Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 132 (2008) 123–126

CATALYSIS TODAY

www.elsevier.com/locate/cattod

$Pt_{45}Ru_{45}M_{10}/C$ (M = Fe, Co, and Ni) catalysts for methanol electro-oxidation

Min Ku Jeon [a], Ki Rak Lee [a], Hideo Daimon [b], Akemi Nakahara [b], Seong Ihl Woo [a,*]

[a] *Department of Chemical and Biomolecular Engineering (BK21 Graduate Program) & Center for Ultramicrochemical Process Systems (CUPS), Korea Advanced Institute of Science and Technology, 373-1, Daejeon 305-701, Republic of Korea*

[b] *Development & Technology Division, Hitachi Maxell Ltd., 6-20-1 Kinunodai, Tsukubamirai, Ibaraki 300-2496, Japan*

Abstract

$Pt_{45}Ru_{45}M_{10}/C$ (M = Fe, Co, and Ni) catalysts were synthesized and physical and electrochemical properties were analyzed by XRD, TEM, CO stripping and methanol electro-oxidation activity measurement. Among these catalysts, the $Pt_{45}Ru_{45}Fe_{10}/C$ catalyst exhibited the highest mass activity of 2.6 A/g catal. while those of the $Pt_{45}Ru_{45}Co_{10}/C$ and $Pt_{45}Ru_{45}Ni_{10}/C$ catalysts were 2.2 and 2.5 A/g catal., respectively. In the case of specific activity, the catalysts exhibited much higher activities of 110 (130%), 120 (140%) and 150 (170%) mA/m^2 for the Fe, Co and Ni incorporated catalysts, respectively, than 88 mA/m^2 of a commercial PtRu/C catalyst.

Keywords: Electrocatalysts; Methanol electro-oxidation; Direct methanol fuel cell

1. Introduction

Direct methanol fuel cell (DMFC) is widely studied for application in portable power sources such as cellular phones and notebook computers. Present lithium batteries for these portable electronics are suffering from long recharge and short operation time. DMFC should be one of the most promising alternatives to replace lithium batteries because of its short refuel time and easy handling of liquid fuel, methanol. However, low catalytic activity for methanol electro-oxidation in the anode is one of the major problems of low power density of DMFC [1].

Platinum was firstly used for methanol electro-oxidation, however, it was easily poisoned by intermediate CO. Improved CO tolerance was obtained by alloying Ru with Pt [2]. The PtRu catalyst showed higher activity for methanol electro-oxidation by the bifunctional mechanism [3]. Though the PtRu catalyst largely improved the catalytic activity of Pt, higher activity for methanol electro-oxidation and cost down by replacing expensive Pt and Ru are essential for commercialization of DMFC.

Various efforts were made to improve catalytic activity of PtRu. Changing oxidation state of Ru [4,5] and incorporation of non-metals could greatly improve methanol electro-oxidation activity [6]. Modification by adding a third metal into the PtRu catalyst resulted in higher methanol electro-oxidation activity in the PtRuIr [7] and PtRuNi [8] catalysts. Strasser et al. reported that, from their theoretical screening results, alloying PtRu with Fe, Co, Rh, Ir and Ni could provide higher activity than the PtRu catalyst [9].

In this study, we incorporated a third metal into the PtRu/C catalyst to synthesize $Pt_{45}Ru_{45}M_{10}/C$ (M = Fe (PtRuFe/C), Co (PtRuCo/C), and Ni (PtRuNi/C)) catalysts. We selected Fe, Co, and Ni as a third member because their precursors are much cheaper than novel metals. Characterization of the synthesized catalysts was carried out by X-ray diffraction (XRD), transmission electron microscopy (TEM), CO stripping and methanol electro-oxidation.

2. Experimental

Conventional sodium borohydride reduction method was used for synthesis of the catalysts. Carbon support (Vulcan XC72R) was dispersed in mixture of de-ionized water and isopropyl alcohol, and then metal precursors were dissolved.

---

[*] Corresponding author. Tel.: +82 42 869 3918; fax: +82 42 869 8890.
E-mail address: siwoo@kaist.ac.kr (S.I. Woo).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.12.011

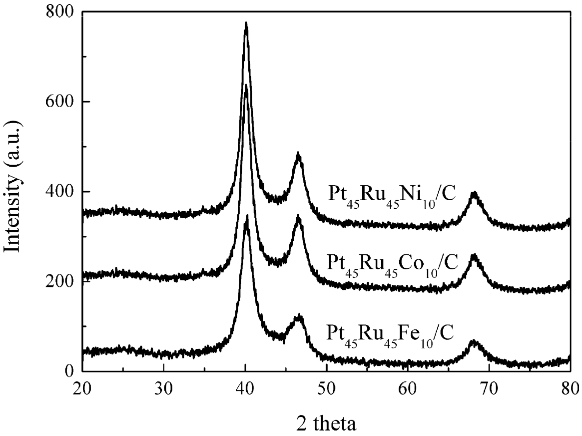

Fig. 1. XRD results of $Pt_{45}Ru_{45}Fe_{10}/C$, $Pt_{45}Ru_{45}Co_{10}/C$ and $Pt_{45}Ru_{45}Ni_{10}/C$ catalysts.

H_2PtCl_6, $RuCl_3$ were used for Pt and Ru precursors, respectively. For Fe, Co, and Ni metals $(NH_4)Fe(SO_4)_2$, $CoCl_3$ and $NiCl_2{\cdot}6H_2O$ were used as precursors, respectively. Loading of metals was adjusted to be 60 wt% vs. carbon support. The mixture was heated to 80 °C and kept for 1 h with stirring. $NaBH_4$ solution (0.2 M) was added to the mixture solution for reduction and the mixture was kept for 3 h with stirring. The catalyst and solvent mixture was filtered and washed with hot water. The final catalyst slurry was dried at 100 °C overnight.

A three-electrode-type beaker cell was used for electrochemical characterization. Platinum wire and Ag/AgCl electrode (BAS Co. Ltd., MF-2052 RE-5B) were used as counter and reference electrodes, respectively. Glassy carbon electrode with 3 mm diameter (BAS Co. Ltd., MF-2012) was used as a working electrode. The working electrode was prepared by the thin-film method suggested by Schmidt et al. [10]. Catalyst was dispersed in de-ionized water and sonication

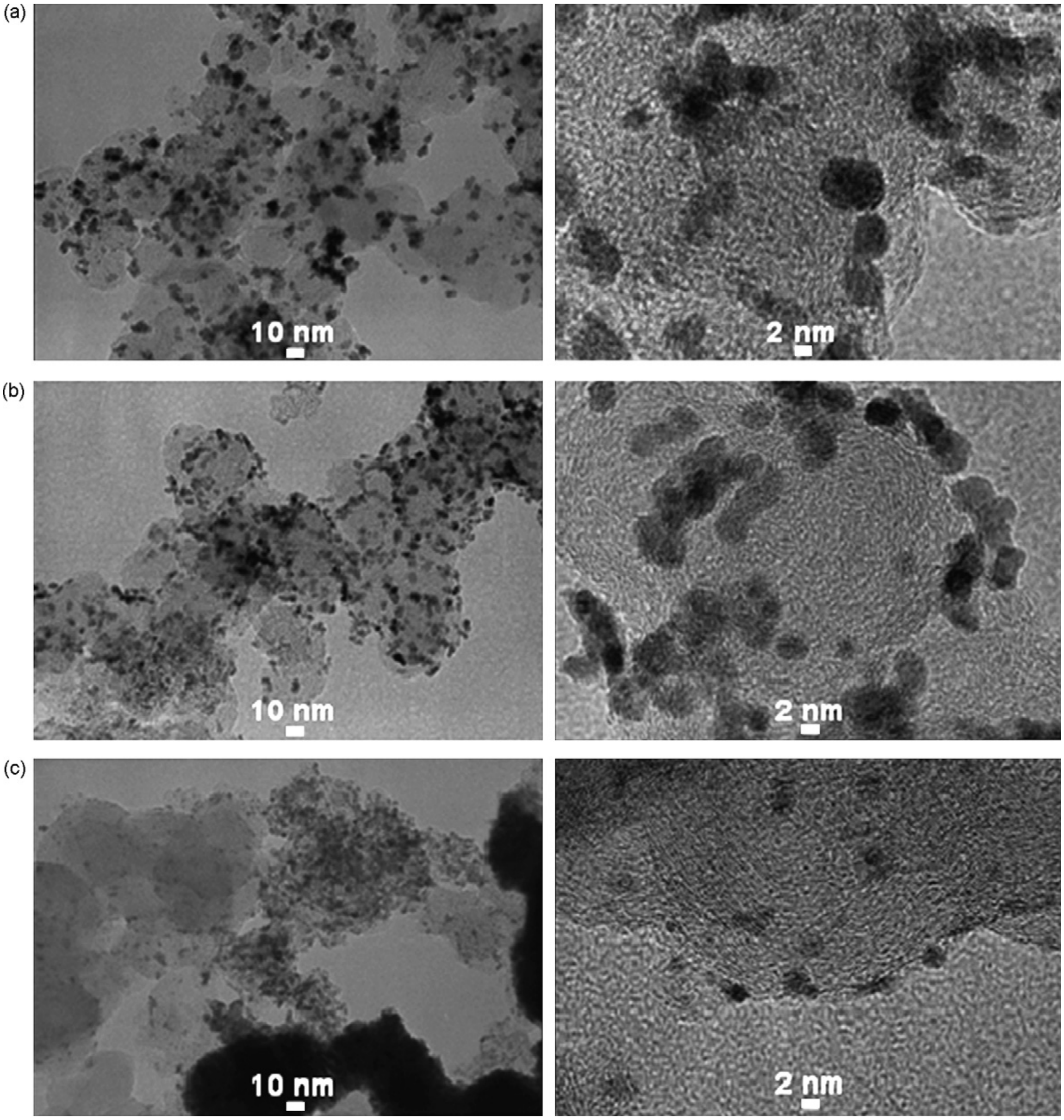

Fig. 2. TEM images of (a) $Pt_{45}Ru_{45}Fe_{10}/C$, (b) $Pt_{45}Ru_{45}Co_{10}/C$ and (c) $Pt_{45}Ru_{45}Ni_{10}/C$ catalysts.

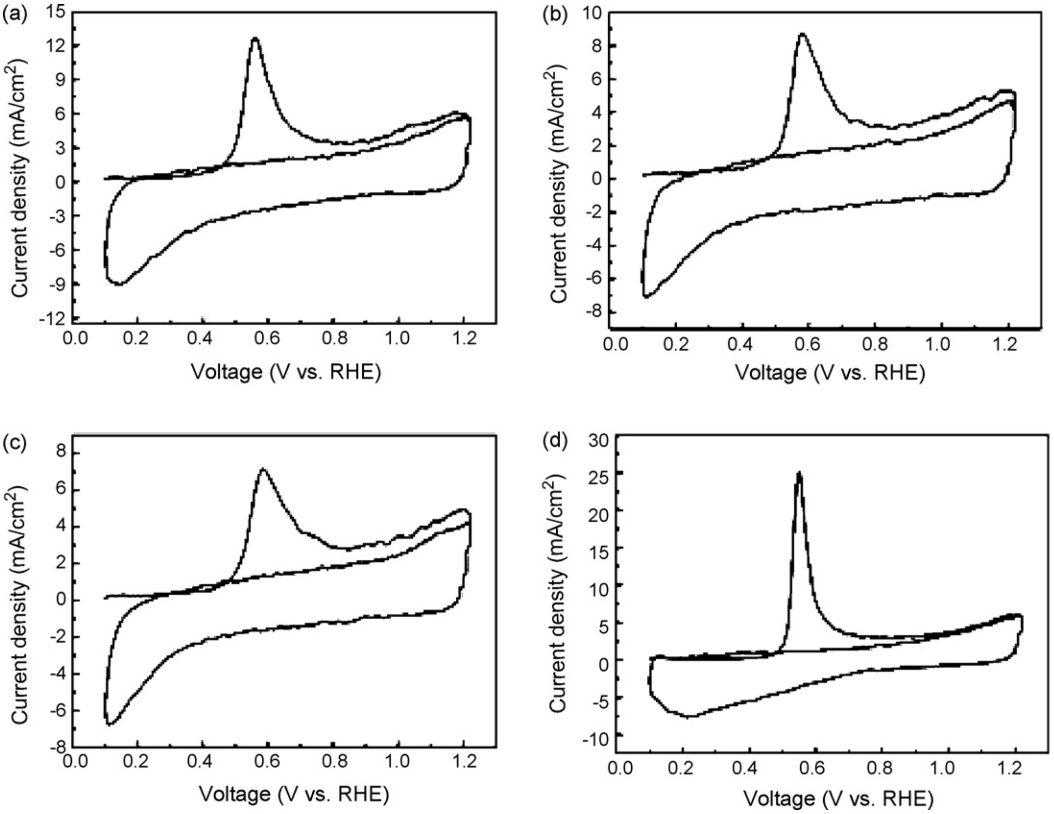

Fig. 3. CO stripping results of (a) $Pt_{45}Ru_{45}Fe_{10}/C$, (b) $Pt_{45}Ru_{45}Co_{10}/C$, (c) $Pt_{45}Ru_{45}Ni_{10}/C$ and (d) PtRu/C catalysts.

was carried out. The resulting catalyst dispersion was dropped on the glassy carbon electrode. After drying in the air, 5 wt% Nafion ionomer solution was dropped on the working electrode to stabilize the catalyst layer. CV and CO stripping were carried out in a 1 M $HClO_4$ solution, while methanol electro-oxidation was carried out in a 1 M H_2SO_4 + 1 M CH_3OH solution. All the electrochemical experiments were done at a scan rate of 15 mV/s. In CO stripping, CO was bubbled for 1 h keeping the working electrode at a constant voltage of 0.1 V. Dissolved CO in the electrolyte was purged by N_2 gas bubbling for 50 min. All voltages shown in this paper were converted to reversible hydrogen electrode (RHE) scale.

3. Results and discussion

Fig. 1 shows X-ray diffraction results of the synthesized catalysts. Peaks from oxides of Ru or third metals were not observed, indicating well-mixed alloy formation. Average particle sizes calculated by the Debye–Scherrer equation for the catalysts incorporated with Fe, Co, and Ni were 4.6, 5.2, and 5.0 nm, respectively. TEM images are displayed in Fig. 2. Uniform dispersion of the catalysts without agglomeration was observed for the all catalysts.

CO stripping results of the synthesized catalysts and a commercial PtRu/C catalyst (60 wt%, Pt:Ru = 1:1 at.%, E-tek) are shown in Fig. 3. Decrease of on-set voltage for CO electro-oxidation was observed in the synthesized catalysts. The PtRuFe/C catalyst exhibited lowered CO electro-oxidation on-set voltage of 0.46 V compared with 0.48 V of the PtRuCo/C and PtRuNi/C catalysts and 0.49 V of the PtRu/C catalyst. This lowered CO electro-oxidation on-set voltage might have originated from Pt–Fe alloy formation. Watanabe et al. reported that alloying Pt with Fe could weaken Pt–CO bonding by preventing electron back-donation from Pt to CO [11,12].

Electrochemically active surface area (EAS) was calculated from the CO electro-oxidation area with an assumption that the charge of CO monolayer adsorption is 420 μC/cm^2. The calculated EAS were 23, 18 and 17 m^2/g catal. for the PtRuFe/C, PtRuCo/C and PtRuNi/C catalysts, respectively. EAS of the PtRu/C catalyst was 26 m^2/g catal., which was higher than the

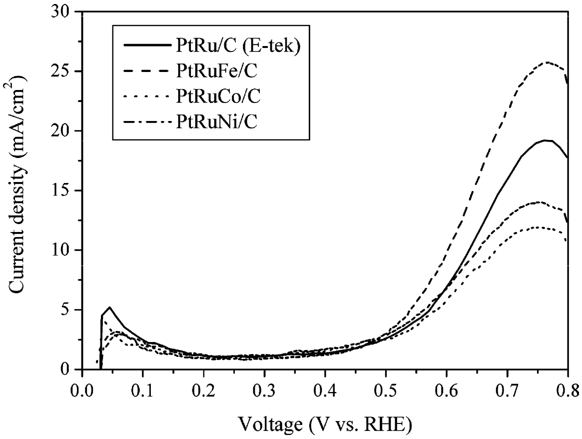

Fig. 4. Methanol electro-oxidation activity measurement results in 1 M H_2SO_4 + 1 M methanol electrolyte. Scan rate was 15 mV/s.

Table 1
Electrochemical properties of $Pt_{45}Ru_{45}Fe_{10}/C$, $Pt_{45}Ru_{45}Co_{10}/C$, $Pt_{45}Ru_{45}Ni_{10}/C$ and PtRu/C catalysts

Catalysts	EAS (m^2/g catal.)	On-set voltage for CO electro-oxidation	Current density at 0.5 V (mA/cm^2)	Mass activity (A/g catal.)	Specific activity (mA/m^2)
$Pt_{45}Ru_{45}Fe_{10}/C$	23	0.46	3.0	2.6	110
$Pt_{45}Ru_{45}Co_{10}/C$	18	0.48	2.5	2.2	120
$Pt_{45}Ru_{45}Ni_{10}/C$	17	0.48	2.9	2.5	150
PtRu/C (E-tek)	26	0.49	2.6	2.3	88

other catalysts because of larger amount of Pt and smaller particle size. Though the synthesized catalysts have only 10% smaller amount of Pt than the PtRu/C catalyst, the PtRuCo/C and PtRuNi/C catalysts showed largely reduced EAS. This result indicates that exposure of Pt to the surface of catalyst particles was hindered by incorporation of Co and Ni.

Fig. 4 shows methanol electro-oxidation activity measurement results. Current densities of the catalysts at 0.5 V are listed in Table 1. The current densities were converted into mass and specific activities. In the case of mass activity, the PtRuFe/C and PtRuNi/C catalysts showed mass activities of 2.6 and 2.5 A/g catal., respectively, which were higher than 2.3 A/g catal. of PtRu/C. However, PtRuCo/C catalyst exhibited slightly lower mass activity of 2.2 A/g catal. than that of PtRu/C. To remove surface area dependence on the activity of the catalysts, specific activity was calculated by dividing mass activity by EAS obtained from the CO stripping. Specific activities of the catalysts were 110, 120, and 150 mA/m^2 for the PtRuFe/C, PtRuCo/C, and PtRuNi/C catalysts, respectively. When compared to specific activity of 88 mA/m^2 of the PtRu/C catalyst, increase of specific activities by addition of a third metal is clear. The specific activity of $Pt_{45}Ru_{45}Ni_{10}/C$ catalyst was 70% higher than that of PtRu/C.

4. Conclusion

The $Pt_{45}Ru_{45}M_{10}/C$ (M = Fe, Co, and Ni) catalysts were synthesized and physical and electrochemical properties were analyzed. CO stripping results revealed that the $Pt_{45}Ru_{45}Fe_{10}/C$ catalyst had a similar EAS to that of the PtRu/C catalyst, while EAS of the $Pt_{45}Ru_{45}Co_{10}/C$ and $Pt_{45}Ru_{45}Ni_{10}/C$ catalysts were largely decreased. In methanol electro-oxidation activity measurement, the $Pt_{45}Ru_{45}Fe_{10}/C$ catalyst exhibited the highest mass of 2.6 A/g catal. and the $Pt_{45}Ru_{45}Ni_{10}/C$ catalyst showed highest specific activity of 150 mA/m^2, which was 70% higher than that of commercial PtRu/C catalyst. These new catalyst of high methanol electro-oxidation activity are promising candidate for DMFC anode catalyst.

Acknowledgements

This work was supported by Center for Ultramicrochemical Process Systems (CUPS) sponsored by KOSEF (2007).

References

[1] A.S. Arico, S. Srinivasan, V. Antonucci, Fuel Cells 1 (2001) 133.
[2] M. Watanabe, M. Uchida, S. Motoo, J. Electroanal. Chem. 229 (1987) 395.
[3] N.M. Markovic, H.A. Gasteiger, P.N. Ross, X.D. Jiang, I. Villegas, M.J. Weaver, Electrochim. Acta 40 (1995) 91.
[4] M.K. Jeon, J.Y. Won, S.I. Woo, Electrochem. Solid-State Lett. 10 (2007) B23.
[5] Q. Lu, B. Yang, L. Zhuang, J. Lu, J. Phys. Chem. B 109 (2005) 1715.
[6] H. Daimon, Y. Kurobe, Catal. Today 111 (2006) 182.
[7] P. Sivakumar, V. Tricoli, Electrochem. Solid-State Lett. 9 (2006) A167.
[8] Z.B. Wang, G.P. Yin, P.F. Shi, Y.C. Sun, Electrochem. Solid-State Lett. 9 (2006) A13.
[9] P. Strasser, Q. Fan, M. Devenney, W.H. Weinberg, P. Liu, J.K. Norskov, J. Phys. Chem. B 107 (2003) 11013.
[10] T.J. Schmidt, H.A. Gasteiger, G.D. Stab, P.M. Urban, D.M. Kolb, R.J. Behm, J. Electrochem. Soc. 145 (1998) 2354.
[11] M. Watanabe, H. Igarashi, T. Fujino, Electrochemistry 67 (1999) 1194.
[12] M. Watanabe, Y. Zhu, H. Uchida, J. Phys. Chem. B 104 (2000) 1762.