

Synthesis and anode property of Pt-CeO₂ electrode materials for direct methanol fuel cells applications

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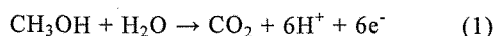
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The nano-size Pt-CeO₂ anode materials supported by carbon black (CB) were prepared using combined process of co-precipitation and impregnation methods. The morphology and size of CeO₂ particle were changed by preparation condition. The nano-size round shaped CeO₂ particles (approximately 40nm) could be obtained. The current density for methanol oxidation on the Pt-CeO₂/CB with round shaped CeO₂ particles was much higher than that on the Pt-CeO₂/CB with mixed shape CeO₂ particles. The onset potential on aforementioned anode shifted to a lower potential. It is concluded that a control of morphology of CeO₂ particle in Pt-CeO₂/CB anode is important for a decrease of the onset potential and an improvement of methanol oxidation activity. In addition, the onset potential on Pt-CeO₂/CB anode was lower than that on commercially available Pt-Ru/CB anode. The activation energy of this anode was lower than that of the Pt-Ru/CB anode. These results indicate that the anode performance of the Pt-CeO₂/CB at operation temperature (80°C) of fuel cells is higher than that of the Pt-Ru/CB anode. The rare earth Ru is not required in the present anode material. Also, it would be able to reduce the Pt content in our anode. Therefore, it is concluded that the Pt-CeO₂/CB anode in the present study will be one of promising anode materials for development of direct methanol fuel cells.

Key words: Pt-CeO₂ nano particle, methanol oxidation, onset potential, anode material, direct methanol fuel cells

1. INTRODUCTION

Polymer membrane fuel cells (PMFCs) have been expected as a next power generation system for clean and efficient power source for generating electricity from hydrogen. However, PMFCs have the problems of production, storage, and distribution of hydrogen. An alternative to the use of hydrogen as fuel is methanol which is a liquid fuel easy to handle. There is no need to use a reformer system, which make it easier to design a small and lightweight fuel cell. Direct methanol fuel cells (DMFCs) are being especially developed for the portable system applications such as the mobile phone. The overall electrochemical reaction for methanol oxidation is expressed by Eq. (1).



The standard electrode potential for methanol oxidation is 0.016V vs. standard hydrogen electrode at 25°C.¹⁻² However, Pt anode needs a high overpotential (approximately 0.6V) because it is difficult to oxidize the strongly adsorbed carbon monoxide (CO) as reaction intermediate on Pt surface. To decrease the overpotential, the Pt based alloy electrodes with transition metal

additives such as Ru,¹⁻² Sn,³ Ni,⁴ or Fe⁵ were developed. The overpotential of methanol oxidation on Pt-Ru or Pt-Sn alloy anode shifted to a lower potential as compared with that on Pt anode. Watanabe et al.¹ reported that the onset potential for methanol oxidation on Pt-Ru alloy anode was approximately 0.4V recorded from cyclic voltammetry with in-situ ATR-FTIR. But the overpotential for methanol oxidation on Pt-Ru alloy anode was still too high for development of high quality anode materials in DMFCs. Ru of second metal was rare metal. It is important to reduce the Pt and Ru content in anode for lowering of environmental burden and production cost. As a consequence, a new high quality anode material with the low onset potential should be identified.

Recently, precious metal such as Pt or Pd supported ceria (CeO₂) has been focused on catalysts for CO oxidation reaction of water-gas shift (WGS) reaction for fuel processing application.⁶⁻⁹ It is well known that the pure CeO₂ is a thermally and chemically stable catalyst with high capacity of oxygen storage and oxygen release. The CeO₂ promotes oxidation of the adsorbed CO on precious metal. Bunluesin et al.⁶ proposed CeO₂ mediated redox process as a key

reaction in the WGS reaction on CeO₂ catalyst. According to Bunluesin et al., CO adsorbed on the precious metal was oxidized by the released oxygen from surface of CeO₂. And CO₂ was formed on the surface of precious metal. Oxygen deficient CeO₂ was oxidized by water-gas. This catalysis can be repeated in the WGS reaction. The activity of precious metal supported by CeO₂ for the WGS reaction was higher than that of precious metal supported by non-redox materials like alumina and silica.⁶⁻⁷ The authors expected that the redox reaction on CeO₂ surface can be used for enhancement of CO oxidation on Pt electrode.

In the present study, to reduce the overpotential for methanol oxidation reaction, the Pt-CeO₂ anodes supported by carbon black (CB) were synthesized and methanol oxidation reaction on aforementioned anode materials was examined.

2. EXPERIMENTAL

Pt-CeO₂ anode materials supported by CB were synthesized using a combined process of precipitation and co-impregnation methods. To impregnate Pt particles on pure CeO₂ particles, H₂PtCl₆·6H₂O (Purity: ≥98.5%, Kishida Chemical Co.), synthesized pure CeO₂ particles, and CB (Vulcan XC-72R, Cabot Co.) particles were dispersed into ethanol. The mixture was dried at room temperature in N₂ gas flow. The dried powder was reduced at 400°C for 2h in mixed gas H₂ (10%) and He (90%) flow. The content of Pt particles was 30% by weight in the mixture of Pt,

CeO₂, and CB. Pt/Ce atomic ratio was 1.4. Commercially available 30wt.%Pt+15wt.%Ru supported by CB (Pt:Ru atomic ratio of 1:1, Johnson Matthey Company, USA) was examined for comparison of anode property difference between the Pt-Ru/CB and synthesized Pt-CeO₂/CB anodes.

In the present study, the pure CeO₂ particles were synthesized using ammonium carbonate precipitation method. The starting materials used were Ce(NO₃)₃·6H₂O (Purity: >99.99, Kanto Chemical Co.) and (NH₄)₂CO₃ (Ultrapurity, Wako Pure Chemical Ind.). The Ce(NO₃)₃·6H₂O powder (7.57g) was dissolved into distilled water (174ml). To prepare the homogeneous precipitation, this solution was dropped into 0.25M (NH₄)₂CO₃ solution (174ml) which was heated at 75°C under mild stirring for 1h or 96h. After repeated washing, the precipitate was dried at room temperature in N₂ gas flow. Also the dried powder was calcined at 800°C for 2h in O₂ gas flow.

The morphology and size of Pt-CeO₂/CB anode were observed using field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM). Platinum, cerium, and carbon particles in the anode materials were detected using energy dispersive spectrometer (EDS).

The anode property of synthesized Pt-CeO₂/CB anodes was examined by cyclic voltammetry (CV) and chronoamperometry (CA) experimentation.

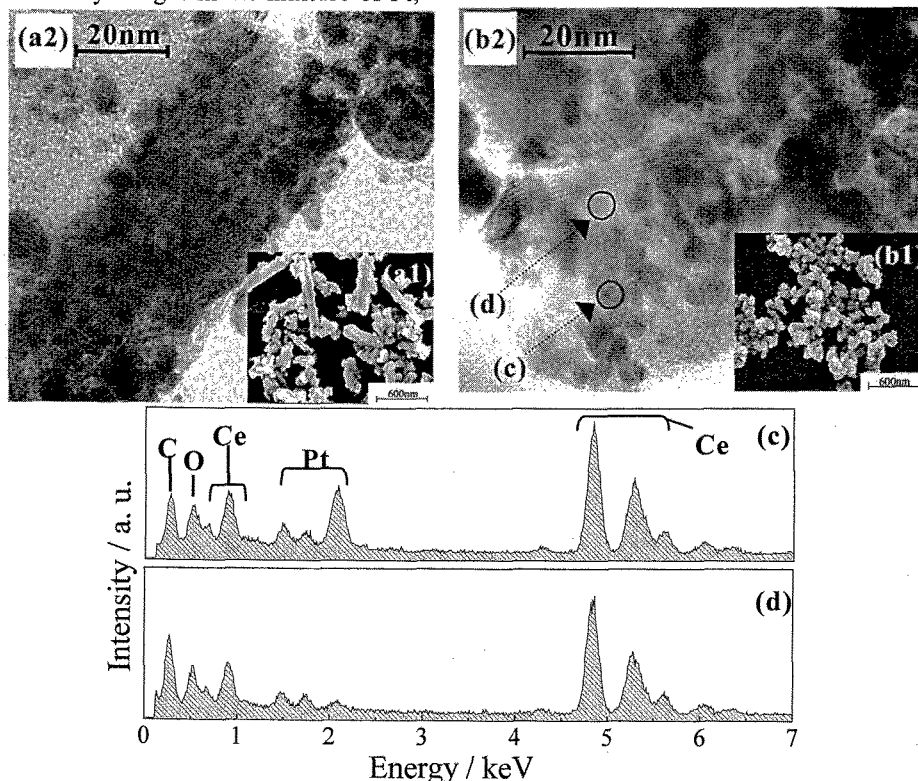


Fig. 1 a1) and b1): SEM images of calcined CeO₂ particles, a2) and b2): TEM images of Pt-CeO₂/CB particles, c) and d): EDS profiles of Pt-CeO₂/CB particles. Aging time at 75°C for preparation of CeO₂ in a1): 1h, aging time at 75°C for preparation of CeO₂ in b1): 96h. The arrow line indicates the analysis area by EDS.

The measurement carried out in a mixed solution of 0.5M H₂SO₄ aqueous solution and 0.5M CH₃OH aqueous solution. Pt foil and Ag/AgCl were used as counter and reference electrodes, respectively. The anode materials were suspended into CH₃OH aqueous solution (2mg/ml). The suspension was spread onto the surface of Au electrode (area: 0.20cm²) using a micro-pipette. Amount of the anode materials spread was 0.01mg. The measured potentials were converted to the reversible hydrogen electrode (RHE) scale. The current density as a function of RHE (V vs. RHE) was plotted after cyclic measurements of 30 times in CV experimentation for examination of electrode performance. The current density was normalized to the Pt surface area calculated from the charge of desorbed hydrogen in 0.5M H₂SO₄ aqueous solution, using 210μC/cm² as the conversion factor. To estimate activation energy on anode, the current density for methanol oxidation was measured at electrolyte temperature between 40°C to 60°C after 10min at 0.6V in CA experimentation.

3. RESULT AND DISCUSSION

3.1 Preparation of Pt-CeO₂/CB anode

Figure 1 displays particle morphology, particle size and element analysis of our anode materials using FE-SEM and TEM. In SEM images, The CeO₂ particles which consisted of both elongated and round shaped particles (Fig. 1(a1)) were observed when the precipitation was formed at 75°C for 1h of aging time. To prepare the nano-size round shaped CeO₂ particles, the precipitation was formed at 75°C for 96h of aging time. The only round shaped CeO₂ particles were obtained, as shown in Fig. 1(b1). The average particle size of this CeO₂ (40nm) was smaller than that of the round shaped CeO₂ (60nm) in aforementioned CeO₂ particles (Fig. 1(b2)). It was found that the morphology and size of CeO₂ particle were controllable by a change of aging time. In TEM images, the black color particles (5-10nm) and the gray color particles were observed. To observe the distribution of Pt particles on CeO₂ particle, the element analysis was performed using EDS. The Pt/Ce ratio of EDS profiles between black color particle (Fig. 1(c)) and gray color particle (Fig. 1(d)) was different. The much amount of Pt was detected on the black color particle. These results indicate that the black color particle and gray color particle are Pt and CeO₂, respectively. It is found that Pt particles in these Pt-CeO₂/CB anodes are dispersed on CeO₂ particle well.

3.2 Methanol oxidation on Pt-CeO₂ anode material

Figure 2 shows cyclic voltammograms of methanol oxidation on two kinds of Pt-CeO₂/CB anodes and commercially available Pt-Ru/CB anode at 28°C in the mixed solution of 0.5M H₂SO₄ aqueous solution and 0.5M CH₃OH aqueous solution. The anodic peaks for methanol oxidation reaction appeared on three kinds of

anodes in forward and return sweeps. In forward sweep, the peak current density of the Pt-CeO₂/CB anode with round shaped CeO₂ particles for methanol oxidation was higher than that of the Pt-CeO₂/CB anode with mixed shape CeO₂ particles. Moreover, the peak current density of the Pt-round shaped CeO₂/CB anode was 1.5 times bigger than that of the commercially available Pt-Ru/CB anode. However, the most important thing for development of high quality anode material is lowering of onset potential of methanol oxidation reaction.

Figure 3 presents the onset potential of methanol oxidation reaction on the Pt-CeO₂/CB and the Pt-Ru/CB anodes in the forward sweep of cyclic voltammograms. The measured onset potential on the Pt-mixed shape CeO₂/CB, Pt-round shaped CeO₂/CB and Pt-Ru/CB anodes were 0.51V, 0.43V and 0.46V at 0.02mA/cm²Pt, respectively. The onset potential on Pt-round shaped CeO₂/CB anode shifted to a lower potential as compared with that on the Pt-mixed shape CeO₂/CB anode. This result indicates that a control of particle morphology of CeO₂ particle in Pt-CeO₂/CB anode is important for a decrease of the onset potential and an improvement of

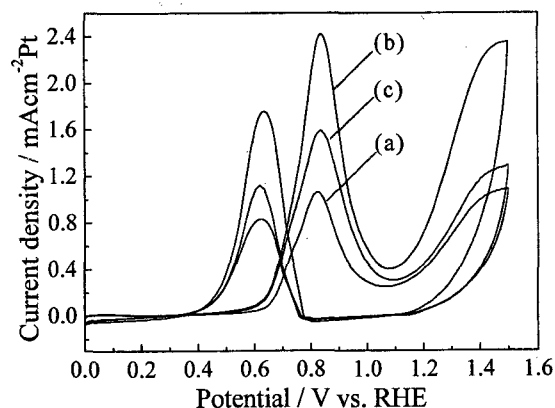


Fig. 2 Cyclic voltammograms of (a): Pt-mixed shape CeO₂/CB anode, (b): Pt-round shaped CeO₂/CB anode and (c): commercially available Pt-Ru/CB anode in forward and return sweeps.

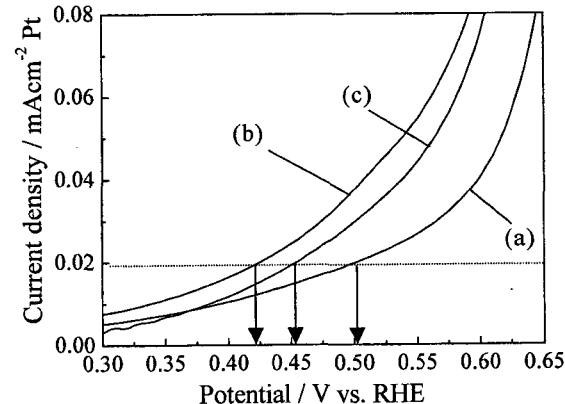


Fig. 3 Cyclic voltammograms of (a): Pt-mixed shape CeO₂/CB anode, (b): Pt-round shaped CeO₂/CB anode and (c): commercially available Pt-Ru/CB anode in forward sweep.

methanol oxidation activity. In addition, the onset potential of the Pt-round shaped CeO₂/CB was lower than that of the Pt-Ru/CB anode. It is concluded that the anode performance of the aforementioned Pt-CeO₂/CB is superior to that of the Pt-Ru/CB. These results indicate that it is possible to reduce Pt and Ru content in anode materials for lowering of environmental burden and production cost.

3.3 Temperature dependence for methanol oxidation

Figure 4 shows temperature dependence of current density of methanol oxidation on the three kinds of anodes. The activation energies of Pt-mixed shape CeO₂/CB anode, Pt-round shaped CeO₂/CB anode and Pt-Ru/CB anode were 97kJ/mol, 59kJ/mol, and 66kJ/mol, respectively. The activation energies of previously reported Pt-Ru alloy anodes were from 60 to 95kJ/mol.¹⁰⁻¹³ The previously reported activation energies of Pt-Ru alloy anodes almost agreed with the value of Pt-Ru anode in the present study. In Fig. 4, the activation energy of Pt-round shaped CeO₂/CB anode was lower than that of Pt-Ru/CB anode. The current density on this anode for methanol oxidation was the highest among three kinds of anodes at whole measurement temperature. From these results, it is concluded that the anode performance of Pt-round shaped CeO₂/CB at operation temperature of fuel cells (80°C) is higher than that of the commercially available Pt-Ru/CB.

4. SUMMARY

The authors investigated anode performance of the Pt-CeO₂/CB for development of high quality anode in DMFCs. This anode was synthesized using a combined process of precipitation and co-impregnation methods. To develop the Pt-CeO₂/CB anode, the characterization of the Pt-CeO₂/CB anode was examined using FE-SEM, TEM, and EDS. The electrochemical activity of methanol oxidation reaction was also examined. The morphology and size of CeO₂ particles were

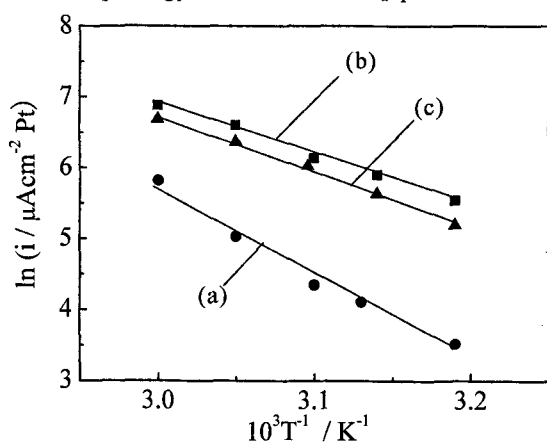


Fig. 4 Temperature dependence on current density of methanol oxidation on (a): Pt-mixed shape CeO₂/CB anode, (b): Pt-round shaped CeO₂/CB anode and (c): commercially available Pt-Ru/CB anode at 0.6V.

changed by preparation condition. The round shaped CeO₂ particles (approximately 40nm) could be obtained. The peak current density for methanol oxidation on Pt-CeO₂/CB anode with round shaped CeO₂ particles was much higher than that on Pt-CeO₂/CB anode with mixed shape CeO₂ particles. The onset potential on aforementioned anode shifted to a lower potential as compared with that on Pt-CeO₂/CB anode with mixed shape CeO₂ particles. It is concluded that a control of particle morphology of CeO₂ particle in Pt-CeO₂/CB anode is important for a decrease of the onset potential and an improvement of methanol oxidation activity. In addition, the onset potential of our anode was lower than that of commercially available Pt-Ru/CB anode. Also, the activation energy of our anode for methanol oxidation was lower than that of the Pt-Ru/CB anode. These results indicate that the anode performance of the Pt-CeO₂/CB anode at operation temperature (80°C) of fuel cells is higher than that of the Pt-Ru/CB anode. The high performance and low cost anode could be obtained by using nano size CeO₂ particles instead of Ru as rare metal. Therefore, it is expected that the Pt-CeO₂/CB anode in the present study will be one of promising anode materials for development of direct methanol fuel cells.

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