Minimization of Pt content in Pt-CeO$_2$ composite anode

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Direct methanol fuel cells (DMFCs) are attracting much attention as clean and efficient power sources. Pt-Ru alloy anode has been developed for industrial applications. However, the resources of both Pt and Ru are limited on our planet. In the present work, Pt-CeO$_2$ composite anodes were prepared. We examined the influence of surface activity of substrate CeO$_2$ on anode performance of Pt-CeO$_2$ composites for development of high quality anodes in DMFCs. The surface area of CeO$_2$ particles was changed by a control of dropping speed of cerium nitrate aqueous solution into ammonium carbonate aqueous solution. The peak current density of methanol oxidation on Pt(30wt%)-CeO$_2$ composite anodes increased with an increase of surface area of CeO$_2$ up to 51m^2/g. The current density of Pt(30wt%)-CeO$_2$ (CeO$_2$: 51m^2/g) composite anode was 1.8 times higher than that on commercially available Pt-Ru alloy anode. On the other hand, the current density of Pt(5wt%)-CeO$_2$ (CeO$_2$: 51m^2/g) was also higher than that on Pt-Ru alloy anode. Those results indicate that the anode performance on Pt-CeO$_2$/CB can be maximized and Pt content in Pt-CeO$_2$/CB can be minimized by a design of interface between Pt and active CeO$_2$.
Key words: DMFC, Pt-CeO$_2$ composite anode, anode property, methanol oxidation reaction, cyclic voltammetry

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are attracting much attention as clean power sources for electric vehicles or residences.[1] However PEFCs require the use of pure hydrogen as the fuel. And the transportation of high-purity hydrogen has not been met yet. Direct methanol fuel cells (DMFCs) are attracting much attention as power sources for potable system applications. An alternative to the use of hydrogen as fuel is methanol which is much easier to handle and store.

The standard electrode potential for the methanol oxidation reaction is 0.016 V versus the standard hydrogen electrode at 25°C.[2, 3] However, an absorbance of carbon monoxide (CO) on the surface of the Pt anode introduces a very large over potential (approximately 0.6 V). To decrease the onset potential of methanol oxidation reaction, the anodes based on Pt alloys with transition metal additives such as Ru[2-5] have been developed. The onset potential of methanol

Table 1 Preparation condition and specific surface area of CeO$_2$.

| CeO$_2$ | Preparation condition | | | | Specific surface area / m^{2}g^{-1} |
	Temp. / °C	Time. / h	Dropping time / min	Calcine temp. / °C	
(A)	55	24	60	400	51
(B)	75	96	60	800	20
(C)	75	96	60	1000	11
(D)	58	24	90	400	86

oxidation reaction on the Pt-Ru alloy anode shifts to a lower potential side as compared with that on a pure Pt anode. However, the onset potential on the Pt-Ru alloy anode is still high. In addition, the limited resources of Pt and Ru in ore bodies on the planet will make the cost of large-scale production expensive and so it is imperative that the Pt and Ru contents of any potential electrode be reduced to a minimum. To overcome those problems, Pt-oxide anode materials such as Pt-SnO$_2$ or Pt-WO$_3$ have been reported.[6, 7] However, the onset potential of methanol oxidation reaction on these anodes is higher than that of the Pt-Ru alloy anode. As a consequence, a development of new environmental friendly anode material with a low onset potential and a high current density is required.

In the present study, we proposed the Pt-CeO$_2$/carbon black (CB) anode material. To decrease the onset potential and Pt content in anode, the influence of specific surface area of CeO$_2$ and Pt content in Pt-CeO$_2$ composite anode on anode properties was examined.

2. Experimental Procedure

Pure CeO$_2$ particles were synthesized using the ammonium carbonate precipitation method. The starting materials were Ce(NO$_3$)$_3$·6H$_2$O (Purity: > 99.99%, Kanto Chemical Co.) and (NH$_4$)$_2$CO$_3$ (Ultrahigh purity, Wako Pure Chemical Ind.). The Ce(NO$_3$)$_3$·6H$_2$O powder (7.57g) was dissolved into distilled water (174ml). To prepare the homogeneous precipitation, this solution was dropped into 0.25M (NH$_4$)$_2$CO$_3$ solution (174ml) for 60min or 90min, which was heated at 55°C to 75°C while undergoing mild stirring for 24h to 96h. After repeated washing, the precipitate was dried at room temperature in N$_2$ gas flow before being calcined at 400°C-1000°C for 2h in O$_2$ gas flow. The specific surface area and average pore size of synthesized CeO$_2$ particles were summarized in **Table 1**.

Pt-CeO$_2$ anode materials supported by CB were synthesized using a combined process of precipitation and co-impregnation methods. To impregnate Pt particles on pure CeO$_2$ particles, H$_2$PtCl$_6$·6H$_2$O (Purity: ≥ 98.5%, Kisida Chemical Co.) and synthesized pure CeO$_2$ particles were dispersed in ethanol. The mixture was dried at room temperature under an argon atmosphere in a glove box with less than 10ppm H$_2$O. The dried powder was reduced at 400°C (a-d) or 350°C (f-h) for 2h in a mixed gas H$_2$ (10%) and He (90%) flow. The prepared Pt-CeO$_2$ and CB (Vulcan XC-72R, Cabot Co.) particles were dispersed in ethanol. The

Table 2 Characteristic properties of Pt-CeO$_2$ composite anodes.

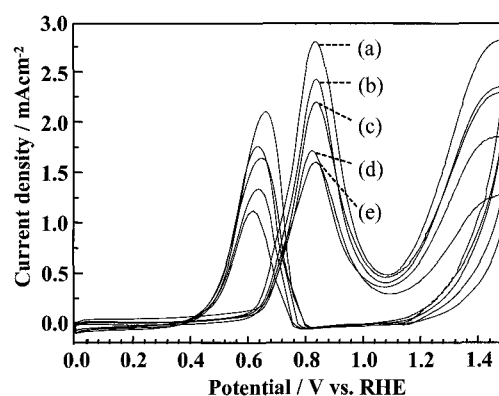| Anode	Pt content / wt%	Pt particle size / nm	Specific surface area of CeO$_2$ / m^{2}g^{-1}
(a)	30	8	51
(b)	30	8	20
(c)	30	7	11
(d)	30	16	86
(f)	10	9	51
(g)	5	4	51
(h)	3	4	51

Figure 1 Cyclic voltamograms of methanol oxidation reaction on Pt(30wt%)-CeO$_2$ composite anodes (a-d) and commercially available Pt-Ru alloy anode (e). (a-d): Reduction temperature of the anodes is 400°C. Specific surface area of CeO$_2$ in Pt(30wt%)-CeO$_2$ composite anodes: (a) 51m^2/g, (b) 20m^2/g, (c) 11m^2/g and (d) 86m^2/g.
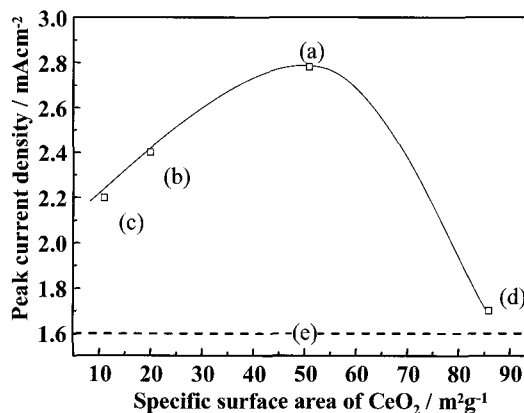

Figure 2 Relationship between specific surface area of CeO$_2$ and peak current density of methanol oxidation reaction on Pt-CeO$_2$ composite anodes (a-d), and peak current density of methanol oxidation reaction on commercially available Pt-Ru alloy anode (e).

mixture was dried at room temperature in N$_2$ gas flow.

The content of Pt particles was 30%, 10%, 5% and 3% by weight in the mixture of Pt, CeO_2 and CB. We compared the performance of these anodes with that of a commercially available Pt-Ru/Carbon (C) anode (Pt:Ru atomic ratio of 1:1, Pt: 30wt%, Ru: 15wt%, Johnson Matthey Co.). The characteristic properties of Pt-CeO_2 composite anodes were summarized in **Table 2**. The anode properties of Pt-CeO_2/CB and Pt-Ru/C were examined by cyclic voltammetry (CV). Pt foil and Ag/AgCl were used as counter and reference electrodes, respectively. The measurement was carried out in a mixed solution of 0.5M H_2SO_4 solution and 0.5M methanol solution. The measured potential was converted to the reversible hydrogen electrode (RHE) scale. The Pt surface area was calculated by the CO stripping method.[8]

3. Results and Discussion

3.1 Influence of specific surface area of CeO_2 on anode performance

To compare the anode performance of Pt-CeO_2 composite anodes with that of commercially available Pt-Ru alloy anode, the cyclic voltamograms of methanol oxidation reaction on Pt-CeO_2 composite anodes and Pt-Ru alloy anode is shown in **Figure 1**. The peak current density of methanol oxidation on the four kinds of Pt-CeO_2 composite anodes (a-d) was much higher than that on Pt-Ru alloy anode (e). Moreover, the peak current density of methanol oxidation on Pt-CeO_2 composite anode (a) was 1.8 times higher than that on Pt-Ru alloy anode. **Figure 2** presents the relationship between the specific surface area of CeO_2 in our composite anodes and the peak current density of methanol oxidation. The peak current density on Pt-CeO_2 composite anodes (a-c) increased with increasing specific surface area of CeO_2. However, the peak current density on Pt-CeO_2 composite anode (d) was lower than that on Pt-CeO_2 composite anode (a). The anode (d) (CeO_2: 86m^2/g) consisted of meso-porous structure. The number of interface between Pt particles and CeO_2 particles in Pt-CeO_2 composite anode (d) would not be increased on the meso-porous CeO_2 with high surface area. Therefore, it is concluded that the processing route design for optimization of active interface structure between Pt particles and CeO_2 particles in our composite anode is a key for enhancement of anode performance.

Figure 4 displays the tafel plots of methanol oxidation reaction on Pt-CeO_2 composite anodes and Pt-Ru alloy anode. The tafel slopes of methanol oxidation reaction on Pt-CeO_2 composite anode (a) and
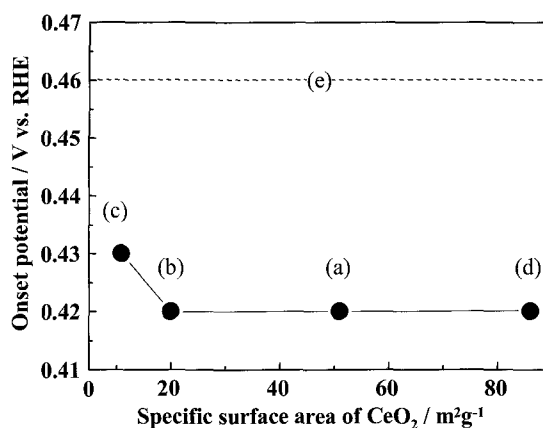
Figure 3 Relationship between specific surface area of CeO_2 and onset potential of methanol oxidation reaction on Pt-CeO_2 composite anodes (a-d), and onset potential of methanol oxidation reaction on commercially available Pt-Ru alloy anode (e).

Pt-Ru alloy anode were 89mV/decade and 112mV/decade, respectively. Tafel slopes of 110-140mV/decade have been reported for Pt-Ru alloy anode.[9-11] The observed tafel slopes on Pt-CeO_2 composite anode agreed with the preciously reported value of Pt-Ru alloy anode. This suggests that proton and electron are catalytically created from methanol on Pt-CeO_2 composite anode as same as Pt-Ru alloy anode. In addition, the onset potential of methanol oxidation reaction on Pt-CeO_2 composite anode (a) shifted to a low potential side as compared with that on Pt-Ru alloy anode. These results tell that the anode performance on Pt-CeO_2 composite electrode is superior to that on Pt-Ru alloy anode.
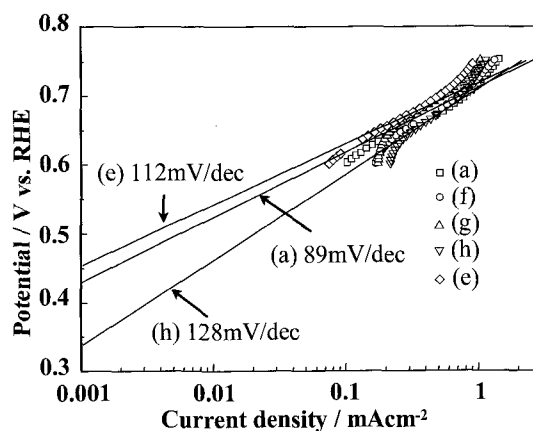
Figure 4 Tafel plots of methanol oxidation reaction on Pt-CeO_2 composite anodes (a, f-h) and commercially available Pt-Ru alloy anode (e).

3.2 An influence of Pt content on anode performance

Figure 5 shows Pt content dependence of peak

current density (A) and onset potential of methanol oxidation reaction (B) on the composite anodes. The peak current density on composite anodes (a, f and g) was higher than that on the Pt-Ru alloy anode. Also onset potential of methanol oxidation on aforementioned anodes was lower than that on composite anodes (a. f and g). Those suggest that Pt content in our composite anode can be lowered from 30wt% to 5wt% in the anodes. We conclude that the interface between Pt and CeO₂ plays a key role to lower Pt content in our composite anode. We expect that careful analysis of interface region between Pt and CeO₂ and optimization of the interface structure in the composite anode will minimize Pt content and maximize anode performance on Pt-CeO₂ composite anode.
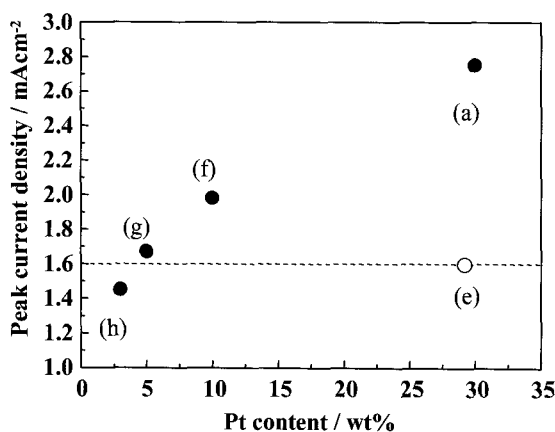

Figure 5(A) Pt content in anodes dependence of peak current density of Pt-CeO₂ composite anodes (a, f, g and h) and   commercially available Pt-Ru alloy anode (e) and peak current density of methanol oxidation reaction on the anodes.
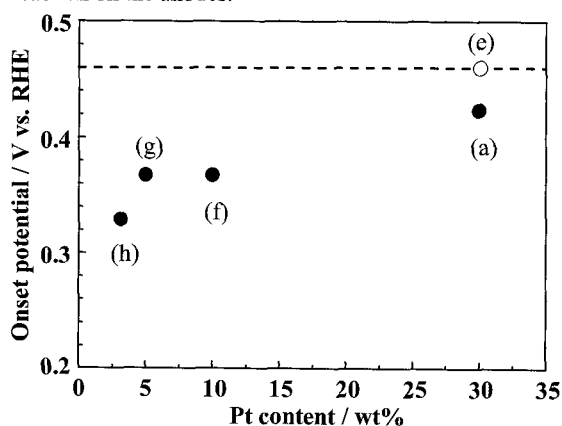

Figure 5(B) Pt content in anodes dependence of onset potential of methanol oxidation reaction of Pt-CeO₂ composite anodes (a, f, g and h) and commercially available Pt-Ru alloy anode (e).

4. Summary

We examined the influence of specific surface area of

CeO₂ on anode performance of Pt-CeO₂ composite anodes to minimize Pt content and maximize anode performance on Pt-CeO₂ composite anode. The peak current density on the composite anode increased with increasing surface area of CeO₂ up to 51m²/g of specific surface area. But the peak current density was lowered when the specific surface are of CeO₂ over 51m²/g. The peak current density of methanol oxidation on Pt-CeO₂ (CeO₂: 51m²/g) composite anode (a) was 1.8 times higher than that on the commercially available Pt-Ru alloy anode. But this peak current density decreased with decreasing the specific surface area of CeO₂ in the composite anode. This indicates that a careful design of interface between Pt and CeO₂ is important for development of high quality composite anodes. In addition, we examined the influence of Pt content in the composite anodes on anode performances (i.e. onset potential and peak current density). Since the performance on 5wt% Pt loaded CeO₂ was better than Pt(30wt%)-Ru alloy anode, we concluded that Pt contents in the composite anodes can be lowered from 30wt% to 5wt%. Also we expect that the anode performance on 5wt% Pt loaded CeO₂ composite anode will be improved by a careful analysis and optimization of interface structure between Pt and CeO₂ in our anodes.

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