Influence of Pt and CeO_2 iteraction in Pt-CeO_2 electrode on anode and cathode performance for fuel cell applications

Motoi Takahashi[*], Toshiyuki Mori[*], Hirotaka Togasaki[*,**], Keisuke Fugane[**], Akio Tada[**], Vladimir Matolin[***] and John Drennan[****]

[*]Nation Institute for Materials Science,
1-1 Namiki, Tsukuba, Ibaraki, Japan
Fax: 81029-860-4667, Mori.Toshiyuki@nims.go.jp
[**]Kitami Institute of Technology,
165 Koen-cho, Kitami, Hokkaido, Japan
[***]Charles University,
V Holesovickach 2, Prague 8, Czeech Republic
[****]The University of Queensland
St.Lucia, Brisbane, Qld, Australia

A Pt on nano-size CeO_2 particles which in turn are supported on carbon black (CB) was synthesized using co-impregnation method. The pure CeO_2 was synthesized using an ammonium carbonate precipitation method. The electrochemical activities of methanol oxidation reaction and oxygen reduction reaction on the Pt-CeO_2 composite electrode were investigated using cycle voltammetry and hydrodynamic voltammetry experimentation. It was found that the anode performance on Pt-CeO_2 composite electrode for methanol oxidation reaction was superior to that on the commercially available Pt-Ru alloy electrode. In addition, the cathode performance on composite electrode for oxygen reduction reaction was higher than that on the commercially available Pt electrode. Based on SPring-8 XPS observation, we conclude that a change of $5d$-electron density on Pt induced by an interaction between Pt and CeO_2 plays a key role for improvement of the performance on Pt-CeO_2 composite electrodes. It is expected that the anode and cathode performance on Pt-CeO_2 composites will be maximized by a design of interface between Pt and CeO_2 on the surface of electrodes.
Key words: Pt-CeO_2 composite anode, methanol oxidation, oxygen reduction, 5d-electron vacancy, fuel cells

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) are being especially developed as efficient power source for portable system applications. However, one of the serious problems for DMFCs is a low cell potential. Since IR loss of electrode at operation temperature of DMFCs is small, the low cell potential is attributable to the big overpotential on both anode and cathode. On the anode side, the performance of Pt is conspicuously decreased by adsorption of carbon monoxide (CO) as intermediate of methanol oxidation reaction. To oxidize the adsorbed CO and convert methanol to proton, the overpotential on Pt anode becomes high level. To overcome this CO poisoning effect on Pt, the Pt-Ru alloy anode has been developed. However, its performance doesn't reach the sufficient level from the view point of practical use of that alloy anode. In addition, the limited resources of Pt and Ru in ore bodies on the planet will make the cost of large scale production expensive. To minimize the environmental burden and maximize the performance of anode and cathode materials, a development of new environmental friendly anode and cathode

materials with the low overpotential and high current density is required.

In our previous works, we have developed Pt-CeO_2 composite electrode for methanol oxidation reaction.[1,2] The anode performance on Pt-CeO_2 composite electrode became higher than that on the commercially available Pt-Ru alloy electrode. The anode performance on Pt-CeO_2 composite electrode was improved using the high surface area of CeO_2 in the composite electrodes. It was concluded that the interaction between Pt and CeO_2 played an important role for enhancement of anode performance on Pt-CeO_2 composite electrode.

In order to propose a new design paradigm of anode and cathode materials, the authors examined the influence of interaction between Pt and CeO_2 on both anode and cathode properties.

2. EXPERIMENTAL

Pt-CeO_2 composite electrode supported by carbon black (CB) was synthesized using a combined process of precipitation and co-impregnation methods. To impregnate Pt particles on pure CeO_2 particles, $H_2PtCl_6 \cdot 6H_2O$

(Purity: ≥98.5%, Kishida Chemical Co.) and synthesized pure CeO_2 particles were dispersed into ethanol. The mixture was dried at room temperature under argon atmosphere in a glove box with less than 10ppm H_2O. The dried powder was reduced at 400°C for 2h in mixed gas H_2 (10%) and He (90%) flow. The synthesized Pt-CeO_2 particles were dispersed with CB (Vulcan XC-72R, Cabot Co.) particles in ethanol. The mixture was dried at room temperature in a N_2 gas flow. The content of Pt particles was 30% by weight in the mixture of Pt, CeO_2 and CB. Pt/Ce atomic ratio was 1.4. The anode and cathode performance of composite electrodes were compared with that of a commercially available Pt-Ru/C (HiSPEC7000, Johnson Matthey Company, Pt:Ru atomic ratio of 1:1, Pt: 30wt%, Ru: 15wt%) electrode and a commercially available Pt/C (HiSPEC3000, Johnson Matthey Company, Pt: 20wt%) electrode, respectively. The pure CeO_2 particles were synthesized using ammonium carbonate precipitation method. The starting materials used were $Ce(NO_3)_3 \cdot 6H_2O$ (Purity: >99.99, Kanto Chemical Co.) and $(NH_4)_2CO_3$ (Ultrahigh purity, Wako Pure Chemical Ind.). The $Ce(NO_3)_3 \cdot 6H_2O$ powder was dissolved into distilled water. To prepare the homogeneous precipitation, this solution was dropped into $(NH_4)_2CO_3$ solution which was heated at 55°C under mild stirring for 24h. After repeated washing, the precipitate was dried at room temperature in N_2 gas flow. Also the dried powder was calcined at 400°C for 2h in O_2 gas flow.

The anode performance on synthesized Pt-CeO_2 composite electrode for methanol oxidation reaction was examined by cyclic voltammetry (CV) experimentation. The measurement of CV was carried out in a mixed solution of 0.5M H_2SO_4 aqueous solution and 0.5M CH_3OH aqueous solution. Pt foil and Ag/AgCl were used as counter and reference electrodes, respectively. The electrode materials were suspended into CH_3OH aqueous solution (2mg/ml). The suspension was spread onto the surface of Au electrode (area: 0.20cm²) using a micro-pipette. Amount of the electrode materials spread was 0.01mg. The measured potentials were converted to the reversible hydrogen electrode (RHE) scale. The current density on the anode was normalized by the Pt surface area calculated from CO stripping method.[3] The cathode performance on synthesized Pt-CeO_2 composite electrode for oxygen reduction reaction was examined by hydrodynamic voltammetry experimentation on rotating disk electrode. The difference between the measured current in electrolyte aqueous solution saturated by O_2 and N_2 was regarded as oxygen reduction current.

The surface composition of Pt in electrodes was characterized by X-ray photoelectron spectroscopy (XPS) analysis. The measurement of XPS was carried out using the high-energy synchrotron radiation at super photon ring

(5946.8eV, SPring-8, BL15XU) in Japan. The binding energy was corrected using the observed value of C1s peak at 284.5eV.

3. RESULTS AND DISCUSSION

3.1 Anode performance on Pt-CeO₂ composite electrode

Figure 1(A) presents cyclic voltammograms of methanol oxidation reaction on Pt-CeO_2 composite electrode and commercially available Pt-Ru alloy electrode. The anodic peaks appeared in forward and reverse sweeps on both electrodes. The peak current density on Pt-CeO_2 composite electrode was 1.8 times higher than that on commercially available Pt-Ru alloy electrode. The tafel plots of methanol oxidation reaction were shown in **Figure 1(B)**. Tafel slopes of methanol oxidation reaction on Pt-CeO_2 composite electrode and Pt-Ru alloy electrode were 112mV/decade and 108mV/decade, respectively. The tafel slopes of 110-140mV/decade have been reported for carbon-supported Pt-Ru alloy electrodes.[4-6] The observed tafel slope of Pt-CeO_2 composite electrode agreed with the previously reported value of Pt-Ru alloy electrode. This suggests that proton is catalytically created from methanol on Pt-CeO_2 composite electrode as same as Pt-Ru alloy electrode. In addition, the onset potential of methanol oxidation reaction on Pt-CeO_2 composite electrode shifted to a low potential side as compared with that on Pt-Ru alloy electrode. These results indicate that the anode performance on Pt-CeO_2 composite electrode is superior to that on the Pt-Ru alloy electrode.

3.2 Cathode performance on Pt-CeO₂ composite electrode

Potential-current curves of oxygen reduction reaction on Pt-CeO_2 composite electrode and commercially available Pt electrode on 2000rpm are displayed in **Figure 2**. The cathodic current on Pt-CeO_2 composite electrode was observed. This indicates that
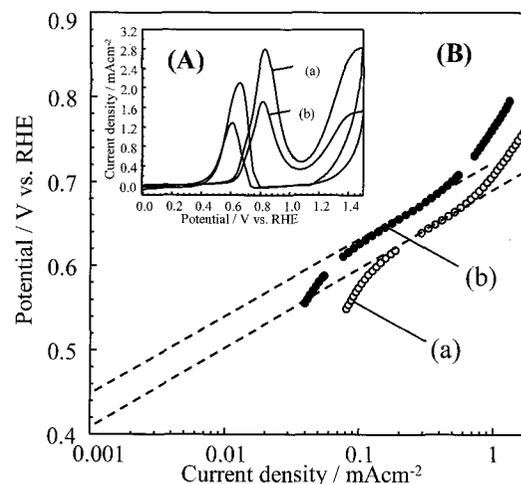

Figure 1 Cyclic voltammograms (A) and tafel plots (B) of methanol oxidation reaction on Pt-CeO_2 composite electrode (a) and commercially available Pt-Ru alloy electrode (b) at 28°C. Sweep rate: 50mV/s.
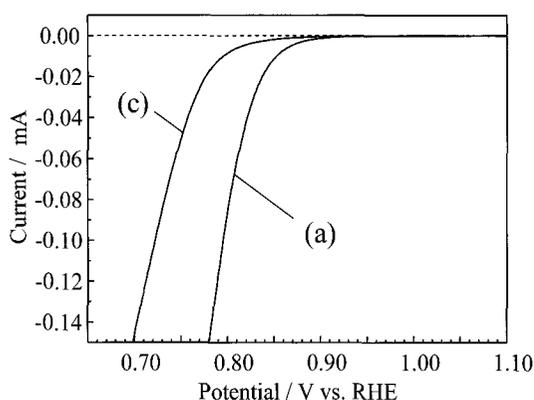
Figure 2 Potential-current curves of oxygen reduction reaction on Pt-CeO₂ composite electrode (a) and commercially available Pt electrode (c) at 28°C. Sweep rate: 10mV/s. Rotation rate: 2000rpm.

Pt-CeO₂ composite electrode shows a stable activity of oxygen reduction reaction. Moreover, the cathodic current at a constant potential on Pt-CeO₂ composite electrode was higher than that on Pt electrode. This result tells that the onset potential of oxygen reduction reaction on Pt-CeO₂ composite electrode shifts to a higher potential side as compared with that on Pt electrode.

The tafel plots of oxygen reduction reaction were demonstrated in **Figure 3**. Two kinds of tafel slopes recorded from Pt-CeO₂ composite electrode and Pt electrode were observed. In the case of Pt electrode, the tafel slopes of the high potential region and low potential region were -64mV/decade and -128mV/decade, respectively. These values agreed with the tafel slopes of the previously reported data on Pt electrode well.[7-8] The tafel slopes recorded from Pt-CeO₂ composite electrode (-58mV/decade and

-113mV/decade) were comparable to that recorded from Pt electrode. It suggests that the oxygen molecule completely reduces on Pt-CeO₂ composite electrode based on four electron process. In addition, the potential at a constant value of $I/(I_d-I)$ on Pt-CeO₂ composite electrode was higher than that on Pt electrode. This indicates that the onset potential of oxygen reduction reaction on Pt-CeO₂ composite electrode shifts to a higher potential side. Since the onset potential on cathode must be high level for a design of high quality cathode materials, it is concluded that the cathode performance on Pt-CeO₂ composite electrode is improved by the interaction between Pt and CeO₂ on our composite electrode.

3.3 Surface composition of Pt in Pt-CeO₂ composite electrode

Figure 4 presents XPS spectra of Pt4f recorded from Pt-CeO₂ composite electrode, Pt-Ru alloy electrode and Pt electrode. The binding energies of Pt4f spectra recorded from aforementioned electrodes are summarized in **Table 1**. The Pt4f spectra showed two doublets from the spin-orbital splitting of the $4f_{7/2}$ and $4f_{5/2}$ states. The binding energies of Pt$4f_{7/2}$ peak recorded from Pt-Ru alloy electrode and Pt electrode were 71.4eV and 71.2eV, respectively. The binding energy of Pt4f peak observed from Pt electrode in the present study was almost same as previously reported one.[9] However, that of $4f_{7/2}$ peak of Pt-Ru alloy was slightly higher than that of Pt electrode. This suggests that the density of valence electron $(5d)$ on Pt surface in Pt-Ru alloy electrode is lower than that in Pt electrode. This small change on the Pt surface of Pt-Ru alloy would contribute to a lowering of CO poisoning effect of Pt electrode. On the other hand, two kinds of binding energies of Pt$4f_{7/2}$ peak were observed from the surface of Pt-CeO₂ composite electrode. The observed binding energies of Pt$4f_{7/2}$ peak were 71.1eV and 72.6eV. The lower binding energy of
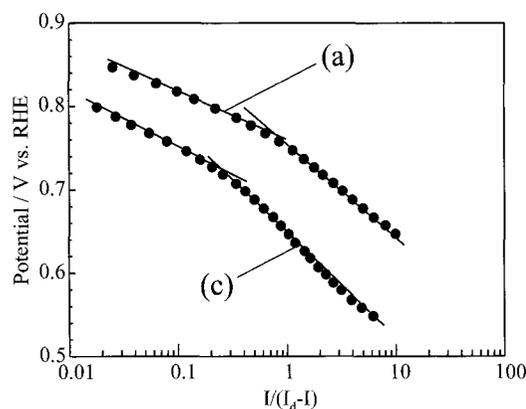

Figure 3 Tafel plots of oxygen reduction reaction on Pt-CeO₂ composite electrode (a) and commercially available Pt electrode (c) at 28°C. I is current and I_d is limiting current. Sweep rate: 10mV/s. Rotation rate: 2000rpm.
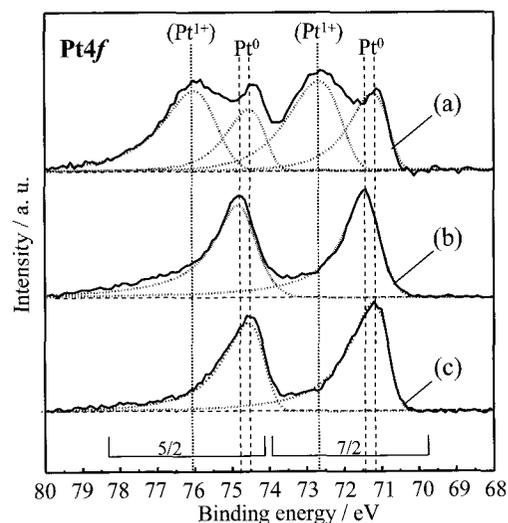

Figure 4 XPS spectra of Pt4f recorded from Pt-CeO₂ composite electrode (a), Pt-Ru alloy electrode (b) and Pt electrode (c).

Table 1 Binding energies of Pt4f spectra recorded from Pt-CeO₂ composite electrode, Pt-Ru alloy electrode and Pt electrode.

Electrodes	Binding energies			
	Pt4$f_{7/2}$		Pt4$f_{5/2}$	
	eV	eV	eV	eV
Pt-CeO₂	71.1	72.6	74.4	76.0
Pt-Ru	71.4	-	74.8	-
Pt	71.2	-	74.6	-

Pt4$f_{7/2}$ peak observed from Pt-CeO₂ composite electrode corresponds to metallic Pt (Pt^0) on Pt electrode. The peak position of higher binding energy of 4$f_{7/2}$ was in a middle between metallic Pt (Pt^0) and di-valent Pt (Pt^{2+}: 73.8eV).[10] This indicates that the higher binding energy of 4$f_{7/2}$ peak observed from Pt-CeO₂ composite electrode corresponds to mono-valent Pt (Pt^{1+}). Based on this observation, we conclude that the density of valence electron (5d) on Pt surface of Pt-CeO₂ composite electrode is much lower than that of Pt-Ru alloy and Pt electrodes. That valence electron density would be drastically decreased by an interaction between Pt and CeO₂ in our composite electrode.

As mentioned in the introduction section, the performance of Pt was lowered by CO poisoning effect. On this Pt electrode, the electron back-donation from Pt 5d orbital to CO 2π* orbital makes the bond strength between Pt and CO quite strong. On the Pt surface of Pt-CeO₂ composite electrode, the electron back-donation would be conspicuously decreased by a lowering of 5d electron density on Pt surface of Pt-CeO₂ composite electrode. This means that the bond strength of Pt-CO on the surface of our composite electrode is much lower than that of Pt-Ru alloy and Pt electrodes. As a consequence, we conclude that the anode performance on Pt-CeO₂ composite electrode becomes better than that on Pt-Ru alloy and Pt electrodes.

Watanabe et al.[7] reported that the rate-determining step for oxygen reduction reaction on Pt electrode was an adsorption step of O₂ molecule accompanied with an electron transfer from O₂ molecule to Pt surface. In the present study, the electron transfer in the rate-determining step would be increased by a lowering of 5d electron density on Pt surface of Pt-CeO₂ composite electrode. The reduction of O₂ molecule on Pt surface of Pt-CeO₂ composite electrode becomes easier than that of Pt electrode. Therefore, it is concluded that the cathode performance on Pt-CeO₂ composite electrode is superior to that on Pt electrode.

Based on all observed results, it is concluded that the interaction between Pt and CeO₂ plays a key role for improvement of anode and cathode performance on Pt-CeO₂ composite electrode. We expect that the anode and cathode performance on Pt-CeO₂ composite electrode will be maximized by a design of interface between Pt and CeO₂ on the surface of our composite electrodes.

4. SUMMARY

We examined the anode and cathode performance on synthesized Pt-CeO₂ composite electrode for development of high quality anode and cathode in DMFCs. Pt-CeO₂ composite electrode was synthesized by a combined process of precipitation and coimpregnation methods. The electrochemical activities of methanol oxidation reaction and oxygen reduction reaction on synthesized Pt-CeO₂ composite electrode were investigated by cyclic voltammetry and hydrodynamic voltammetry experimentation. The surface composition of Pt in electrodes was also characterized by high-energy synchrotron radiation X-ray photoelectron spectroscopy analysis. It was found that the anode performance on Pt-CeO₂ composite electrode for methanol oxidation reaction was superior to that on the commercially available Pt-Ru alloy electrode. The cathode performance of our composite electrode became better than that of the commercially available Pt electrode. In addition, the surface composition of Pt in Pt-CeO₂ composite electrode was quite different from that in Pt-Ru alloy electrode and Pt electrode. The 5d-electron density on Pt surface of Pt-CeO₂ composite electrode was much lower than that of Pt-Ru alloy electrode and Pt electrode. That 5d-electron density would be drastically decreased by an interaction between Pt and CeO₂ in our composite electrode. Therefore, it is concluded that the interaction between Pt and CeO₂ plays an important role for enhancement of anode and cathode performance on Pt-CeO₂ composite electrode.

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