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Combinatorial investigation of Pt–Ru–M as anode electrocatalyst for direct methanol fuel cell

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Abstract

The addition of Au/TiO_2 and zeolites as active components to PtRu/C electrode in DMFC was investigated by using combinatorial high-throughput-screening test. Addition of Au/TiO_2 to PtRu/C electrode, especially in the ratio of PtRu/C: Au/TiO_2 9:1, 8:2, 7:3, were effective to improve the performance of direct methanol fuel cell. The electrochemical properties of the prepared electrodes were compared using cyclic voltammetry, impedance spectroscopy and a single cell performance test of a direct methanol fuel cell (DMFC). The adsorbed CO on Pt might be easily oxidized on the surface of Au/TiO_2 by interaction between PtRu/C and Au/TiO_2. The addition of the solid acid proton conducting materials (ZSM-5) on PtRu/C anode leads to the high temperature operation. The cell performance was maintained over the cell temperature 120 °C (maximum current density was 200 mA/cm^2 at 160 °C) by the addition of ZSM-5 as proton conducting materials.

Keywords: DMFCs; Au/TiO_2; ZSM-5; Platinum–ruthenium; CO poisoning

1. Introduction

A direct methanol fuel cell (DMFC) is one of the most attractive power sources for a variety of wide applications from vehicles to portable electrical equipment, due to the simplicity of the system and the adaptability of the liquid fuel (methanol). Methanol and water react to produce carbon dioxide, electrons and protons at anode (Eq. (1)). The electrons and protons, which are transferred via external circuit and electrolyte membrane, respectively, react with oxygen to produce water at cathode (Eq. (2)).

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (1)$$

$$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad (2)$$

Extensive studies on DMFCs have been carried out [1–3], mainly aiming at improving its poor performance compared with that of polymer electrolyte membrane fuel cells (PEMFCs) supplied with hydrogen. However, the main drawbacks limiting the practical realization of DMFC are the high over potential at the anode catalyst. It is well known that the electro-oxidation of methanol on platinum catalysts generates CO and various intermediates, which are poisons that adsorb on the active sites of catalysts [4–6]. In order to solve these problems, considerable efforts have been made in search for an alternative DMFC anode catalyst or improvement of the properties of the existing catalyst, especially for methanol electro-oxidation [7–9]. Making alloys with a second or third metal is a convenient way to modify the electrocatalytic properties of platinum in order to overcome the poisoning. To date, Pt–Ru alloy catalysts are still considered the most active catalysts to improve the effective polarization characteristics of methanol electro-oxidation for DMFCs. Ruthenium forms oxygenated species at lower potentials than platinum and its presence in the catalysts promotes the oxidation of CO to CO_2 by bifunctional mechanism [10–15]. However, there is a need to further reduce the poisoning of Pt and/or Pt–Ru catalysts to improve the performance of DMFC at the desired level.

Combinatorial chemistry, while most popularly used in the discovery of biochemicals and pharmaceuticals, has also been

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used to identify and optimize inorganic materials of complex compositions for many years [16,17]. The combinatorial method entails the synthesis of large libraries of compounds, in which composition or processing conditions are systematically varied, followed by screening for a particular property of interest. Recently, this approach has been used with some success in the discovery of a new electrocatalyst [18]. The more sophisticated methods for rapid screening of catalyst libraries have been developed by Chen et al. [19].

In our previous work, the influence of Nafion ionomer in DMFC anode was evaluated by combinatorial electrochemistry and electrochemical characterization method. From this work, we could identify that the most active composition was in the ratio of 63.6:36.4 of Pt/Ru (1:1, molar ratio) and Nafion. By optimization of the Nafion ionomer composition in DMFC anode, the CO oxidation environment was modified because of the acid characteristic of the Nafion ionomer, and a synergistic effect of the methanol electro-oxidation on Pt–Ru–Nafion electrocatalyst was verified [21]. When the Nafion ionomer was used as proton conducting material, we cannot increase the cell operation temperature over than 100 °C, because of the dehydration of Nafion membrane and Nafion ionomer in electrode. By the addition of solid acid proton conducting material (heteropoly acid) into the PtRu/C anode, we could improve the cell operation temperature up to 160 °C [22].

Table 1
Chemical properties of zeolites

Zeolite	SiO_2/Al_2O_3 (molar ratio)	Supplier
4A	1	Aldrich
13X	2.4	Aldrich
US-Y	5	Shokubai Kasei Co.
DAY	21	Degussa
ZSM-5	23.8	Zeolyst

To improve the DMFC performance, easy removal of CO and high temperature operation of system could be beneficial. Au/TiO_2 is known to be a catalyst which oxidize CO to CO_2 in air [20,23], and zeolites are traditional solid acid materials, which have proton-conducting ability [24], therefore in the present study, the addition of these materials to the platinum–ruthenium (Pt–Ru) alloy electrocatalyst were examined using a combinatorial electrochemisty method. Cyclic voltammetry, impedance spectroscopy and a direct methanol fuel cell performance test were used, to elucidate the electrochemical properties of the electrodes with different compositions.

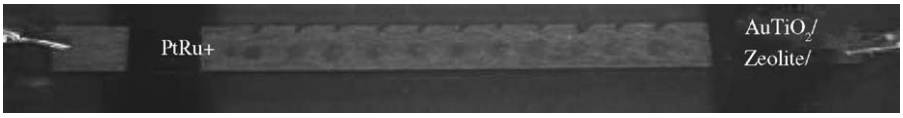


Fig. 1. One-dimensional array of Pt–Ru–M[Au/TiO_2 and Zeolite] for the high-throughput-screening test.

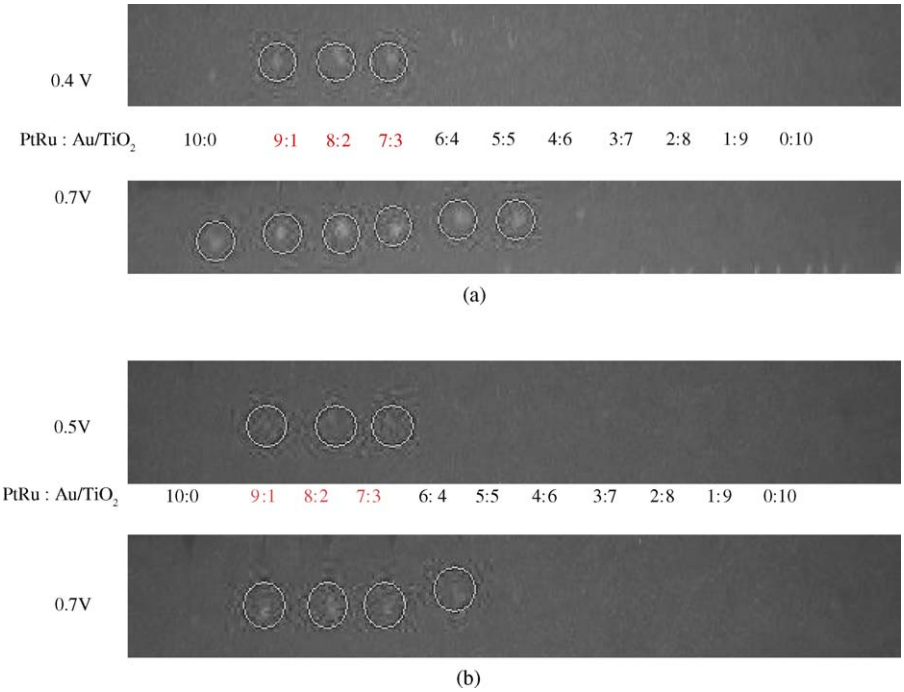


Fig. 2. Fluorescence images of PtRu/C–Au/TiO_2 electrocatalysts array with the potential sweep. (a) In CO-free 6 M methanol solution. (b) In CO saturated methanol solution.

2. Experimental

2.1. Factorial method

To prepare the Pt–Ru–Au/TiO_2 and Pt–Ru–Zeolite ternary electrodes, commercial electrocatalyst PtRu/C (E-tek, Pt:Ru:C = 40:20:40, wt.%) was mixed with Au/TiO_2(nano particle prepared by sol–gel method [20,25]) or commercially available zeolites (4A[Aldrich], ZSM-5[Zeolyst], US-Y[Shokubai Kasei Co.], DAY[Degussa], 13X[Aldrich]). The exchanged-ion in the zeolites was H^+(proton). Table 1 shows the chemical properties of the zeolites. The preparation method of Au/TiO_2 nano particle was presented in our previous work and the content of gold was fixed at 1 wt.% on TiO_2 [25]. These manually prepared slurries were deposited onto a Teflon-coated Toray carbon sheet as shown in Fig. 1. The completed array was reduced by 0.5 M sodium borohydride, and the reduced array was thoroughly washed with nanopure water. To measure the methanol electro-oxidation potential of CO adsorption on the array with this combinatorial method, CO gas was adsorbed onto the selected composition (the most active composition) by immersion of that array into CO purged electrolyte solution for 5 h.

The electrolyte solution was composed of 100 μM quinine as a proton indicator, 6 M of reactant methanol, and the diluted H_2SO_4 which was added to adjust the pH to 7. The potential-step experiments were carried out using a potentiostat/galvanostat controlled by an IBM PC. Each composition was used as a working electrode. Cyclic voltammetry experiments were conducted between −0.3 and 0.8 V RHE at a sweep rate of 20 mV/s. The most active working electrode was selected by the brightest spot of the array obtained by fluorescence emission excited by UV of 254 nm [21].

2.2. Electrochemical experiments

Anodes were prepared having different loadings of additive materials to evaluate the additive materials. A single direct methanol fuel cell was operated at a temperature of 80–160 °C. To analyze the DMFC anode impedances, the anode was supplied with a 2 M aqueous solution of methanol at the flow rate of 1.0 ml/min. The cathode was operated on hydrogen: this served as a reference and counter electrode. For impedance measurements, the current was modulated by a small sinusoidal signal so that the potential amplitude did not exceed 15 mV. Impedance spectra were usually obtained at frequencies between 40 kHz and 3 mHz [26]. The cyclic voltammetry experiments were carried out at 25 °C in a conventional three-electrode cell, oxygen free (purged and blanked with nitrogen) electrolyte solution. The prepared anodes were mounted into a Teflon holder containing a platinum ring as current collector and a platinum mesh was used as counter electrode. An Ag/AgCl reference electrode was placed next to the cell and connected to the main compartment through a Luggin capillary whose tip was placed near to the working electrode surface. The electrochemical cell was connected to an impedance analyzer (AUTOLAB FRA2) for electrochemical impedance spectroscopy and an AUTOLAB potentiostat/galvanostat for cyclic voltammetry.

3. Results and discussion

3.1. CO tolerance effect

Fig. 2 (a) shows the fluorescence images of PtRu/C–Au/TiO_2 array for electro-oxidation of methanol at various potentials. At the potential of 0.4 V, the spots of PtRu/C:Au/TiO_2 = 9:1, 8:2 and 7:3 were brighter than the other spots. The addition of Au/TiO_2 lowered the initial oxidation potential of methanol. This indicates that Au/TiO_2 helped the platinum for methanol electro-oxidation. It has been well known that the CO or CO-like substances produced on the Pt surface act as self-poisons during the electro-oxidation of methanol [27]. Au/TiO_2 might be effective to the decomposition of these deactivating species at room temperature to improve the activity of electro-oxidation of methanol. However, Au/TiO_2 catalyst (the last spot) never emitted any fluorescence which indicates that the acidic proton did not formed on Au/TiO_2 system. Since the methanol is

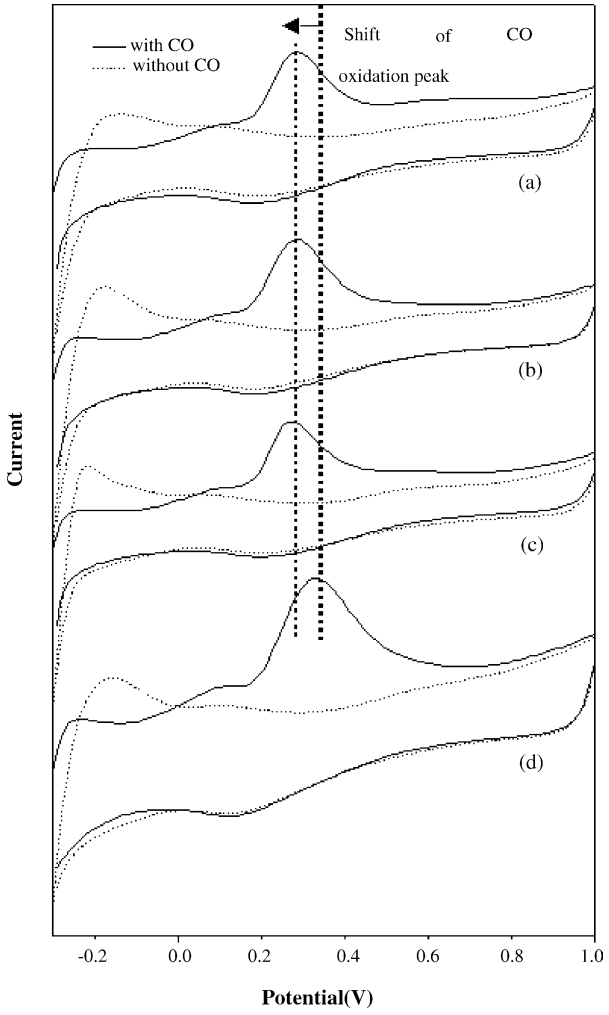


Fig. 3. Cyclic voltammograms of PtRu/C–Au/TiO_2 electrode in 0.25 M H_2SO_4 at scan rate of 20 mV/s. (a) PtRu/C: Au/TiO_2 = 70: 30. (b) PtRu/C: Au/TiO_2 = 80: 20. (c) PtRu/C: Au/TiO_2 = 90: 10. (d) PtRu/C: Au/TiO_2 = 100: 0.

generally decomposed to acetic acid and/or formic acid at low temperature [28], no detection of acidic proton means that Au/TiO_2 does not have any activity for the oxidation of methanol in our experimental condition. It proves that Au/TiO_2 might selectively remove the CO which was produced during the electro-oxidation of methanol over PtRu catalyst.

The effect of CO on electro-oxidation of methanol over PtRu/C–Au/TiO_2 was examined by using CO-saturated methanol electrolyte. The fluorescence was detected from 0.5 V at PtRu: Au/TiO_2 = 9:1, 8:2 and 7:3 as shown in Fig. 2 (b). The active regions were same as the case of pure methanol as shown in Fig. 2 (a). The initial oxidation potential of PtRu/C–Au/TiO_2 was lower than that of PtRu/C catalysts. It means that the catalytic activity for methanol electro-oxidation and CO tolerance of PtRu/C was improved by the addition of Au/TiO_2.

Fig. 3 shows the cyclic voltammograms of PtRu/C–Au/TiO_2 catalysts. The onset potential of CO oxidation for PtRu/C catalyst started at 0.2 V. This indicates that PtRu/C had higher activity for the oxidation of CO than pure platinum, being consistent with many other studies so far [15,29,30]. According to the bifunctional mechanism of electro-oxidation [29], the synergistic effect of PtRu is resulted from the fact that Ru activates water molecules to form the active oxidant, i.e., a surface hydroxyl intermediate (Ru–OH). Abundant –OH species subsequently oxidizes CO bound to a neighboring Pt site [30]. The bifunctional mechanism is commonly written as:

$$Ru + H_2O \rightarrow Ru{-}OH + H^+ + e^- \quad (3)$$

$$Pt{-}CO + Ru{-}OH \rightarrow CO_2 + H_+e^- + Pt + Ru \quad (4)$$

As shown in Fig. 3, the addition of Au/TiO_2 in PtRu/C electrode lowered the potential for onset CO oxidation potential by

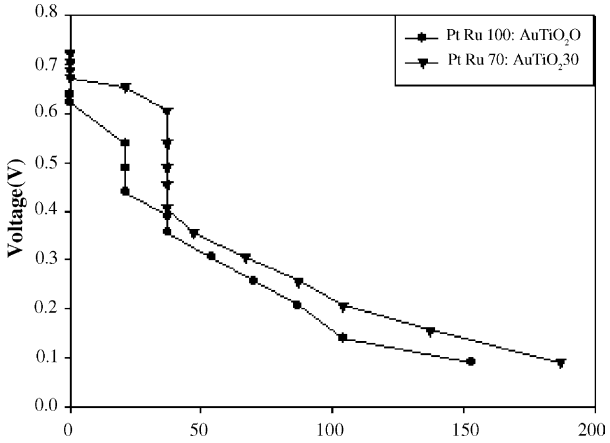


Fig. 4. The single cell performance of PtRu/C–Au/TiO_2 electrode at 25 °C. Fuel: 2 M methanol solution, 1.0 ml/min. O_2: 300 ml/min, 2 atm.

20 mV. And, CO stripping peak potential was also negatively shifted. CO easily oxidized to CO_2 over Au/TiO_2 by following reactions in 2 M MeOH solution [22].

$$CO{-}(Au/TiO_2) + 1/2O_2 \rightarrow AuTiO_2 + CO_2 \quad (5)$$

$$CO{-}(Au/TiO_2) + H_2O \rightarrow AuTiO_2 + CO_2 + H_2 \quad (6)$$

The adsorption energy of CO on Au/TiO_2 was 52 kJ/mol [31] and the activation energy for the reaction between adsorbed CO and Au/TiO_2 was nearly zero [22]. In the case of Ru–OH, the adsorption energy of CO was about 60 kJ/mol calculated by Neurock et al. [32]. Therefore, if the CO is movable from the platinum site to the surface of Au/TiO_2 and/or Ru, the oxidation of CO over Au/TiO_2 could energetically occur preferentially or

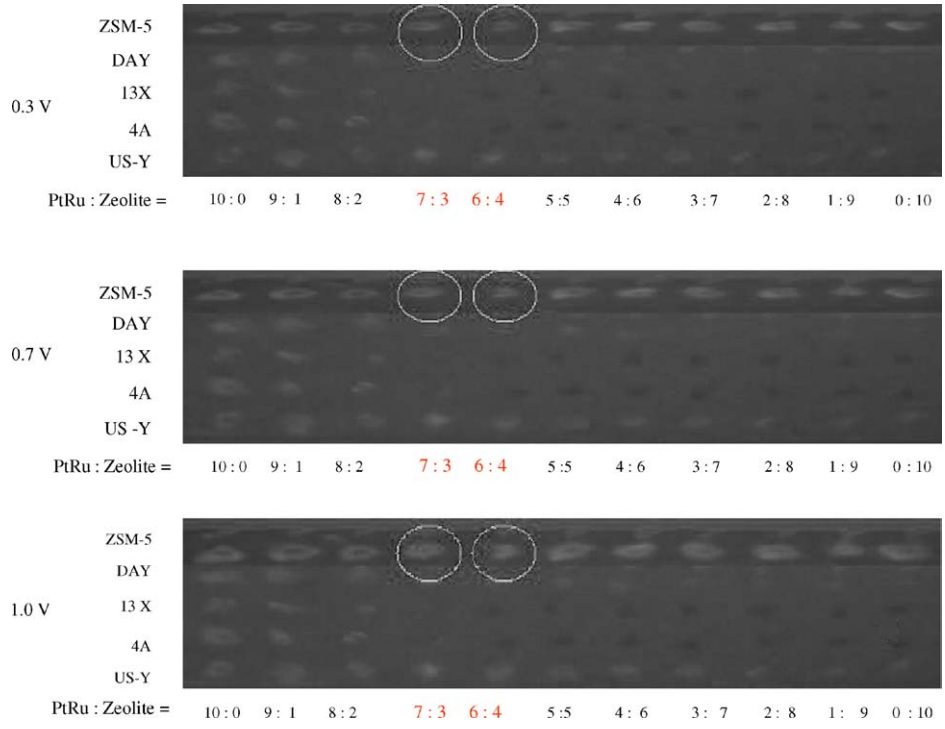


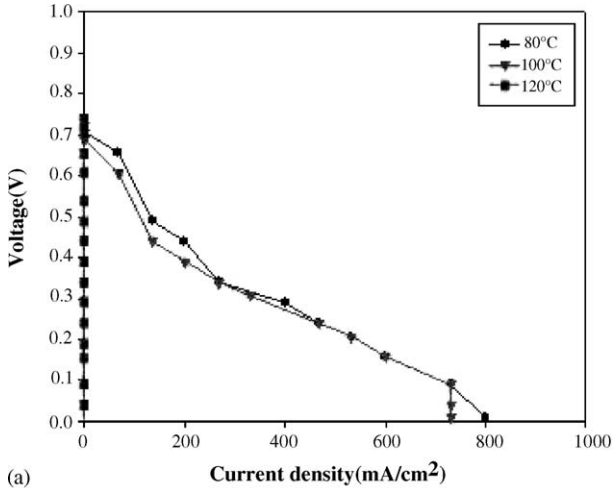
Fig. 5. Fluorescence images of PtRu/C–zeolite electrocatalysts array with the potential sweep in 6 M methanol solution.

simultaneously with that over Ru–OH. Since the PtRu/C–Au/TiO_2 catalysts were thermally reduced at 350 °C, the interaction between PtRu/C and Au/TiO_2 could make it possible to move the CO adsorbed on Pt to the surface of Au/TiO_2. The oxidation of CO over Au/TiO_2 could reduce the coverage of CO on PtRu surface and promote the electro-oxidation of CO. This might shift the onset and peak voltages for CO oxidation as shown in Fig. 3. Fig. 4 shows the single cell performance with the PtRu/C–Au/TiO_2 anode at 25 °C. The single cell performance test was performed with the addition of Au/TiO_2 into the anode at room temperature (25 °C). As shown in Fig. 4 the single cell performance was improved and the OCV was also increased from 0.64 to 0.73 V by the addition of Au/TiO_2.

3.2. High temperature operating anode

The fluorescence image of Pt–Ru–zeolite electrodes for methanol electro-oxidation was shown in Fig. 5. We applied zeolites (ZSM-5, DAY, 13X and US-Y) as the new proton conducting materials, which endure at the high operating temperature over 120 °C beside the Nafion ionomer. At the potential of 0.3 V, the spots of PtRu:ZSM-5 = 7:3 and 6:4 were brighter than the other spots. The addition of ZSM-5 lowered the initial oxidation potential of methanol. This indicates that ZSM-5 helped the platinum for electro-oxidation of methanol among the zeolites tested. This may be due to the acid strength of ZSM-5. Among the zeolites tested, the ZSM-5 is known to have the strongest acidity. This implies that the proton mobility in the anode may be remarkably governed by the acid strength.

Fig. 6 shows the performance of the single direct methanol fuel cell using (a) PtRu/C–Nafion and (b) PtRu/C–Nafion-[ZSM-5], respectively at temperature from 80 to 160 °C. Without ZSM-5, the cell performance was sustained up to 100 °C (210 mA/cm^2 at 0.4 V), but it decreased abruptly at 120 °C (0 mA/cm^2 at 0.4 V) due to dehydration from Nafion structure. Fig. 6 (b) shows the cell performance of the anode



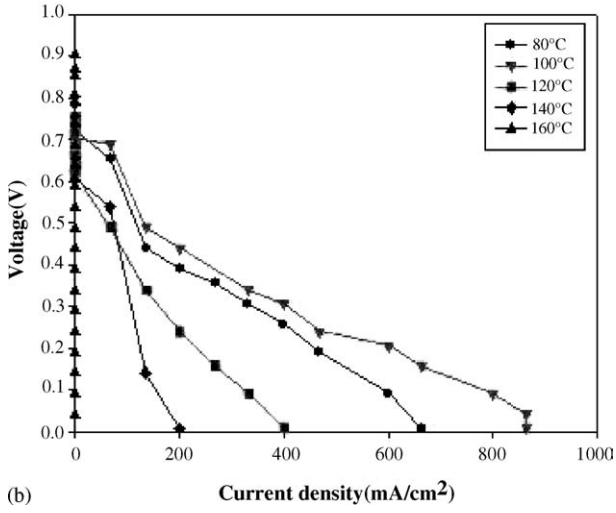
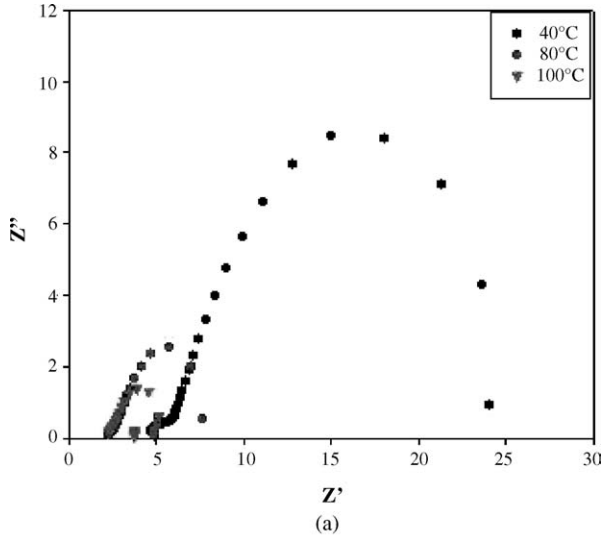


Fig. 6. The single cell performance of the prepared anode. Fuel: 2 M methanol solution, 1.0 ml/min. O_2: 300 ml/min, 2 atm. (a) PtRu/C–Nafion, PtRu: Nafion = 10: 3 (wt. ratio) (b). (b) PtRu/C–Nafion-[ZSM-5], PtRu: Nafion: ZSM-5 = 7: 2.1: 3 (wt. ratio).



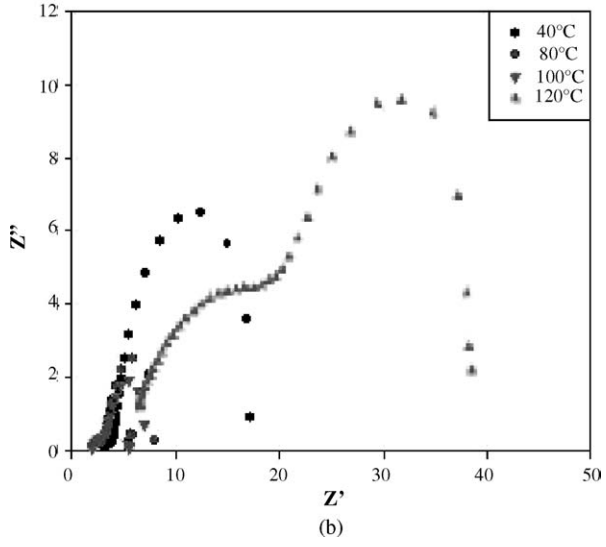


Fig. 7. Impedance spectrum of the prepared anode. (a) PtRu/C–Nafion, PtRu: Nafion = 10: 3 (wt. ratio). (b) PtRu/C–Nafion-[ZSM-5], PtRu: Nafion: ZSM-5 = 7: 2.1: 3 (wt ratio).

Table 2
Impedance spectrum analysis of the prepared anode

Temperature (°C)		40	80	100	120
PtRu/C–Nafion	Interfacial resistance (Ω cm^2)	19.46	5.35	2.87	∞
	Membrane resistance (Ω cm^2)	4.64	2.27	2.26	∞
PtRu/C–Nafion-[ZSM-5]	Interfacial resistance (Ω cm^2)	14.17	5.96	5.03	32.02
	Membrane resistance (Ω cm^2)	3.09	2.01	1.94	6.49

with the ZSM-5. The open circuit voltage was increased from 0.75 V to 0.9 V as increasing the cell temperature from 80 to 160 °C, indicating the low methanol crossover [33]. Although the maximum current density decreased gradually from 860 to 200 mA/cm^2 as the temperature increased from 100 to 140 °C it does not drop abruptly as the case of the anode without ZSM-5 shown in Fig. 6 (a). Fig. 7 shows the impedance spectra of DMFC anode. It is known that the magnitude of the semicircle in the DMFC anode impedance is the interfacial resistance related to the methanol electro-oxidation kinetics [26], and the intercept of *x*-axis is the membrane resistance (Table 2). The interfacial resistance and membrane resistance decreased as the cell operating temperature increased to 100 °C PtRu/C–Nafion anode. The two resistances increased to infinity at 120 °C because of the dehydration of Nafion membrane in electrode. With the addition of ZSM-5 in PtRu/C anode catalyst, both the methanol electro-oxidation kinetics related resistance and the membrane resistance decreased as the cell operating temperature increased to 100 °C. At 120 °C the resistances were 32.02 and 6.49 Ω cm^2, respectively. It should be noted that these values do not reach to the infinite. It implies that the methanol electro-oxidation ability was sustained by the addition of ZSM-5 zeolite over the cell temperature 120 °C. This may be due to the role of the zeolite as micro-humidifier to the Nafion membrane as well as anode, which was positioned inside anode and the anode–Nafion membrane interface.

From this result, we can conclude that the high temperature endurable anode can be made by the addition of ZSM-5 zeolite as the proton conducting materials.

4. Conclusions

The DMFC anode was developed by the addition of the third materials (Au/TiO_2 and Zeolites) into the PtRu electrocatalysts. Through the high-throughput-screening test the catalysts composition was optimized. Au/TiO_2 were added to PtRu/C electrode to improve the performance of direct methanol fuel cell. The catalysts composed PtRu/C: Au/TiO_2 = 9:1, 8:2 and 7:3 were most active in electro-oxidation of methanol. The adsorbed CO on Pt might be easily oxidized on the surface of Au/TiO_2 by the interaction between PtRu/C and Au/TiO_2. The replacement of polymer proton conducting materials (Nafion ionomer) with the solid acid proton conducting materials (ZSM-5) was performed to prepare the high temperature endurable anode. The cell performance was maintained at the cell temperature 160 °C (maximum current density was 200 mA/cm^2) by the addition of ZSM-5 as proton conducting materials.

Acknowledgements

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References

[1] S. Wasmus, A. Kuver, J. Electroanal. Chem. 461 (1999) 14.
[2] M. Baldauf, W. Predel, J. Power Sources 84 (1999) 161.
[3] B.D. McNicol, D.A.J. Rand, K.R. Williams, J. Power Sources 83 (1999) 15.
[4] G.T. Burstein, C.T. Barnett, A.R. Kucernak, K.R. Williams, Catal. Today 38 (1997) 425.
[5] W.H.L. Valbuena, V.A. Paganin, C.A.P. Leite, F. Galembeck, E.R. Gonzalez, Electrochim. Acta 48 (2003) 3869.
[6] Y.X. Chen, A. Miki, S. Ye, H. Sakai, M. Osawa, J. Am. Chem. Soc. 125 (2003) 3680.
[7] A. Hamnett, Catal. Today 38 (1997) 445.
[8] U.A. Paulus, U. Endruschat, G.J. Feldmeyer, T.J. Schmidt, H. Bonnemann, R.J. Behm, J. Catal. 1995 (2000) 383.
[9] J. Kua, W.A. Goddard III, J. Am. Chem. Soc. 121 (1999) 10928.
[10] M. Watanabe, M. Uchida, S. Motoo, J. Electroanal. Chem. 199 (1986) 311.
[11] H.A. Gasteiger, N.M. Markovic, P.N. Ross Jr., E.J. Cairns, J. Electrochem. Soc. 141 (1994) 1795.
[12] S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. LaConti, J. Kosek, G.K.S. Prakash, G.A. Olah, J. Power Sources 47 (1994) 377.
[13] N.M. Markovic, H.A. Gasteiger, P.N. Ross Jr., X. Jiang, I. Villegas, M.J. Weaver, Electrochim. Acta 40 (1995) 91.
[14] A.S. Arico, P. Creti, E. Modica, G. Monforte, V. Baglio, V. Antonucci, Electrochim. Acta 45 (2000) 4319.
[15] M. Watanabe, S. Motoo, J. Electroanal. Chem. 60 (1975) 267.
[16] J.J. Hanak, J. Mater. Res. 5 (1970) 964.
[17] B. Jandeleit, D.J. Schaefer, T.S. Powers, H.W. Turner, W.H. Weinberg, Angew. Chem. Int. Ed. Engl. 38 (1999) 2494.
[18] W.C. Choi, J.D. Kim, S.I. Woo, Catal. Today 74 (2002) 235.
[19] G. Chen, D.A. Delafuente, S. Sarangapani, T.E. Mallouk, Catal. Today 67 (2001) 341.
[20] M. Date, Y. Ichihashi, T. Yamashita, A. Chiorino, F. Boccuzzi, M. Haruta, Catal. Today 72 (2002) 89–94.
[21] Y.H. Chu, Y.G. Shul, W.C. Choi, S.I. Woo, H.S. Han, J. Power Source 118 (2003) 334.
[22] Y.G. Shul, H.J. Kim, S.W. Ahn, Y.H. Chu, H. Han, High throughput screening test of electrocatalyst and proton conductor for direct methanol fuel cells, in: 206th Meeting of the Electrochemical Society, 2004 October 3–8, Honolulu, Hawaii, 2004, Abstract No., 1899.
[23] M. Haruta, M. Date, Appl. Catal. A: Gen. 222 (2001) 427.
[24] Z. Połtarzewski, W. Wieczorek, J. Przyłuski, V. Antonucci, Solid State Ionics 119 (1999) 301.
[25] H.J. Kim, D. Y. Kim, H. S. Han, Y.G. Shul, J. Power Sources, submitted.
[26] J.T. Muller, P.M. Urban, J. Power Sources 75 (1998) 139.
[27] P.C. Bissawa, Y. Nodasaka, M. Enyo, M. Haruta, J. Electroanal. Chem. 381 (1995) 167.
[28] H. Sakurai, A. Ueda, T. Kobayashi, M. Haruta, Chem. Commun. (1997) 271.
[29] B.R. Gurau, R. Viswanathan, R.X. Liu, J. Phys. Chem. B 102 (1998) 9997.
[30] W. Hou, Z. Zhou, S. Song, W. Li, G. Sun, P. Tsiakaras, Q. Xin, Appl. Catal. B: Environ. 46 (2003) 273.
[31] D.C. Meier, D.W. Goodman, J. Am. Chem. Soc. 126 (2004) 1892.
[32] S. Desai, M. Neurock, Electrochim. Acta 48 (2003) 3759.
[33] P.L. Antonucci, A.S. Arico, P. Creti, E. Ramunni, V. Antonucci, Solic State Ionics 125 (1999) 431.