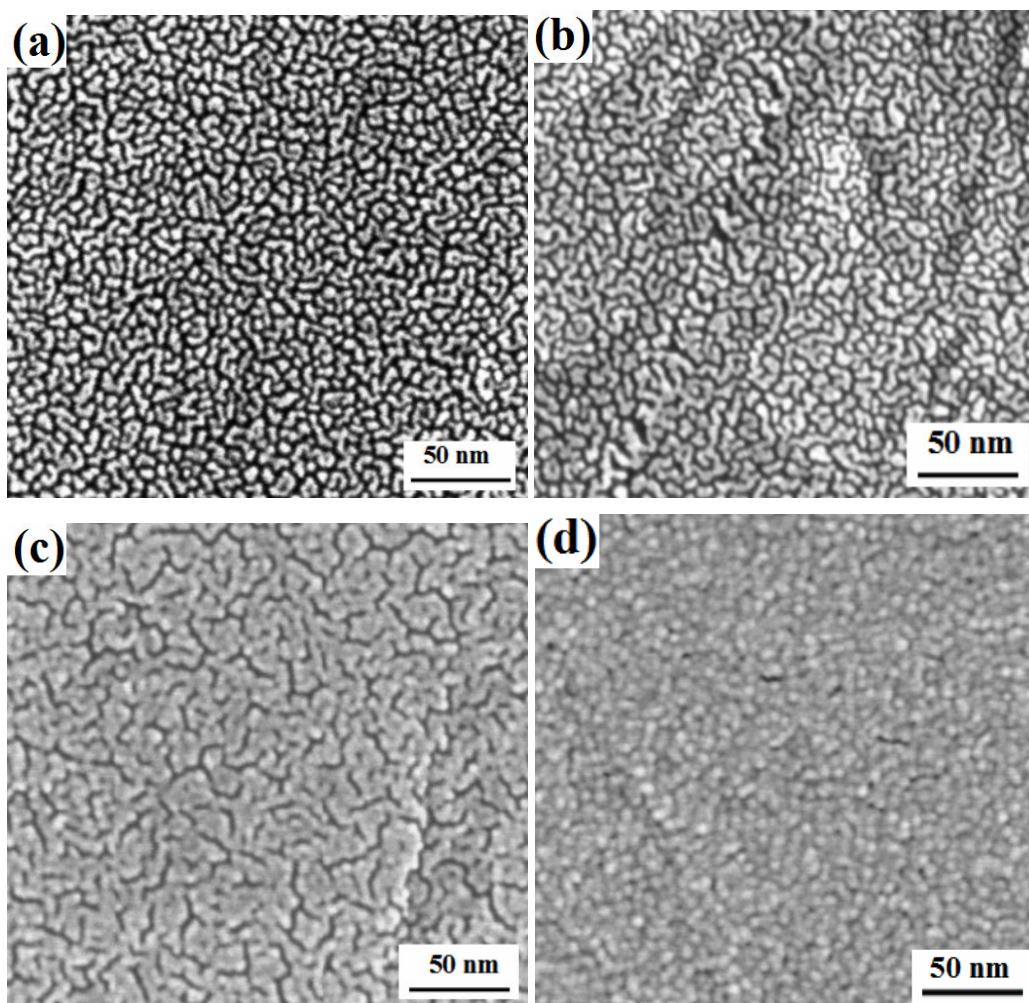


Figure 1. SEM image of Pt nanoparticles supported on Ti, the platinum loading is $0.43 \mu\text{g cm}^{-2}$ (a), $2.14 \mu\text{g cm}^{-2}$ (b), $4.29 \mu\text{g cm}^{-2}$ (c) and $8.58 \mu\text{g cm}^{-2}$ (d)

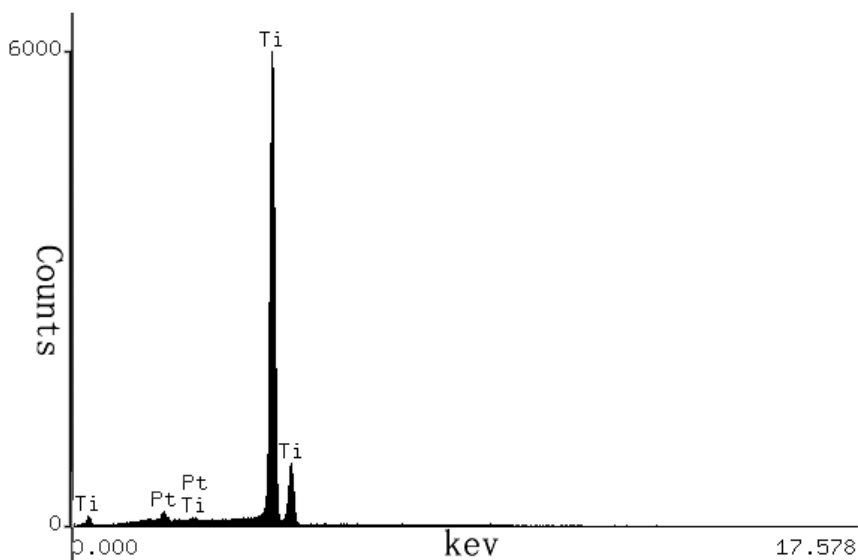


Figure 2. EDAX of Pt/Ti with a platinum loading of $4.29 \mu\text{g cm}^{-2}$.

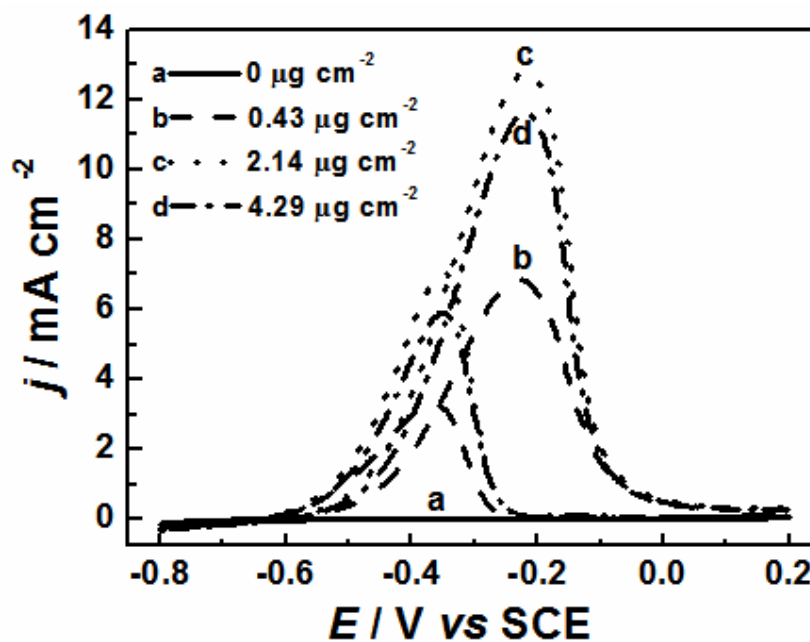


Figure 3. Cyclic voltammograms of methanol oxidation on Pt/Ti electrode with a platinum loading of $0 \mu\text{g cm}^{-2}$ (a), $0.43 \mu\text{g cm}^{-2}$ (b), $2.14 \mu\text{g cm}^{-2}$ (c) and $4.29 \mu\text{g cm}^{-2}$ (d) in 1.0 M KOH solution containing 1.0 M methanol with a sweep rate of 50 mV s^{-1} .

A linear relation is obtained from the plot for the peak potential of methanol oxidation (E_p) and natural logarithm of sweep rate ($\ln v$) in Fig.5, showing the methanol electrooxidation on Pt/Ti is an irreversible electrode process. The plot slope is 0.023. The plot slope between E_p and $\ln v$ is

$$K = \frac{RT}{2\alpha nF} \tag{1}$$

Where α is the anodic transfer coefficient and n is the number of transferred electrons. The value of αn is calculated as 0.56. The number of transferred electrons is associated with the overall oxidation process and given as 1.3 [24]. So the α is 0.43.

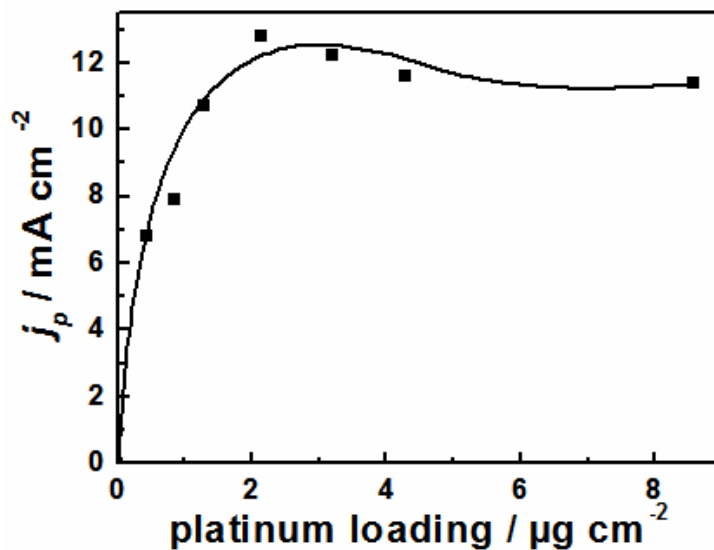


Figure 4. The relation between peak current density (j_p) of methanol oxidation and platinum loading

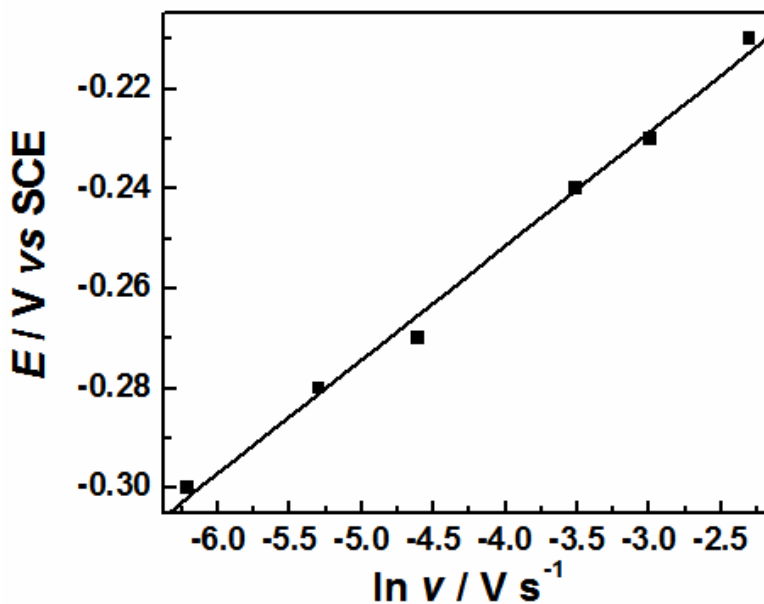


Figure 5. The relation between the peak potential of methanol oxidation (E_p) and natural logarithm of sweep rate ($\ln v$)

The relation between the peak current density (j_p) and $v^{1/2}$ is shown in Fig.6. A linear relationship is obtained, showing the methanol oxidation reaction on Pt/Ti in alkaline media is controlled by methanol diffusion [25]. The diffusion coefficient (D) of methanol can be calculated according to the following equation [26]:

$$j_p = 0.4958 \times 10^{-3} nFC_{\text{methanol}} \left(\frac{\alpha n F}{RT} \right)^{1/2} D^{1/2} v^{1/2} \quad (2)$$

The average value of D is calculated as $6.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (298 K).

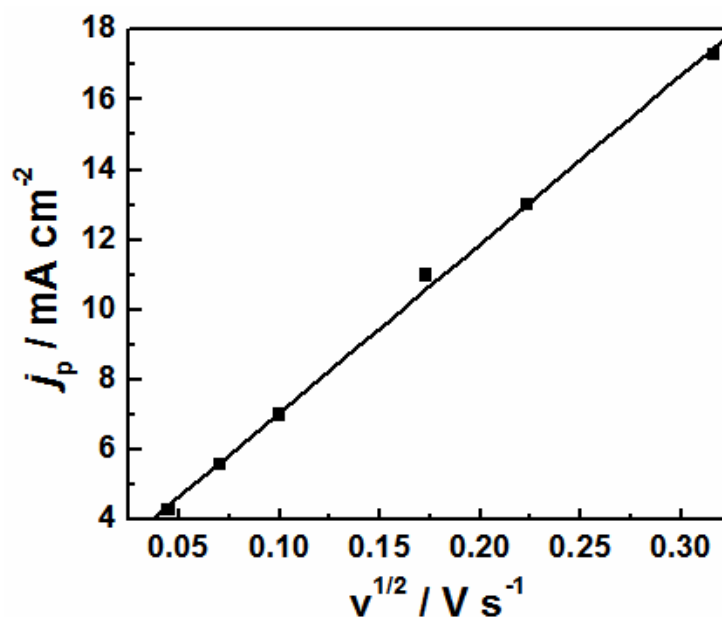


Figure 6. The relation between the peak current density (j_p) and $v^{1/2}$

4. CONCLUSIONS

Pt nanoparticles dispersed on Ti were successfully prepared by the magnetron sputtering method used in this study. The results show that the platinum loading is very low and the catalyst shows a very high activity for methanol oxidation in alkaline media. The electrochemical oxidation performance increases with the increasing platinum loading on Ti. The best platinum loading was found at $2.14 \mu\text{g cm}^{-2}$. A linear relation is obtained from the plot for the peak potential of methanol oxidation and natural logarithm of sweep rate, showing the methanol electrooxidation on Pt/Ti is an irreversible electrode process. A linear relationship is obtained from the plot for the relation between the peak current density (j_p) and $v^{1/2}$, showing the methanol oxidation reaction on Pt/Ti in alkaline media is controlled by methanol diffusion. The anodic transfer coefficient (α) is 0.43. The diffusion coefficient (D) of methanol is calculated as $6.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (298 K) when the concentration of KOH

and methanol is both 1.0 M. The Pt nanoparticles dispersed well on Ti in this study possess good electrocatalytic properties for methanol electrooxidation in alkaline media and may be a great potential in methanol sensor and direct methanol fuel cells.

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