

Anode properties of Pt-CeO₂ composite electrode materials for direct methanol fuel cells application

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A Pt on nano-sized CeO₂ particles which in turn are supported on carbon black (CB) was synthesized using co-impregnation method. The electrochemical activity of methanol oxidation reaction on the composite anode Pt-CeO₂/CB was investigated using cyclic voltammetry and chronoamperometry experimentation. The onset potential of methanol oxidation reaction on the Pt-CeO₂/CB anodes was shifted to a lower potential as compared with that on commercially available Pt-Ru/Carbon (C) alloy anode. In addition, the activation energy of the Pt-CeO₂/CB anode was much lower than that of the Pt-Ru/C alloy anode at temperature between 28°C to 60°C. Moreover, the composite anode showed better stability of performance in a cycle test as compared with that of the Pt-Ru/C alloy anode. Importantly, the rare metal, Ru is not required in the present anode material and the amount of Pt required would be also significantly reduced. Based on those results, we expect that our composite anode will be one of promising new anode materials for fuel cell applications.

Key words: Pt-CeO₂, composite anode, on-set potential, hetero interface, fuel cell application, high stability

1. Introduction

Polymer membrane fuel cells (PMFCs) have the potential to be the next generation power production system for clean and efficient generation of electricity from hydrogen. However, at this point in time, PMFCs require the use of pure hydrogen as the fuel and the challenges associated with production, storage and transportation of high purity hydrogen have not been met. An alternative to the use of hydrogen as fuel is methanol (CH₃OH). This easily handled liquid fuel has the possibility of being used directly without the usual reforming process—the direct methanol fuel cells (DMFCs). This makes such a system particularly attractive for the design of compact light weight systems such as could be used in mobile phones and personal computers.

The standard electrode potential for the methanol oxidation reaction is 0.016V vs. standard hydrogen electrode at 25°C.[1] The difficulty here is that the intermediate reaction, the adsorbance of carbon monoxide (CO) (adsorbed CO is very difficult to oxidize) on the surface of the Pt electrode introduces a very large overpotential (approximately 0.6V). To decrease this overpotential, electrodes based on Pt alloys with transition metal additives such as Ru [1-3] have been developed. The overpotential associated with methanol oxidation on a Pt-Ru alloy anode shifts to a lower potential as compared with that on a pure Pt anode. However, the overpotential on the Pt-Ru alloy anode is still significant enough to restrict its use as an anode

material. 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 content of any potential electrode be reduced to a minimum. Pt-oxide anode materials such as Pt-SnO₂ or Pt-WO₃ have been reported.[4,5] However, the activity of these anodes for methanol oxidation is lower than that of the Pt-Ru alloy anodes. As a consequence, a new anode material with the low over-potential and high current density is required.

In the present study, nano-sized CeO₂ particles with high specific surface area were prepared for a design of high quality Pt-CeO₂/CB composite anodes. The difference of reaction mechanism on the Pt-CeO₂/CB composite anode and Pt-Ru/C alloy anode was concluded. Also, the stability of anode performance on the Pt-CeO₂/CB composite anode and Pt-Ru/C alloy anode 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. The performance of this electrode was compared with that of a commercially available Pt-Ru on carbon (Pt:Ru atomic ratio of 1:1, Pt: 30wt%, Ru: 15wt%, Johnson Matthey Company, USA) electrode material. In the present process, 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 (Ultrahigh purity, 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 55°C or 75°C whilst undergoing mild stirring for 24h or 96h. After repeated washing, the precipitate was dried at room temperature in N₂ gas flow before being calcined at 400 and 800°C for 2h in O₂ gas flow.

The particle size of synthesized Pt-CeO₂/CB was observed using transmission electron microscope (TEM). Platinum, cerium and carbon in the anode materials were identified using an energy dispersive spectrometer (EDS). The average particle size and surface area of active species in anode materials were summarized in Table 1.

Table 1 Chemical and physical properties of anode materials

Sample	Pt (wt%)	Ru (wt%)	Ce (wt%)	Average particle size of Pt (nm)
a	30	-	20	7.5
b	30	15	-	4.5
c	30	-	20	7.5

Sample	Specific surface area of CeO ₂ (m ² /g)
a	51
b	-
c	20

The anode properties of Pt-CeO₂/CB and Pt-Ru/C were examined by cyclic voltammetry (CV) and chronoamperometry (CA). The measurements were carried out in a mixed solution of aqueous 0.5M H₂SO₄ and aqueous 0.5M CH₃OH. Pt foil and Ag/AgCl were used as counter and reference electrodes, respectively. The samples for measurement were prepared from a suspension of the anode material (2mg/ml) in an aqueous CH₃OH solution. The suspension was spread onto the surface of a Au electrode (area: 0.20cm²) using a micro-pipette. The amount of material 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 30 cycles in the cyclic voltammetry experiment. The current density was normalized to the Pt surface area calculated by CO stripping method.[6] To estimate activation

energy for methanol oxidation reaction on the anode, the current density was measured at electrolyte temperature between 40°C to 60°C after 10min at 0.6V in CA experimentation. The cycle test (1200cycle) of anode performance on Pt-CeO₂/CB composite and Pt-Ru/C alloy anodes was examined at a sweep ranging from 0 to 1.2V.

3. Results and discussion

Figure 1 displays particle morphology and , particle size of our composite anodes and commercially available Pt-Ru/C alloy anode using FE-SEM.

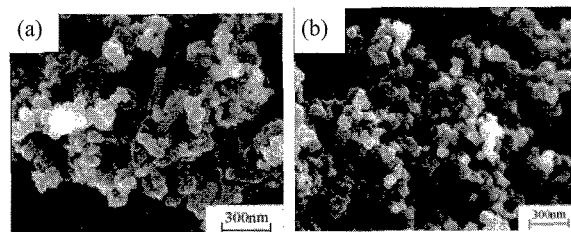


Figure 1 Particle morphologies and particle size of (a): Pt-CeO₂/CB (Sample (a) in Table 1), and (b): commercially available Pt-Ru/C (Sample (b) in Table 1).

In SEM images, the CeO₂ particles which consisted of both elongated and round shaped particles (Fig. 1(a)) were observed in the Pt-CeO₂/CB composite anode. 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. But the specific surface areas of CeO₂ of both specimens were almost same when calcination temperature was the same in each case. Since the authors concluded that the specific surface area of CeO₂ was a key parameter for development of anode materials with high performance, the specific surface area of CeO₂ was controlled using different calcination temperature (Sample (a): 400°C, Sample (c): 800°C) On the other hand, it was hard to observe elongated shaped particles in commercially available Pt-Ru alloy anode. It looks quite homogeneous. (Fig. 1(b)) To observe the distribution of Pt particles on CeO₂ particle, the element analysis was performed using TEM equipped with EDS. This microanalysis indicates that almost all Pt particles were on CeO₂ particles. A quite few Pt particle was on the CB. This tells us that the heterogeneous interface between Pt and CeO₂ is in everywhere on the surface of CeO₂ particles of composite anode.

In Figure 2, we present the cyclic voltammograms of methanol oxidation on the Pt-CeO₂/CB and Pt-Ru/C anodes at 28°C in the mixed aqueous solution of 0.5M H₂SO₄ and 0.5M CH₃OH. In Fig. 2(A), the anodic peaks for methanol oxidation appeared on both Pt-CeO₂/CB and Pt-Ru/C anodes in the forward and reverse sweeps. In the forward sweep, the peak current density of the Pt-CeO₂/CB anode was 1.9 times

larger than that of the Pt-Ru/C anode at the maximum. However, the most important observation which has implications for the development of high quality anode materials is the clear lowering of onset potential for the methanol oxidation reaction. The onset potential of methanol oxidation reaction on the Pt-CeO₂/CB and Pt-Ru/C anodes in the forward sweep of the cyclic voltammograms was shown in **Fig. 2(B)**. The measured onset potential on the Pt-CeO₂/CB composite anode shifted to a lower potential as compared with that on the Pt-Ru/C alloy anode. The values of the onset potential on the Pt-CeO₂/CB (a), Pt-CeO₂/CB (c) and Pt-Ru/C (b) anodes were 0.380V, 0.402V and 0.45V at 0.02mA/cm², respectively.

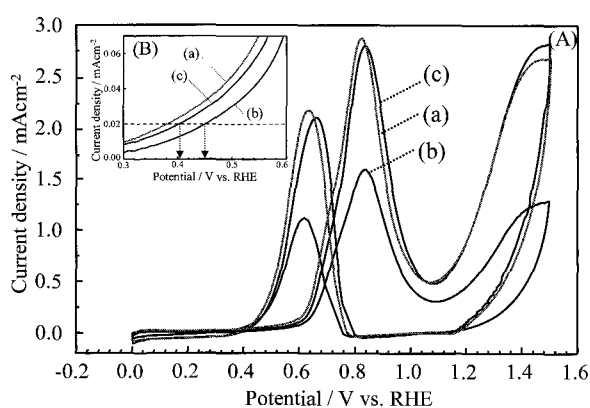


Figure 2 Cyclic voltammograms of methanol oxidation in both forward and reverse sweeps (A) and in forward sweep (B) on Pt-CeO₂/CB anodes (a, c) and commercially available Pt-Ru/C anode (b) at 28°C in the mixed solution of 0.5M H₂SO₄ aqueous solution and 0.5M CH₃OH aqueous solution at 50mV/s.

This clearly indicates that the anode performance of Pt-CeO₂/CB composite anodes is superior to that of the Pt-Ru/C anode.

Figure 3 shows Chronoamperometry results and the temperature dependence of the current density for methanol oxidation on the Pt-CeO₂/CB (Sample (a)) and Pt-Ru/C anodes. The **Fig. 3(B)** was plotted using the current density at 600 seconds in **Fig.3(A)** to estimate the activation energy. The activation energy of the Pt-CeO₂/CB anode was lower than that of the Pt-Ru/CB anode in whole measurement temperature region. The activation energies of the Pt-CeO₂/CB and Pt-Ru/C anodes were 32kJ/mol and 66kJ/mol, respectively. Also the measured activation energy of Pt-Ru/C alloy anode agreed with the previously reported activation energies for Pt-Ru alloys. This suggests that our measurement is consistent with previous experimentation and the anode performance of the Pt-CeO₂/CB at the usual operation temperature (80°C) of a fuel cell is superior to that of the more standard Pt-Ru/C systems.

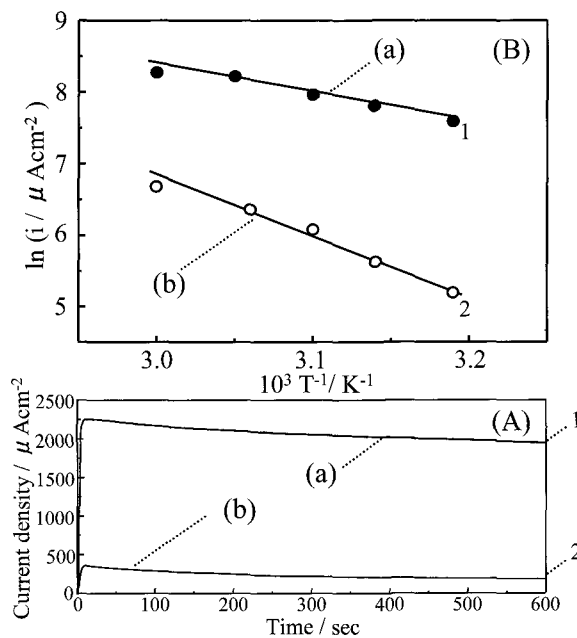


Figure 3 Chronoamperometry results (A) and the temperature dependence of the current density (B) for methanol oxidation on the Pt-CeO₂/CB (Sample (a) in Table 1) and Pt-Ru/C (Sample (b) in Table1) anodes.

Based on the series of the results, the following anode reaction mechanism was considered. Oxygen vacancies made the surface of CeO₂ activated under applied potential. The H₂O molecule was adsorbed to the active sites of oxygen vacancies. (Step I) The electron between O and H was drawn to Ce sites in CeO₂, the bonding strength between H and OH was consequently decreased and H₂O was converted to OH at the active oxygen vacancy sites. (Step II) Then OH was converted to active O atm at the same site. (Step III) The active oxygen atom was diffused to the adsorbed CO on Pt atom, the CO on Pt was oxidized to CO₂ by the active O released from CeO₂. (Step IV) These electrode catalysts returned to the original oxygen vacancy structure. This cycle reaction (Step I -> Step IV -> Step I) proceeded continuously on the surface of our anode. Moreover, the diffusion of oxygen released from oxygen vacancy sites onto the sample surface was increased with increasing anode reaction temperature. The detailed reaction mechanism is not clear, but it can be clarified by careful surface analysis (i.e. high power XPS using synchrotron and In-situ EXAFS).

The cycle test presented in Figure 4 compares the durability of Pt-CeO₂/CB composite anode and Pt-Ru/C alloy anode. In a higher potential region such as 1.1V, it is well known that the surface of Ru is oxidized and the performance on Pt-Ru alloy anode is drastically decreased. Fig.4 clearly demonstrates this big decrement of performance of Pt-Ru alloy anode at a sweep ranging from 0 to 1.2V. The peak current

density of Pt-Ru/C alloy anode decreased with increasing cycle number in the cycle test. On the other hand, the peak current density of Pt-CeO₂ composite anode was stable after 800 cycles, although a lowering of peak current density of Pt-CeO₂ composite anode was observed at initial stage of cycle test as shown in Fig.4.

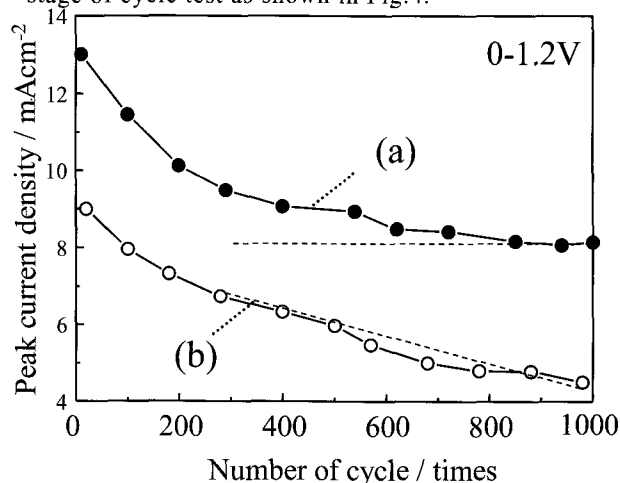


Figure 4 Relationship between peak current density and number of cycle of (a) Pt-CeO₂/CB composite anode (Sample (a) in Table 1) and (b) Pt-Ru alloy anode (Sample (b) in Table 1) at a sweep ranging from 0 to 1.2V. Measurement temperature: 60°C.

This result indicates that the performance of our composite anode is quite stable for long time at higher potential region, even though the performance of commercially available Pt-Ru/C alloy anode is drastically decreased in the cycle test. Therefore, we expect that Pt-CeO₂/CB composite anode will be one of promising anodes in the fuel cells.

4. Summary

The authors investigated anode performance of the Pt-CeO₂/CB composite anode for development of high quality anode in DMFCs. The composite anode was synthesized using a combined process of precipitation and co-impregnation methods. To develop the Pt-CeO₂/CB composite 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 peak current density for methanol oxidation on Pt-CeO₂/CB anode which consists of CeO₂ particles with high surface area was much higher than that on Pt-low surface area CeO₂/CB anode. But the peak current density of both composite anodes was much higher than that of commercially available Pt-Ru/C alloy anode. Also, the onset potential on aforementioned composite anodes clearly shifted to a lower potential as compared with that on the Pt-Ru/C alloy anode. This suggests that an interface between active surface of CeO₂ and

nano-sized Pt particles on CeO₂ is an active site of anode reaction. A design of the nano-hetero interface structure between Pt and CeO₂ is important for a lowering of the onset potential and an improvement of methanol oxidation activity. Also, the activation energy of our composite anode for methanol oxidation was lower than that of the Pt-Ru/CB anode in whole measurement temperature region. This result indicates that the anode performance of the Pt-CeO₂/CB composite anode at operation temperature (80°C) of fuel cells is higher than that of the Pt-Ru/CB alloy anode. In addition, our composite anode has quite high stability in the severe cycle test condition which makes the anode performance of Pt-Ru alloy quite low. Therefore, the high and stable anode performance could be obtained by using Pt-CeO₂/CB composite anode. It is expected that the Pt-CeO₂/CB composite anode in the present study will be one of promising anode materials for development of direct methanol fuel cells.

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