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Effect of Deposition Potential on the Structure, Electrocatalytic Activity and Stability of Pt Films for Methanol Oxidation

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The effect of deposition potential on the structure and electrocatalytic properties of Pt films electrodeposited on Ti was investigated. By controlling a constant deposition potential either at -0.15 V, -0.20 V, -0.25 V or -0.30 V, various shapes of Pt structures such as cauliflower-like, durian-like, needle-like and worm-like can be observed by FESEM. The face-centered cubic (fcc) structure of all the prepared Pt films was confirmed by XRD. The highest specific electrochemically active surface area (ECSA) was obtained for Pt films with durian-like shape prepared at -0.2 V with 6.0 m² g⁻¹ which gave the best catalytic activity and stability for methanol oxidation in alkaline medium.

Keywords: Pt films, electrodeposition, methanol oxidation, electrocatalytic activity

1. INTRODUCTION

The methanol oxidation reaction (MOR) on anode surface has been extensively studied in recent years due to methanol is the simplest alcohol and its electrochemical reaction kinetics is faster as compared to other alcohol fuel cells [1]. However, the difficulty in finding the anode catalyst with high activity for methanol oxidation is a significant challenge in the development of Direct Methanol Fuel Cell (DMFC).

Platinum (Pt) is the most known excellent catalyst due to its ability to catalyse specific chemical reactions [2, 3]. Unfortunately, the limited resources and high price of Pt have become major problems in making the Pt electrodes as an anode for commercialization [4, 5]. Because of that reason, deposition of Pt onto a conducting substrate such as Ti could be a good attempt to minimize the cost of using solid Pt. In order to achieve a high catalytic activity towards methanol oxidation, a highly active Pt with high surface area needs to be synthesized. The control of shape or morphology of the deposited Pt is extensively studied by many researchers since the catalytic activity of the catalyst was found to be

strongly related with the facets terminated surface of the particles [6, 7]. Meanwhile, the stability of Pt during methanol oxidation can be affected by the formation of carbonaceous species (ie: CO). [8, 9]. It was found that the catalytic dissociation of the methanol at electrode surface is a topic of longstanding interest in electrochemistry [10]

Recently, a variety of structures of Pt centres such as polyhedral [7, 11], porous nanostructures [12], dendritic [13, 14] and nanowires [15] have been prepared using chemical and electrochemical methods. However, the complicated preparation process of the chemical method was the major problem in preparing the Pt films with high surface area. Thus, the electrodeposition technique is found to be more convenient and promising method since the electrodeposition condition can be manipulated in order to produce high surface area of Pt.

The aim of this project is to produce high catalytic and stability of Pt films electrodeposited on Ti for MOR in alkaline solution. Thus, in this paper, the effect of the deposition potential on the formation of Pt films catalyst on Ti was studied. The catalytic activity and the stability of the prepared Pt electrodes towards methanol oxidation in alkaline medium were also investigated.

2. EXPERIMENTAL

2.1. Chemicals

H₂PtCl₆.5H₂O, CuSO₄, CH₃OH, H₂SO₄, KOH were obtained from Chemical Reagent Company of Shanghai (Shanghai, China). All chemicals used are of analytical grade. Doubly distilled water was used in the preparation of all solutions.

2.2. Electrodeposition of Pt on Ti surface

Prior to each experiment, the Ti substrate was etched in HCl at 80 °C for 15 min in order to remove oxide layer of Ti and to increase the roughness of the Ti surface for better adhesion of Pt films on the Ti surface. A one-compartment three-electrode cell system was used consisting of the etched Ti substrate as working electrode, a Pt rod as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. A solution containing 0.01 M hydrogen hexachloroplatinate (IV) hydrate in 0.3 M H₂SO₄ was used for the electrochemical deposition of Pt. The reduction of Pt (IV) to Pt was carried out using chronoamperometric technique by applying different potentials such as at -0.15, -0.20, -0.25 and -0.30 V for 30 min. All potentials in the present study were given verses SCE reference electrode.

2.3. Characterization

Morphology of the Pt films prepared at different potentials was observed by Field-emission Scanning Electron Microscope (FESEM, Carl Zeiss SMT Supra 40VP). Crystal structures of the Pt/Ti electrodeposited at different potentials were characterized by X-ray diffraction (XRD, shimadzu XRD-6100 diifractometer). All experiments were carried out at room temperature.

2.4. Electrochemical measurements

A conventional three-electrode system was used throughout this work which consisted of a Pt/Ti prepared at various deposition potentials (Working electrode), a Pt rod (auxiliary electrode) and a saturated calomel electrode (reference electrode). The ECSA was calculated from the charge associated with the hydrogen desorption on Pt/Ti in 0.5 M KOH. The electrocatalytic activity for the methanol oxidation reaction was performed in a 0.5 M KOH containing 1.0 M CH₃OH at a scan rate of 50 mVs^{-1} .

3. RESULTS AND DISCUSSION



Figure 1. Voltammogram of etched Ti substrate in 0.3 M H₂SO₄ containing 0.01 M H₂PtCl₆.6H₂O at a scan rate of 50 mV s⁻¹. The arrows indicate the scanning direction.

Linear sweep voltammetry (LSV) was performed in a range of +0.20 V to -0.40 V vs SCE for etched Ti in 0.3 M H₂SO₄ containing 0.01 M H₂PtCl₆.6H₂O solutions at scanning rate of 50 mVs⁻¹. The reduction potential of Pt centres on the Ti substrate can be determined based on the voltammogram as in Fig. 1. From the voltammogram, it was observed that the reduction of electroactive species (ie: Pt⁴⁺ ions) in the bath solution started to occur at about -0.10 V. At this potential, the electrodeposition of Pt centres was controlled by electron transfer process. Then, the current density slowly increased until potential -0.20 V indicating the formation of more Pt centres on Ti surface which correspond to a mixed control process. Later, a plateau region between -0.25 V to -0.30 V indicates the deposition of Pt centres on the Ti surface was controlled by mass transport process. The number of Pt centres increases with more negative deposition potentials applied. The scanning potential was stopped at -0.35 V due to the evolution of hydrogen. A lot of bubbles can be seen on the Ti surface if potential is applied more than -0.35 V. It can be concluded that the desirable potential range for electrodeposition of Pt on the etched Ti surface is between -0.10 V to -0.30 V in order to avoid the interference of hydrogen bubbles. Thus, four different potentials (i.e.: -0.15 V, -0.20 V, -0.25 V and -0.30 V) between the range were used to study the effect of deposition potentials on the formation of Pt films catalyst in terms of its surface properties and catalytic activity.



Figure 2. Chronoamperometric curves of electrodeposition process of Pt films on etched Ti substrate from $0.3M H_2SO_4$ containing $0.01 M H_2PtCl_6.6H_2O$ at different constant potential of -0.15V, -0.20 V, -0.25 V and -0.3V vs SCE for 30 min.

Fig. 2 shows the deposition of Pt films on Ti substrate at various deposition potentials via chronoamperometry for 1800 s. At the beginning of 30 s, it was observed that a non-faradaic process involves which known as double layer charging which the Pt ions were arranged at the electrode surface [16, 17]. A stable faradaic current was steadily flowing after 30 s resulting the growth of the Pt nuclei onto the Ti substrate. From the chronoamperometric curves, it was found that the current density increased with increasing deposition potential applied.





Figure 3. FESEM images of Pt films at 1000 X magnification deposited electrochemically at (a) -0.15 V (b) -0.20 (c) -0.25 V and (d) -0.30 V vs SCE for 30 min from 0.01 M H₂PtCl₆.6H₂O + 0.3 M H₂SO₄ solution. Magnification at 5000 X for (a'), (b'), (c'), (d'); Inset: 25000 X magnification.

FESEM images as in Fig. 3 display the different morphologies of Pt films formed on Ti deposited using various deposition potentials. The amount of deposited Pt centres on Ti surface was obviously depended on the deposition potential applied. It was due to various deposition charge densities were passed during deposition process at a fixed deposition time. From the FESEM images, it can be suggested that deposition potential has significantly affected the nucleation rates of Pt centres on Ti surface resulting in production of various morphologies of Pt structures.

At -0.15 V with low deposition rate, the current limits the nucleation of the Pt centres on the Ti surface leading to the formation of isolated and agglomerated round structure of cauliflower-like distributed on the Ti surface as shown in Fig 3 (a and a'). It can be seen that a low surface coverage of

Pt with cauliflower-like formed on Ti surface due to a very slow nucleation process of Pt nuclei on Ti at the very positive potential. Then, the Pt structure was changed to durian-like as can be seen in Fig. 3 (b and b') when deposition potential was applied at -0.20 V. As the deposition potential is applied at more negative potential (ie: -0.25 V), the reduction of Pt ions was accelerated resulting in the formation of needle-like Pt structure as shown in Fig. 3 (c and c'). The needle-like Pt structure looks more dense, compact and quite homogeneous than Pt films prepared at more positive potentials. Fig. 3 (d and d') presents the Pt films with worm-like structure deposited at -0.30 V which the Pt centres are arranged closely to each other with more dense and compact on the Ti surface as compared to other films. It can be concluded that deposition potential applied has strongly affected both the nucleation and growth rates of Pt on the Ti surface. This indirectly led to the formation of various morphologies and shapes of Pt centres on the Ti surface.



Figure 4. XRD patterns of Pt films deposited on Ti substrate at different deposition potentials of -0.15V, -0.20 V, -0.25 V and -0.3V vs SCE for 30 min.

The crystalline structures of the Pt films prepared at various deposition potentials were examined by XRD as shown in Fig. 4. Four peaks appeared at 40.1° , 46.6° , 67.9° and 81.5° are assigned to [111], [200], [220], and [311] crystalline planes, respectively. The XRD results suggest that all the prepared Pt films possess a face-centered cubic (fcc) structure. However, an interesting result from the XRD patterns are the appearance of two peaks at 44.7° and 65.0° for the Pt films prepared at -0.20 V and -0.25 V. These are possibly attributed to the morphologies of Pt films prepared at -0.20 V and -0.25 V which possess spiky structure as can be seen in Fig. 3 (b and b') and Fig. 3 (c and c'), respectively.

The catalytic properties of the Pt films prepared at various different potentials were examined using cyclic voltammetry in alkaline medium. The cyclic voltammetry was scanned from -0.90 V to +0.20 V and back to -0.90 V at 50 mV s⁻¹. The cyclic voltammograms as shown in Fig. 5 can be divided into three distinct potential regions which are the hydrogen adsorption/desorption region (-0.9

V to -0.55 V), the double layer region (-0.55 V to -0.35 V) and the formation of surface Pt oxide /reduction of PtO to Pt (0.1 V to -0.5 V).



Figure 5. Cyclic voltammograms of Pt films deposited on Ti substrate for 30 min at different deposition potentials (ie: -0.15V, -0.20 V, -0.25 V and -0.3V vs SCE) in 0.5 M KOH, scan rate: 50 mV s^{-1} .

The results show that the Pt films prepared at -0.20 V produced the highest current densities of hydrogen adsorption or desorption and also the formation of Pt oxide or reduction of PtO. Moreover, interestingly, the reduction peak of PtO to Pt was obviously shifted to more positive potentials indicating the weaker adsorption of oxide species at the Pt films prepared at -0.20 potential compared to other Pt films.

The electrochemically active surface area (ECSA) of all Pt films can be calculated using hydrogen adsorption or desorption peaks from the cyclic voltammograms in Fig. 5. ECSA can be expressed as equation 1 [18].

$$ECSA = \frac{Q_H}{Q_{mono} \ x \ L_{Pt}} \tag{1}$$

Where Q_H is the integrated hydrogen adsorption or desorption charge (μ C cm⁻²), Q_{mono} the hydrogen adsorption or desorption charge on a smooth platinum electrode (210 μ C cm⁻²) and L_{pt} is the Pt loading (μ g cm⁻²). In this experiment, the Pt films electrodeposited on Ti substrates at various deposition potentials have platinum loadings ranging from 857 to 2075 μ g cm⁻². Table 1 summarizes the specific ECSA of each Pt films obtained from various deposition potentials. The results show that the specific ECSA for Pt films prepared at -0.20 V was the highest with 6.0 m² g⁻¹ meanwhile the lowest ECSA belongs to Pt films prepared at -0.15 V (0.6 m² g⁻¹). Based on the literature, it was found that higher ECSA values have been reported by Tripkovic et al. [19] and Doan et al. [20] which were 10.8 m² g⁻¹ and 8.2 m² g⁻¹, respectively for hydrogen adsorption/desorption on Pt films coated on

glassy carbon. The ECSA can be increased by increasing the Pt loading on the substrate. The surface area of the substrate also can influence the specific Pt surface area as highlighted by Bennett et al. [21].

Table 1. Deposition charge, Pt mass per geometrical area of the electrode using different deposition potentials (ie: -0.15 V, -0.20 V, -0.25 V and -0.30 V) and corresponding electrochemical active surface area in 0.5 M KOH for hydrogen desorption.

Potentials (V)	Q _{passed} (C cm ⁻²)	L _{pt} (µg cm ⁻²)	ECSA (m ² g ⁻¹)
-0.15	1.7	857	0.6
-0.20	2.2	1109	6.0
-0.25	3.0	1519	2.0
-0.30	4.1	2075	3.4

From the table, it was also found that the total amount of deposition charge passed at -0.30 V was 2.4 higher than the lowest deposition charge at -0.15 V. These results demonstrate that, even at deposition potentials of -0.20 V was applied with the deposition charge was only 2.20 C cm⁻² (Pt loadings: 1109 μ g cm⁻²), it still produced the best catalytic response for electrocatalytic activity than deposition Pt films at -0.25 V and -0.30 V with deposition charge were 3.0 C cm⁻² (Pt loadings: 1519 μ g cm⁻²) and 4.1 C cm⁻² (Pt loadings: 2075 μ g cm⁻²) respectively. This means that even though the platinum loading formed on Ti by applying deposition potential of -0.20 V was lower than higher applied deposition potentials but the Pt catalyst showed higher electrocatalytic activities in alkaline medium.



Figure 6. Cyclic voltammograms of methanol oxidation on Pt films deposited on Ti substrate for 30 min at different deposition potentials (ie: -0.15 V, -0.20 V, -0.25 V and -0.3V vs SCE) in 0.5 M KOH containing 1.0 M CH₃OH, scan rate: 50 mV s⁻¹.

The maximum specific ECSA was achieved for Pt films prepared at -0.2 V when deposition charge density of 2.2 C cm⁻² was passed. This shows that Pt films with durian-like possessed the

highest ECSA. Thus, these results suggest that the amount of Pt during deposition is not the most important factor in producing the best catalytic materials. But, the most essential is to synthesize high surface area of Pt films with high ECSA which can give the best electrocatalytic activity for electrochemical reactions.

The catalytic activities of the prepared Pt films for methanol oxidation in 0.5 M KOH were also investigated using cyclic voltammetry. Fig. 6 shows the cyclic voltammograms for methanol oxidation in 0.5 M KOH at all Pt films scanned from -0.90 V to +0 V and back to -0.90 V at 50 mV s⁻¹. Each cyclic voltammogram has two oxidation peaks which are current density peak for forward scan (I_f) and current density peak for backward scan (I_b). According to Beden et al. [22] and Praburam et al. [23], I_f is associated with the CH₃OH oxidation, meanwhile for I_b is related to the removal of the carbonaceous intermediate. From these cyclic voltammograms, the peak current ratio between I_f and I_b (I_f/I_b) can be used to describe the tolerance of catalyst to accumulation of carbonaceous species (ie: poisoning species) as reported in the literatures [24-26]. The higher I_f/I_b value suggested that the more effective removal of the poisoning species (ie: CO) from the Pt catalyst surface [27]. Table 2 summarizes the methanol oxidation reaction (MOR) at Pt/Ti. The higher values of I_f/I_b of Pt films deposited at -0.20 V and -0.30 V showed better catalyst tolerance towards poisoning species than other Pt films. Both Pt films deposited on Ti have higher I_f/I_b values for methanol oxidation reaction as compared to other types of Pt electrodes as reported by researchers [28-30] as shown in table 3.

Table 2. Comparison of electrochemical performance of methanol oxidation on Pt films deposited at different deposition potentials (ie: -0.15 V, -0.20 V, -0.25 V and -0.30 V) in 0.5 M KOH containing 1.0 M CH₃OH.

Potentials (V)	$\mathbf{E_{f}}$	$\mathbf{I_{f}}$	$\mathbf{E}_{\mathbf{b}}$	$\mathbf{I_b}$	Ratio Ie/Ib
-0.15	-0.35	43.52	-0.36	25.41	1.71
-0.20	-0.29	110.82	-0.41	40.52	2.73
-0.25	-0.34	38.49	-0.39	21.87	1.76
-0.30	-0.25	70.76	-0.34	25.91	2.73

 E_{f} : potential peak for forward scan; I_{f} : current density peak for forward scan; E_{b} : potential peak for backward scan; I_{b} : current density for backward scan.

Table 3. Comparison of I_f/I_b values of methanol oxidation reaction at different Pt electrodes.

Electrodes	I_f/I_b	References
Polycrystalline Pt	2.46	[28]
PtPd/Nafion	2.40	[29]
Pure Pt	2.40	[30]
Pt/Ti	2.73	In this work

The stability of all Pt films for methanol oxidation in 0.5 M KOH was investigated using chronoamperometry. The chronoamperometry data were recorded for the prepared Pt films in 0.5 M KOH containing 1.0 M CH₃OH at -0.5 V for 3600 s. Fig. 7 shows the Pt films prepared at -0.15, -0.20,

-0.25 and -0.30 V have oxidation current densities of 0.11, 1.50, 0.21 and 1.16 mA mg⁻¹, respectively. These results demonstrate that the Pt films prepared at -0.20 V with durian-like structure has the highest electrocatalytic stability as compared to other Pt films. It can be concluded that a slow decay of current densities over time for durian-like Pt indicating that it has good stability and fast removal of the carbonaceous intermediates from the Pt surfaces.



Figure 7. Chronoamperometric curves at -0.5 V on Pt films deposited on Ti substrate at different deposition potentials (ie: -0.15V, -0.20 V, -0.25 V and -0.3V vs SCE) in 0.5 M KOH containing 1.0 M CH₃OH for 3600 s.

4. CONCLUSION

The applied deposition potential during electrodeposition has significantly affected the formation of Pt films on Ti surface. Various Pt structures (ie: cauliflower-like, durian-like, needle-like or worm-like) can be produced by applying a specific constant deposition potential. Durian-like Pt films prepared at -0.20 V has the highest ECSA which gives the most excellent electrocatalytic activities in alkaline solution especially for methanol oxidation reaction (MOR). Compared to other prepared Pt films the durian-like Pt films showed better stability toward methanol oxidation reaction after 3600 s.

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References

1. S. Y. Shen, T. S. Zhao, J. B. Xu, Y. S. Li, J. Power Sources., 195 (2010) 1001.

- 2. Z. Peng, H. yang, Nano Today., 4 (2009) 143.
- 3. S. A. Evans, J. G. Terry, N. O. V. Plank, A. J. Walton, L. M. Keane, C. J. Campbell, P. Ghazal, J. S. Beattie, T. J. Su, J. Crain, *Electrochem. Commun.*, 7 (2005) 125.
- 4. M. Wang, X. Wang, J. Li, L. Liu, J. Mater. Chem. A., 1 (2013) 8127.
- 5. H. Wang, M. Zhang, F. Cheng, C. Xu, Int. J. Electrochem. Sci., 3 (2008) 946.
- 6. Z. Peng, H. You, J. Wu, H. Yang, Nano letters., 10 (2010) 1492.
- 7. N. Tian, Z. Y. Zhou, S. G. Sun, Y. Ding, Z. L. Wang, science., 316 (2007) 732.
- 8. H. Wang, S. Ji, W. Wang, V. Linkov, S. Pasupathi, R. Wang, Int. J. Electrochem Sci., 7 (2012) 3390.
- 9. L. C. Ordonez, P. Roquero, J. Ramirez, P. J. Sebastian, Int. J. Electrochem. Sci, 11 (2016) 5364.
- 10. B. Beden, J. M. Leger, C. Lamy, J. O. M. Bockris, B. E. Conway, R. E. White, Modern aspects of electrochemistry, Plenum Publishers (1992) Kluwer Adcademic, New York.
- 11. H. Song, F. Kim, S. Connor, G. A. Somorjai, P. Yang, J. Phys. Chem. B., 109 (2005) 188.
- 12. G. S. Attard, P. N. Bartlett, N. R. B. Coleman, J. M. Elliott, J. R. Owen, J. H. Wang, *Science.*, 278 (1997) 838.
- 13. X. Teng, H. Yang, Nano letters., 5 (2005) 885.
- 14. X. Zhong, Y. Feng, I. Lieberwirth, W. Knoll, Chem. mater., 18 (2006) 2468.
- 15. D. Fenske, H. Borchert, J. Kehres, R. Kroger, J. Parisi, J. Kolny-olesiak, *Langmuir.*, 24 (2008) 9011.
- 16. D. Pletcher, *A first course in electrode processes*, Royal Society of Chemistry (2009) Cambridge, UK.
- 17. B. Scharifker, G. Hills, Electrochim. Acta., 28 (1983) 879.
- 18. M. Sogaard, M. Odgaard, E. M. Skou, Solid State Ionics., 145 (2001) 31.
- 19. A. V. Tripkovic, K. D. J. Popovic, J. D. Lovic, V. M. Jovanovic, A. Kowal, J. Electroanal. Chem., 572 (2004) 119.
- 20. N. Doan, T. Sundqvist, P. Hiekkataipale, J. Korhonen, T. Kallio, J. Ruokolainen, K. Kontturi, C. Johans, *Int. J. Electrochem. Sci.*, 10 (2015) 2535.
- 21. J. A. Bennett, Y. Show, S. Wang, G. M. Swain, J. Electrochem. Soc., 152 (2005) 184.
- 22. B. Beden, F. Kadirgan, C. Lamy, J. M. Leger, J. Electroanal. Chem. and Interfacial Electrochem., 142 (1982) 171.
- 23. J. Prabhuram, R. Manoharan, J. Power Sources., 74 (1998) 54.
- 24. M. W. Xu, G. Y. Gao, W. J. Zhou, K. F. Zhang, H. L. Li, J. Power Sources., 175 (2008) 217.
- 25. J. Huang, Z. Liu, C. He, L. M. Gan, J. Phys. Chem. B., 109 (2005) 16644.
- 26. L. Zhang, D. xia, Appl. surf. sci., 252 (2006) 2191.
- 27. L. Gao, L. Ding, L. Fan, Electrochim. Acta., 106 (2013) 159.
- 28. J. A. Vega, S. Smith, W. E. Mustain, J. Electrochem. Soc., 158 (2011) 349.
- 29. S. S. Shendage, J. M. Nagarkar, J. Chem. and Chem. Sci., 5 (2015) 99.
- 30. H. Jiang, B. Geng, L. Kuai, S. Wang, Chem. Commun., 47 (2011) 2447.

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