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Synthesis and Electrocatalytic Activity of Pt/Ni/Ti Electrocatalyst for Methanol Oxidation in Alkaline Medium

[1]A.M. Siti Norsafurah, [2]M. Yusairie, [3]J. Khairil Anuar

[1]Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.
[2]Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[3]Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

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ABSTRACT

A high active surface area of the Pt electrocatalyst coated on Ni/Ti surface (Pt/Ni/Ti) was successfully prepared by a two-step electrodeposition process. Initially, Ni underlayer was deposited on Ti substrate by cathodic deposition at a constant current density of -1.5 mAcm^{-2} and followed by cathodic deposition of Pt outer layer at a constant potential of -0.4 V on the Ni/Ti surface. The coatings were characterized by Field-emission scanning electron microscope (FESEM) for surface morphology and cyclic voltammetry for electrocatalytic activity and stability. The FESEM images showed 'hemispherical' centres of Ni, diameter 1µm, covering most of the Ti surface. The FESEM images of the Pt covered Ni showed worm-like fibrils of Pt again covering most of Ni surface. Cyclic voltammogram of hydrogen desorption indicated the Pt/Ni/Ti electrocatalyst had a higher active surface area than Pt/Ti electrocatalyst with surface roughness of 132 cm^2 Pt cm^{-2} and 99 cm^2 Pt cm^{-2}, respectively. It was found that the catalytic activity of Pt/Ni/Ti electrocatalyst for methanol oxidation was greater than Pt/Ti electrocatalyst due to its higher active surface area. A higher of current density peak for methanol oxidation on the Pt/Ni/Ti demonstrates that this electrode could be a good electrocatalyst. Moreover, good stability of Pt/Ni/Ti was observed.

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INTRODUCTION

Direct methanol fuel cell (DMFC) is a device that converts chemical energy into electrical energy by using methanol as fuel. Many studies have contributed to the development of DMFC, primarily on the fabrication of the anode electrocatalyst (Goodenough *et al.*, 1988; Rolison *et al.*, 1999). In DMFC, the type of electrode material and technique of electrode preparation are highly important parameters to produce a highly efficient electrocatalyst. Typically, a higher electrocatalytic activity for methanol oxidation on electrode surface is clearly arisen from a higher surface area of the catalytic coatings on the supporting material. Moreover, the catalysts alloy composition and type of method used play vital roles toward contribution of the shape and size of the catalyst particles on supporting material. These activities contribute to the very critical for designing the active surface and efficient electrocatalyst (Yang *et al.*, 2010; El-Shafei *et al.*, 2004).

Platinum is a well-known excellent catalyst because of its relative inertness, highly active for methanol adsorption and dehydration (Page *et al.*, 2000) and its ability to catalyse specific chemical reaction (Evans *et al.*, 2005). These properties have promoted the use of Pt as an electrode in the fuel cell application. Nonetheless, it has been generally recognized that the inability of the bulk Pt to adsorb oxygen containing species during methanol oxidation. This has driven to the low activity of DMFC due to the formation of CO intermediates on the Pt surface (Mahapatra and Datta, 2011). A group of researchers have revealed that there is an ability of the second metal in Pt which is capable to produce OH$^-$ species to assist the conversion of CO to CO$_2$ during methanol oxidation (Page *et al.*, 2000; Anderson *et al.*, 1996). Various types of binary metals; PtFe, PtCo, PtCr, PtCu, PtNi (Yang *et al.*, 2010; Yang *et al.*, 2005; Venkateswara and Viswanathan, 2009; Hsieh and Lin, 2009), ternary metals; PtRuOs, PtRuRh (Gurau *et al.*, 1998; Choi *et al.*, 2004) and core shell; AuPt (Zeng *et al.*, 2006) that have been introduced in past researches. All of these resulting electrodes have shown considerable promise for methanol oxidation in DMFC.

Corresponding Author: A.M. Siti Norsafurah, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.

The choice of cheaper Ni catalyst as a second material leads to the superior improvement on the reaction kinetics of anode in DMFC as well as the reduction of cost making the electrode to be more commercially viable. This paper aims at exploring the possibility of producing higher surface area of Pt coatings on Ni underlayer deposited earlier on Ti substrate using low cost of electrodeposition technique and examining its catalytic activity performance and stability for methanol oxidation in alkaline medium.

Experimental:

Chemicals:

CH_3OH, HCl, $H_2PtCl_6.5H_2O$, KOH, $NiSO_4.6H_2O$ of high purity were obtained from Merck. Ultrapure water (Milli-Q) was used in the preparation of all solutions.

Pre-treatment of substrate:

Ti plate substrates were cut into small specimens (10 mm x 10 mm). Prior to electrodeposition, Ti substrates were etched in 37% HCl at 80°C for 10 minutes in order to remove the oxide layer and to increase the roughness of the Ti surface for better adhesion of coatings with Ti substrate. After the etching process, etched Ti substrate was rinsed with distilled water and dried before further electrodeposition process.

Pt/Ni/Ti electrocatalyst preparation:

The electrodeposition of Ni and Pt on etched Ti was carried out immediately after etching process in order to minimise the reformation of TiO_2 film on Ti substrate. A conventional three-electrode system was employed for the electrodeposition which comprising of the etched Ti as working electrode, a Pt rod as counter electrode and a saturated calomel electrode as reference electrode. The electrodeposition of Ni coatings on etched Ti substrate was performed at a constant current density of $-1.5\ mAcm^{-2}$ for 400 s through cathodic reduction of 0.01 M KOH containing 0.05 M $NiSO_4.6H_2O$ solution using chronopotentiometry technique. Then, the electrodeposition of Pt was carried out on Ni underlayer coatings at a constant potential of -0.4 V for 1500 s in 0.01 M KOH containing $H_2PtCl_6.6H_2O$ solution. For comparison, the same procedure was followed for the preparation of the Pt coated Ti (Pt/Ti) and Ni coated Ti (Ni/Ti) electrodes. All electrodeposition processes were controlled by an Autolab Potentiostat (AUT302 FRA2).

Instrumentation:

Morphology of etched Ti substrate before and after deposition of Ni underlayer coatings and Pt coatings was observed by Field-emission scanning electron microscope (FESEM, Carl Zeiss SMT Supra 40VP). The electrochemical measurements (ie: catalytic performance and stability) were performed in a conventional three-electrode cell controlled by an Autolab Potentiostat (AUT302 FRA2) which Pt/Ni/Ti, Pt/Ti and Ni/Ti were used as a working electrode. All measurements were carried out at room temperature (25 ± 1°C).

RESULTS AND DISCUSSION

The surface morphology of electrodes:

Figure 1 displays the FESEM images of etched Ti, Ni/Ti, Pt/Ti and Pt/Ni/Ti electrodes at 10,000 x magnification. The Ti substrate needs to be etched in strong acid in order to improve the adhesion of either Ni coatings or Pt coatings on etched Ti due to the advantage of producing rough Ti surface as in Figure 1(a). Additionally, by removing oxide layer out of the Ti surface would make Ti more conducting due to the absence of TiO_2 film on Ti surface. Figure 1(b) shows the morphology of Ni coatings on etched Ti that the coatings made up of hemispherical centres of Ni with 1µm diameters and an equivalent thickness of ~ 0.2µm covering most of the Ti surface. The Pt coatings with round particles consisting of worm-like fibrils on both etched Ti and Ni/Ti are shown in Figure 1(c) and Figure 1(d), respectively. There is no significant difference between these morphologies since the same catalyst (Pt) and the same applied potential were used for the preparation of both electrodes. However, the morphology of Pt coatings on Ni/Ti electrode was more porous than that on etched Ti probably due to the difference of Ni underlayer surface as compared to etched Ti surface.

Figure 2 shows the cyclic voltammograms of the Pt/Ti and Pt/Ni/Ti electrodes with similar profile in 0.5 M KOH solution at a scan rate of $50\ mVs^{-1}$. There are five important peaks (a - e) need to be recognized in this cyclic voltammogram excluding the oxygen oxidation and reduction peaks at about 0.5 V and 0.3 V, respectively. On the positive going scan, peak (a) corresponds to the oxidation of weakly adsorbed hydrogen ($(a)H_w$)) and strongly adsorbed hydrogen ($(a)H_s$)) from the electrode surface at about -0.9 V and -0.78 V, respectively. It can be seen that higher potential is needed to oxidize the adsorbed strongly hydrogen than that of weakly hydrogen. Peak (b) can be observed at the potential of -0.65 V attributed to the adsorption of OH^- on the electrode surface. The passivation oxide film started to form on electrode surface at approximately -0.16V (peak (c)). On the negative going scan, a large peak (peak (d)) emerges at the potential of -0.5 V corresponds to the reduction of PtO to form clean surface of Pt. Peak (e) can be associated to the adsorption of hydrogen on Pt clean surface which is at about -0.83 V. Similar electrochemical behaviour of Pt electrodes has already been described in previous papers in alkaline medium (Yu *et al*., 2004; Manoharan and Prabhuram, 1998). The electrochemical reactions occurred on the Pt electrode surface are shown as follows:

Peak (a) Oxidation of adsorbed hydrogen : $Pt\text{-}H_{ads} + OH^- \longleftrightarrow Pt + H_2O + e^-$ (1)
Peak (b) Adsorption of OH^- : $Pt + OH^- \longleftrightarrow Pt\text{-}OH_{ads} + e^-$ (2)
Peak (c) Oxidation of Pt : $Pt\text{-}OH_{ads} + OH^- \longleftrightarrow Pt\text{-}O + H_2O + e^-$ (3)
Peak (d) Reduction of PtO : $Pt\text{-}O + H_2O + e^- \longleftrightarrow Pt + 2OH^-$ (4)
Peak (e) adsorption of hydrogen : $Pt + H_2O + e^- \longleftrightarrow Pt\text{-}H_{ads} + OH^-$ (5)

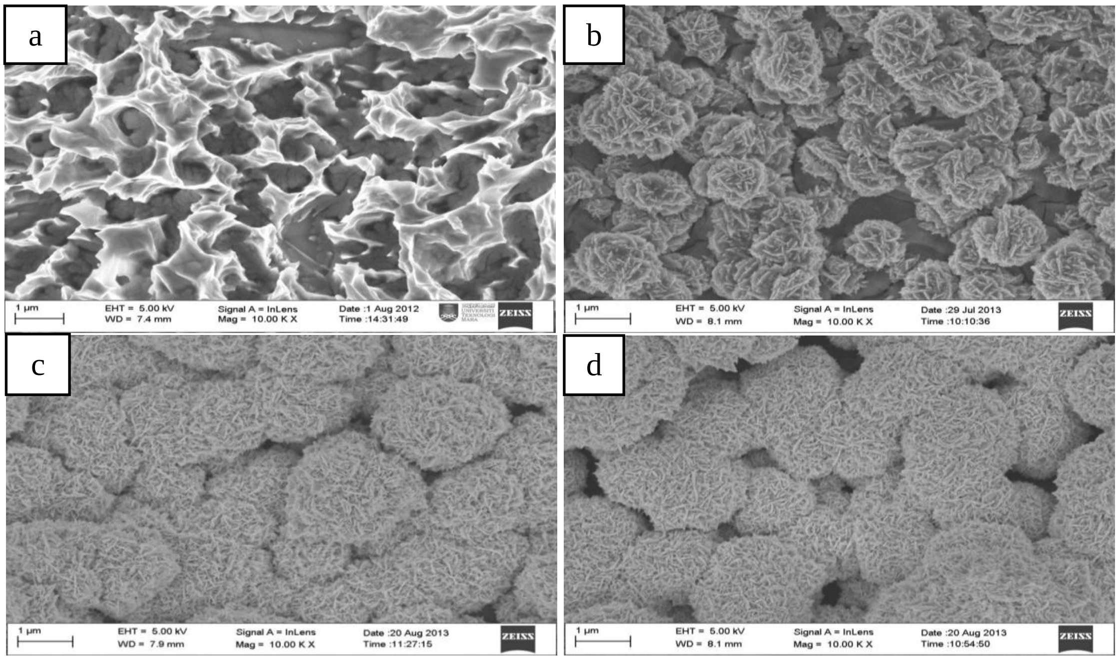

Fig. 1: FESEM images of (a) etched Ti and resulting electrode of (b) Ni/Ti (c) Pt/Ti and (d) Pt/Ni/Ti at 10,000x magnification.

Electrochemical properties of the prepared electrodes:

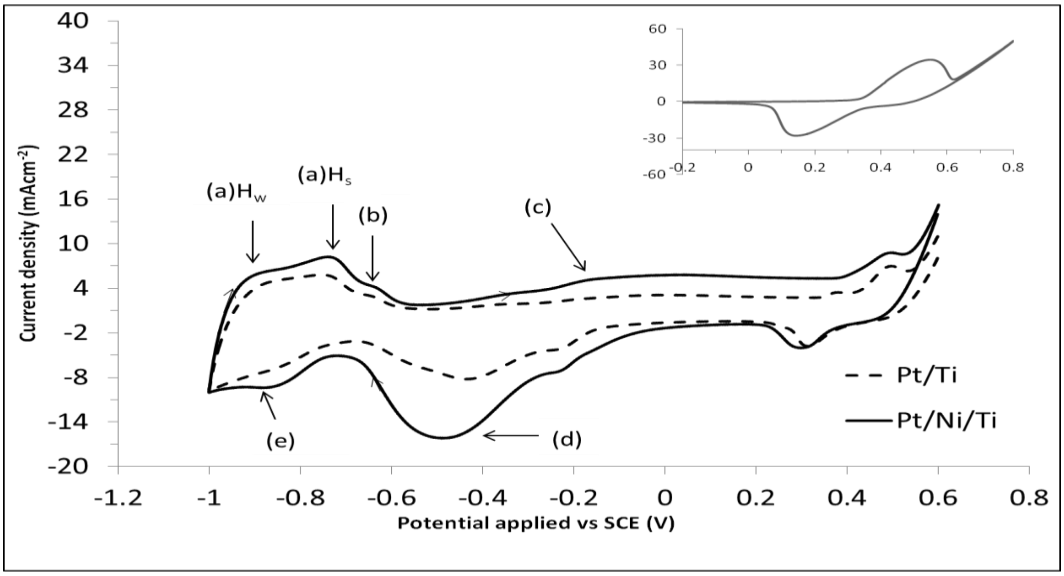

Fig. 2: Cyclic voltammograms of Pt/Ti and Pt/Ni/Ti electrodes in 0.5 M KOH at a scan rate of 50 mVs^{-1}. Inset is the cyclic voltammogram of Ni/Ti electrode in 0.5 M KOH at a scan rate of 50 mVs^{-1}.

The real surface area (A_r) of Pt/Ti and Pt/Ni/Ti electrodes could be calculated based on cyclic voltammograms produced by determining the total charge of hydrogen desorption area (Q_h) with the correction of double layer region as shown in Eq.6. The theoretical charge of 210 $\mu C\ cm^{-2}$ (Q_m) was considered during the measurement which corresponds to the desorption of monolayer hydrogen on smooth Pt (Biegler *et al*., 1971).

$$Q_h = \frac{I}{V_b}\int_{E_1}^{E_2} I.dE \qquad (6)$$

where I is the current density ($mAcm^{-2}$), dE is the potential (mV) and V_b is the scan rate (mVs^{-1}). Thus, the real surface area (A_r) and roughness factors (R_f) (cm^2 platinum cm^{-2}) of resulting electrodes can be calculated as follow (Watt-Smith *et al*., 2008):

$$A_r = \frac{Q_h}{Q_m} \qquad (7)$$

$$R_f = \frac{A_r}{A_g} \qquad (8)$$

where A_g is the geometric area of the prepared electrodes equivalent to the $1cm^2$. The measurement of the real surface area of the Pt coatings is obviously significant since the electrocatalytic activity of electrodes is highly affected by real surface area of the catalyst coatings (Gupta and Datta, 2005). The result shows that the surface roughness of the Pt/Ti and Pt/Ni/Ti are 99 cm^2 Pt cm^{-2} and 132 cm^2 Pt cm^{-2}, respectively. The calculation of roughness factor of resulting electrode has mostly been used by past researchers in order to determine the properties of the catalyst coatings (Page *et al*., 2000; Yu *et al*., 2004; Iwasita, 2002). The higher value of Pt/Ni/Ti surface roughness was evidenced by the higher current density of Pt/Ni/Ti in 0.5 M KOH solution as can be seen in Figure 2. Therefore, in order to investigate the electrochemical behaviour of Ni coatings in Pt/Ni/Ti electrocatalyst, the cyclic voltammetric measurement was carried out. The redox peak as shown in the inset of Figure 2 corresponds to the transformation of $Ni(OH)_2$ to NiOOH in alkaline medium which can be attributed to the following reactions (Fleischmann *et al*., 1971):

$$Ni(OH)_2 + OH^- \longleftrightarrow NiO(OH) + H_2O + e^- \qquad (9)$$

This cyclic voltammogram leads to the discovery of the higher real surface area of Ni coatings on Ti surface by referring to the higher charge density produced by Ni/Ti in alkaline medium at about 112 $mCcm^{-2}$ as compared well with the 2 $mCcm^{-2}$ for bulk Ni in alkaline medium (Li *et al*., 2013). According to this fact, it is important to stress that the higher real surface area of the Ni coatings in Pt/Ni/Ti electrode has contributed to the higher surface area of the Pt coating on Ni underlayer as shown in the schematic diagram of Figure 3 for better understanding.

Figure 4 demonstrates the same cyclic voltammetric profiles of Pt/Ti and Pt/Ni/Ti electrodes in 0.5 M KOH containing 1.0 M CH_3OH solution at a scan rate of 50 mVs^{-1}. On the positive going scan, the methanol started to oxidize at approximately -0.6 V, and then the current density was increased until about the potential of 0.1 V. As potential scan was extended to 0.6 V, the current density was drastically decreased due to the formation of passivation oxide film on the Pt surface. On the negative going scan, the oxidation peak was recognized at the potential of -0.3 V to -0.6 V which probably is associated to the; (i) reduction of the PtO, (ii) oxidation of some methanol on an available active surface of the Pt or (iii) oxidation of intermediates product such as CO, CHO species as reported by Manoharan and Prabhuram (2011) and Morin *et al*. (1990). The results show that the current density produced for methanol oxidation is higher over at all potential on Pt/Ni/Ti electrode than that on Pt coated Ti electrode without the presence of Ni underlayer (Pt/Ti electrode).

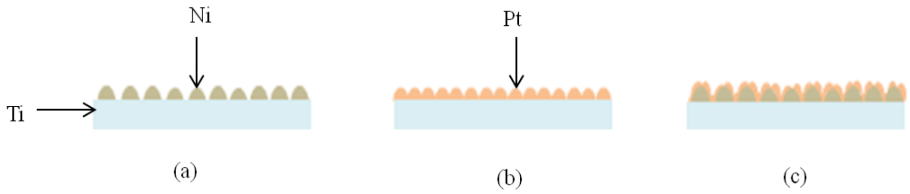

Fig. 3: Schematic diagram of prepared (a) Ni/Ti (b) Pt/Ti and (c) Pt/Ti/Ni electrodes.

In order to investigate the electrochemical behaviour of Ni coatings in Pt/Ni/Ti electrode towards methanol oxidation, cyclic voltammetric experiment of Ni/Ti in 0.5 M KOH containing 1.0 M CH_3OH was performed. The result shows that the methanol oxidation started to occur at approximately 0.35 V as can be seen in the Figure 5. For comparison, a lower current density was found at 0.35 V by referring to the cyclic voltammogram of Pt/Ni/Ti electrode in 0.5 M KOH containing 1.0 M CH_3OH solution as a result of the presence of oxide film on the Pt electrode surface. As scanning to more positive potential than 0.35 V, the oxygen evolution could be observed at this electrode surface which indicated by the sharp of the current density peak as seen in Figure 4. This fact confirming that the Ni coating in Pt/Ni/Ti is not involved in the redox mechanism for the methanol oxidation. This finding is the same with the methanol oxidation on PtNi alloy by Jiang *et al*. (2010). Therefore, it is important to point out that a higher electrocatalytic activity of Pt/Ni/Ti was strongly attributed to the higher real surface area of the Ni coatings which leads to the higher surface area of the Pt.

Electrooxidation of methanol on the prepared electrodes:

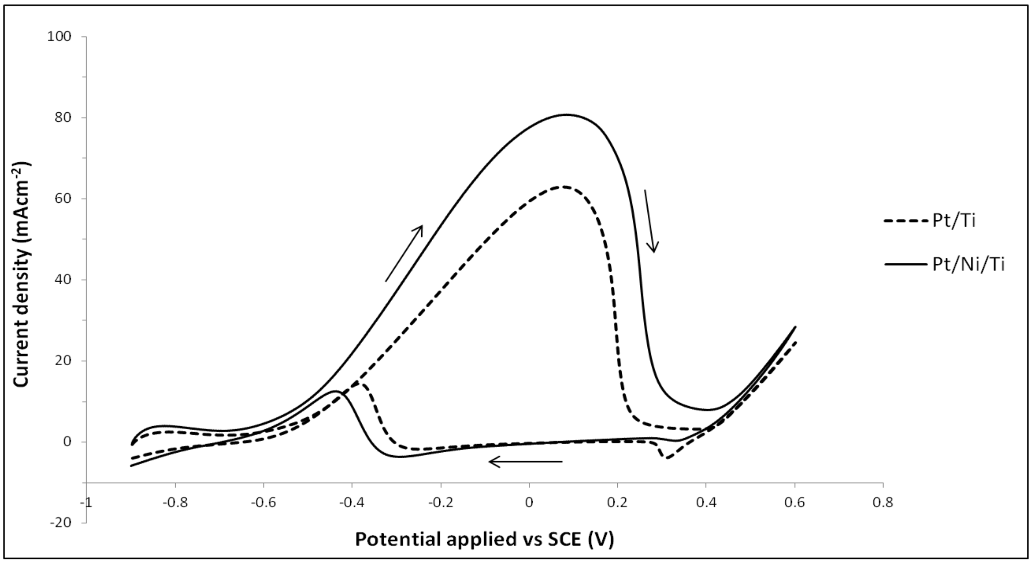

Fig. 4: Cyclic voltammograms of Pt/Ti and Pt/Ni/Ti electrodes in 0.5 M KOH containing 1.0 M CH_3OH solution at a scan rate of 50 mVs^{-1}.

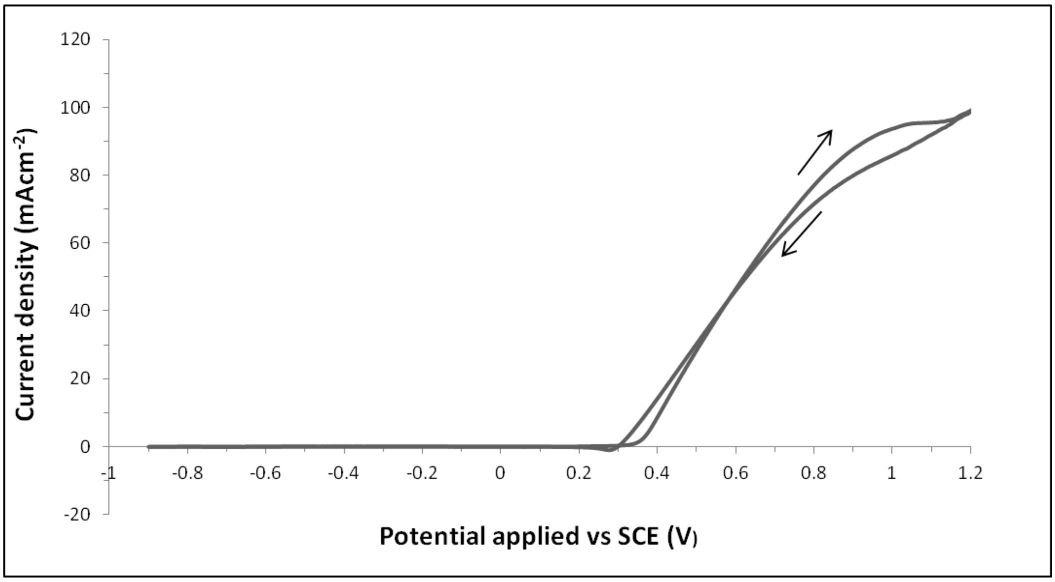

Fig. 5: Cyclic voltammogram of Ni/Ti electrode in 0.5 M KOH containing 1.0 M CH_3OH solution at a scan rate of 50 mVs^{-1}.

Stability of Pt/Ni/Ti electrode during electrooxidation of methanol:

The stability analysis on the prepared Pt/Ni/Ti catalyst was carried out using cyclic voltammetric technique by scanning a potential from -0.9 V to 0.6 V and then back to -0.9 V for 40 cycles in a scanning rate of 50 mVs^{-1} as in Figure 6. It can be clearly seen that the current density peak for methanol oxidation was slightly decreased from the 1st cycle to 40th cycle. Besides, on the negative going scan, there is no significant change in terms of current density peak and the potential. This result indicates that the Pt/Ni/Ti electrocatalyst has high stability for methanol oxidation in alkaline medium.

Conclusion:

The synthesis of Pt coated Ni/Ti substrate (i.e: Pt/Ni/Ti) has significantly improved the performance of electrocatalytic activity of Pt electrode as proven by a higher current density produced over at all potential for methanol oxidation than that on Pt without Ni underlayer (ie: Pt/Ti). The existence of a high real area of Ni underlayer in Pt/Ni/Ti electrode has obviously affected the real surface area of the Pt coatings on Ni which leads to the superior electrooxidation of the methanol. Additionally, the Pt/Ni/Ti electrocatalyst has shown satisfactory stability for methanol oxidation in alkaline medium.

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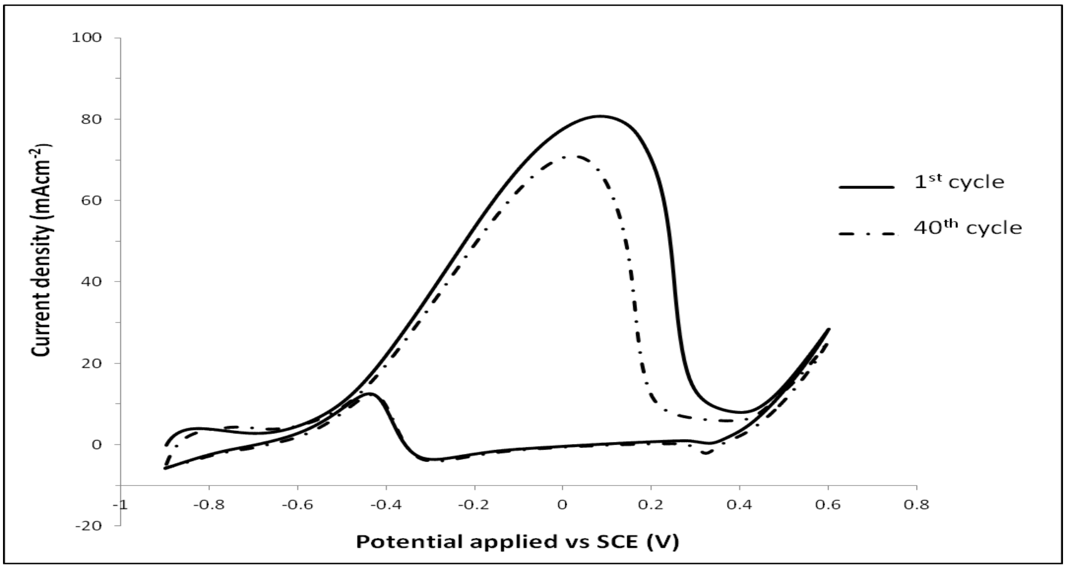

Fig. 6: Cyclic voltammograms of Pt/Ni/Ti electrode at 1st cycle and 40th cycle in 0.5 M KOH containing 1.0 M CH_3OH solution at a scan rate of 50 mVs^{-1}.

REFERENCES

Anderson, A.B., E. Grantscharova and S. Seong, 1996. Systematic theoretical study of alloys of platinum for enhanced methanol fuel cell performance. *Journal of the Electrochemical Society*, 143(6): 2075-2082.

Biegler, T., D. Ran and R. Woods, 1971. Limiting oxygen coverage on platinized platinum; relevance to determination of real platinum area by hydrogen adsorption. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 29(2): 269-277.

Choi, J.H., K.W. Park, I.S. Park, W.H. Nam and Y.E. Sung, 2004. Methanol electro-oxidation and direct methanol fuel cell using Pt/Rh and Pt/Ru/Rh alloy catalysts. *Electrochimica Acta*, 50(2): 787-790.

El-Shafei, A., R. Hoyer, L.A. Kibler and D.M. Kolb, 2004. Methanol oxidation on Ru-modified preferentially oriented Pt electrodes in acidic medium. *Journal of the Electrochemical Society*, 151(6): F141-F145.

Evans, S.A.G., 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, A.R. Mount, 2005. Electrodeposition of platinum metal on TiN thin films. *Electrochemistry Communications*, 7(2): 125-129.

Fleischmann, M., K. Korinek and D. Pletcher, 1971. The oxidation of organic compounds at a nickel anode in alkaline solution. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 31(1): 39-49.

Goodenough, J.B., A. Hamnett, B.J. Kennedy, R. Manoharan and S.A. Weeks, 1988. Methanol oxidation on unsupported and carbon supported Pt + Ru anodes. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 240(1-2): 133-145.

Gupta, S.S. and J. Datta, 2005. An investigation into the electro-oxidation of ethanol and 2-propanol for application in direct alcohol fuel cells (DAFCs). *Journal of Chemical Sciences*, 117(4): 337-344.

Gurau, B., R. Viswanathan, R. Liu, T.J. Lafrenz, K.L. Ley and E.S. Smotkin, 1998. Structural and Electrochemical Characterization of Binary, Ternary, and Quaternary Platinum Alloy Catalysts for Methanol Electro-oxidation 1. *The Journal of Physical Chemistry B*, 102(49): 9997-10003.

Hsieh, C.T. and C.Y. Lin, 2009. Deposition and Electrochemical Activity of Bimetallic Pt-M (M= Fe, Co, and Ni) Nanocatalysts on Carbon Nanotube Electrodes. *Chemical Engineering*, 17: 999-1004.

Iwasita, T., 2002. Electrocatalysis of methanol oxidation. *Electrochimica Acta*, 47(22-23): 3663-3674.

Jiang, Q., L. Jiang, H. Hou, J. Qi, S. Wang and G. Sun, 2010. Promoting effect of Ni in PtNi bimetallic electrocatalysts for the methanol oxidation reaction in alkaline media: experimental and density functional theory studies. *The Journal of Physical Chemistry C*, 114(46): 19714-19722.

Li, X., D. Pletcher, A.E. Russell, F.C. Walsh, R.G.A. Wills, S.F. Gorman, S.W.T. Price and S.J. Thompson, 2013. A novel bifunctional oxygen GDE for alkaline secondary batteries. *Electrochemistry Communications*, 34(0): 228-230.

Mahapatra, S. and J. Datta, 2011. Characterization of Pt-Pd/C electrocatalyst for methanol oxidation in alkaline medium. *International Journal of Electrochemistry*, 2011.

Manoharan, R. and J. Prabhuram, 2001. Possibilities of prevention of formation of poisoning species on direct methanol fuel cell anodes. *Journal of Power Sources*, 96(1): 220-225.

Morin, M.C., C. Lamy, J. M. Leger, J. L. Vasquez and A. Aldaz, 1990. Structural effects in electrocatalysis: oxidation of ethanol on platinum single crystal electrodes. Effect of pH. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 283(1): 287-302.

Rolison, D.R., P.L. Hagans, K.E. Swider and J.W. Long, 1999. Role of hydrous ruthenium oxide in Pt-Ru direct methanol fuel cell anode electrocatalysts: the importance of mixed electron/proton conductivity. *Langmuir*, 15(3): 774-779.

Page, T., R. Johnson, J. Hormes, S. Noding and B. Rambabu, 2000. A study of methanol electro-oxidation reactions in carbon membrane electrodes and structural properties of Pt alloy electro-catalysts by EXAFS. *Journal of Electroanalytical Chemistry*, 485(1): 34-41.

Prabhuram, J. and R. Manoharan, 1998. Investigation of methanol oxidation on unsupported platinum electrodes in strong alkali and strong acid. *Journal of Power Sources*, 74(1): 54-61.

Venkateswara Rao, C. and B. Viswanathan, 2009. ORR Activity and Direct Ethanol Fuel Cell Performance of Carbon-Supported Pt− M (M= Fe, Co, and Cr) Alloys Prepared by Polyol Reduction Method. *The Journal of Physical Chemistry C*, 113(43): 18907-18913.

Watt-Smith, M.J., J.M. Friedrich, S.P. Rigby, T.R. Ralph and F.C. Walsh, 2008. Determination of the electrochemically active surface area of Pt/C PEM fuel cell electrodes using different adsorbates. *Journal of Physics D: Applied Physics*, 41(17): 174004.

Yang, H., C. Coutanceau, J. Leger and N. Alonso-Vante, 2005. Methanol tolerant oxygen reduction on carbon-supported Pt–Ni alloy nanoparticles. *Journal of Electroanalytical Chemistry*, 576(2): 305-313.

Yang, H., L. Dai, D. Xu, J. Fang and S. Zou, 2010. Electrooxidation of methanol and formic acid on PtCu nanoparticles. *Electrochimica Acta*, 55(27): 8000-8004.

Yu, E.H., K. Scott, R.W. Reeve, L. Yang and R.G. Allen, 2004. Characterisation of platinised Ti mesh electrodes using electrochemical methods: methanol oxidation in sodium hydroxide solutions. *Electrochimica Acta*, 49(15): 2443-2452.

Zeng, J., J. Yang, J.Y. Lee and W. Zhou, 2006. Preparation of carbon-supported core-shell Au-Pt nanoparticles for methanol oxidation reaction: the promotional effect of the Au core. *The Journal of Physical Chemistry B*, 110(48): 24606-24611.