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Preparation and Characterization of Nano-hetero Pt-pure CeO_2 Electrodes Supported by Carbon Materials for Direct Methanol Fuel Cells Applications

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The nano-size Pt-pure CeO_2 anode materials supported by conductive carbon materials were prepared using combined process of co-precipitation and impregnation methods. Cyclic voltammetry of the specimens was measured in 0.5M H_2SO_4 containing 0.5M CH_3OH. In the return sweep, the current density value (45mA/cm^2) of the specimen is four times bigger than that of the commercial available Pt-Ru anode material (12mA/cm^2). The current density of the specimen increased with decreasing particle size of pure CeO_2. The nano-size pure CeO_2 particles consist of round shape particles, although course particles of pure CeO_2 includes rod like shape and round shape particles. Therefore, it is concluded that the morphology control of pure CeO_2 particles is important for enhancement of current density of the specimens. In addition, a meso-porous carbon as a new conductive carbon in anode materials was examined. It is expected that the nano-hetero Pt-pure CeO_2 electrodes supported by conductive meso-porous carbon will be one of promising anode materials for direct methanol fuel cells applications.

Key words: Pt-CeO_2 nano particle, methanol oxidation, anode material, polymer membrane fuel cell

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. An alternative to the use of H_2 as fuel is methanol which is a liquid fuel easy to handle. PMFCs are being especially developed as a efficeint power source for the transportation system and the portable system applications. Also, there is no need to use a reformer system, which make it easier to design a small and lightweight fuel cell. But it is well known that the oxidation of methanol on platinum electrode generates CO as reaction intermediate, which is subjected to poisoning even at very low concentrations (10 ppm). The proposal of high quality anode materials which lowered the influence of CO poisoning is required.

In the previous study, the Pt electrode with transition metal additives was developed to lower the CO poisoning on Pt anode materials.[1-16] A number of anodic reactions have been examined especially for supported or unsupported Pt-Ru anode materials. Recently, it was often reported that influence of processing route on the anode catalytic activity for the oxidation of methanol on aforementioned anode materials.[2-7] The mechanism of electro-oxidation reaction of CH_3OH on Pt-Ru anode materials was examined using CO-stripping voltammetry, in-situ FTIR, and EELS experimentation.[8-10] Also an influence of supporting materials such as activated carbon,[11] graphitic carbon nanofibers,[12] highly oriented pyrolytic graphite,[13] multi-wall carbon nanotube,[14] carbon nanohorn[15] and nanofiber polyaniline[16] on anode catalytic activity were examined. On the other hand, the different anode materials from PtRu anode material such as PtNi[17], PtSn[18], PtFe[19], NiTi[20], and Pt/WO_3[21] were developed to decrease Pt content in anode materials or to develop the new electrode materials without Pt element from the perspective of cost performance for the development of electrode materials in the fuel cell.

In the present study, we proposed a new anode material Pt-CeO_2 supported by conductive carbon such as carbon black and meso-porous carbon. It is well known that pure CeO_2 has unique catalytic properties as a thermally and chemically stable material with high capacity of oxygen storage and oxygen release. Pure CeO_2 can enhance the catalytic activity for selective oxidation of CO of water gas shift reaction due to the easy generation of oxygen vacancies.[22-24] In order to increase the active sites on the anode materials and enhance the conversion of CO to CO_2 on the anode, nano-sized Pt-CeO_2 particles supported on carbon black was synthesized and the methanol oxidation reaction on aforementioned materials was investigated. Also the authors discussed the anode performance of Pt/meso-porous carbon for the development of Pt-CeO_2/carbon black anode materials.

2. EXPERIMENTAL

Pt-CeO_2 electrodes supported on conductive carbon were prepared by co-impregnation method. H_2PtCl_6

$\cdot H_2O$, carbon particles and CeO_2 particles were dispersed into ethanol. The mixture was dried at room temperature in N_2 gas flow. The dried powder was reduced at 800°C for 2 h in mixed gas H_2 (10%) and $/N_2$ (90%) flow. The content of Pt particles was 30% by weight in the mixture of Pt and carbon. And Pt:Ce atomic ratio of 1:1 was prepared. Commercially available 30wt.%Pt+15wt.%Ru supported on carbon black (Pt: Ru atomic ration of 1:1) was obtained from ISHIFUKU Metal Industry Co. Ltd. and its electrode performance was compared with that of Pt-CeO_2 anode material.

CeO_2 particles were prepared using ammonium carbonate co-precipitaion method.[25] The starting material used was $Ce(NO_3)_3 \cdot 6H_2O$. This 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 65°-75°C under mild stirring for 1h. After repeated washing, the precipitate was dried at room temperature in N_2 gas flow. Also the dried particles were calcined at 800°C for 2h in O_2 gas flow.

The morphology and size of Pt-CeO_2 particle supported by conductive carbon materials were observed using field emission scanning electron microscopy (FE-SEM) and scanning transmission electron microscopy (STEM). The morphology and size of Pt, Ce and carbon particles in the anode materials were observed by electron diffraction spectrometry (EDS). The content of Pt in anode materials were quantitatively analyzed using inductively coupled plasma atomic emission (ICP-AES) technique. The samples for the FE-SEM analysis were dispersed into ethanol ultrasonically, with the suspensions spread on to a thin layer of aluminum foil. A small portion of the foil with the anode particles was cut, fitted onto a sample plate and then coated with tungsten.

Specific surface areas of carbon black and meso-porous carbon were determined by N_2 gas absorption desorption isotherm. Adsorption of N_2 gas, as probe species, was performed at -196°C. Surface areas of specimens were determined from the BET method.

Electrochemical property of Pt-CeO_2 anode materials was examined by cyclic voltammetry experiment. The measurement 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 anode materials (3mg/ml) were dispersed into CH_3OH aqueous solution. The suspension was spread onto the working electrode using a micro-pipette. Amount of the anode materials spread were 40μL. The measured potentials were converted to the reversible hydrogen electrode (RHE) scale. The potential data was plotted as volts versus RHE (V vs. RHE) after cyclic measurements of 15 times for examination of electrode performance.

3. RESULT AND DISCUSSION

3.1 Preparation of nano-size CeO_2 particle and Pt-CeO_2 anode

Figure 1 shows the SEM images of commercial available reagent CeO_2 and calcined CeO_2 particles prepared by different conditions. The commercial available reagent CeO_2 particles consisted of irregular shape, as shown in **Fig. 1(a)**. In contrast, the pure CeO_2 particle which was consisted of rod-like shape particles (**Fig. 1(b)**) was obtained when the precipitation was formed at 65°C for 1h and calcined at 800°C for 2h in O_2 gas flow. The average particle size in long length was approximately 1.2μm. And this powder had small amount of round shape particles, its average primary particle size of round shape particle was 80nm. To prepare the large amount of round shape CeO_2 nano size particles, the precipitation was formed at 75°C for 1h (**Fig. 1(c)**). The size of rod like shape particle in Fig.1(c) was much shorter than that of the

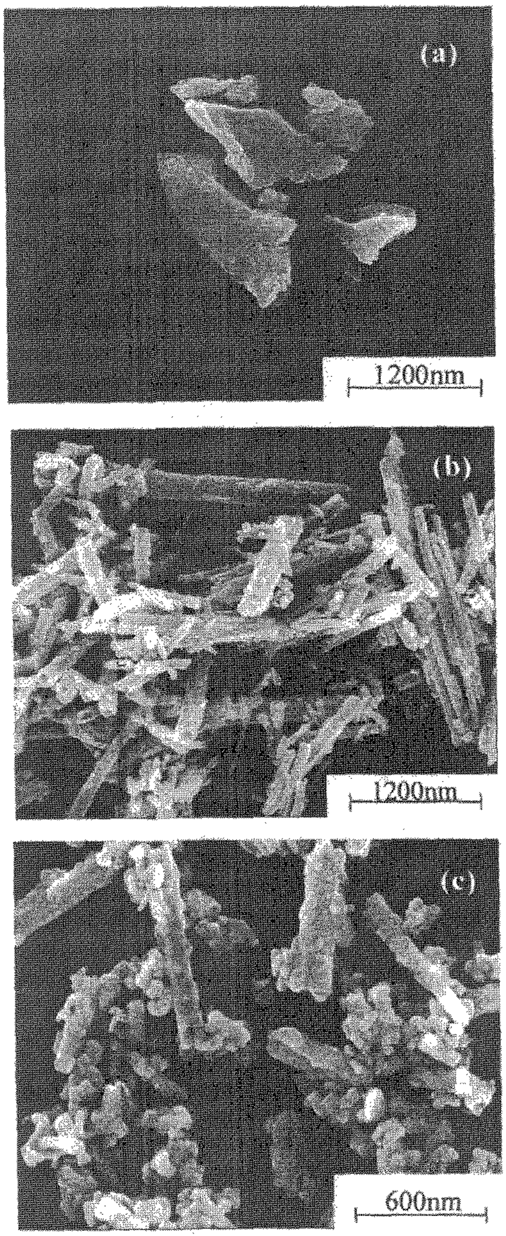

Fig. 1 FE-SEM images of calcined CeO_2 particles. The condition of precipitation formation; (a) reagent, (b) at 65°C for 1h, and (c) at 75°C for 1h. The calcination conditions; at 800°C for 2h in O_2 gas flow.

aforementioned pure CeO_2 particles which were prepared at 65°C for 1h. The amount of round shape particles in Fig. 1(c) was much larger than that in Fig. 1(b). Therefore, the synthesized pure CeO_2 particles in Fig. 1(c) were used as one of starting materials for preparation of Pt-CeO_2 anode materials.

The Pt-CeO_2 anode was prepared by co-impregnation of pure CeO_2 particles displayed in Fig. 1(c), H_2PtCl_6 •H_2O, and carbon black as support. STEM and EDS analysis indicated that Pt particles were dispersed well on pure CeO_2 particles and carbon black particles. The size of Pt particles was below 30nm.

3.2 Methanol oxidation on Pt-CeO_2 anode material

Figure 2 shows cyclic voltammograms of Pt-CeO_2 anode materials and the commercial available Pt-Ru anode supported by carbon black in the mixed solution of 0.5M H_2SO_4 and 0.5M methanol aqueous solution. The anodic peaks on aforementioned two anode materials were appeared in both forward and reverse sweeps. The peak potential of methanol oxidation in voltammograms recorded from the commercial available Pt-Ru-carbon black anode materials were agreed with the previous reported peak potential recorded from Pt-Ru-carbon black anode materials.[2,7] In the negative sweep, the current peak potential (0.70V vs. RHE) of methanol oxidation on Pt-CeO_2 anode shifted towards anodic direction as compared with the commercial available Pt-Ru anode material (0.63V vs. RHE). The current density value (45mA/cm^2) of Pt-CeO_2 anode was about four times bigger than that of the commercial available Pt-Ru anode material (12mA/cm^2). This result suggested that Pt-CeO_2 anode material had high activity of CH_3OH oxidation.

3.3 Effects of meso-porous carbon as support material

In the present study, meso-porous carbon (MC) as a new conductive carbon was employed for the support material of anode. **Figure 3** displays the SEM image of Pt lodings MC. It was observed that the meso-porous carbon consisted of both large size particles (500nm) and small size particles (80nm). The particles size of MC is bigger than that of CB (50nm). However, specific surface area of MC (1,000m^2/g) was much larger than that of CB (150m^2/g).

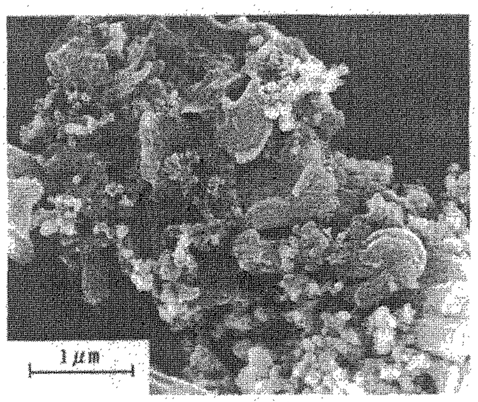

Fig. 3 FE-SEM images of 30wt.%Pt supported by meso-porous carbon. The reduction conditions; at 400°C for 2h in H_2 (10%) gas flow.

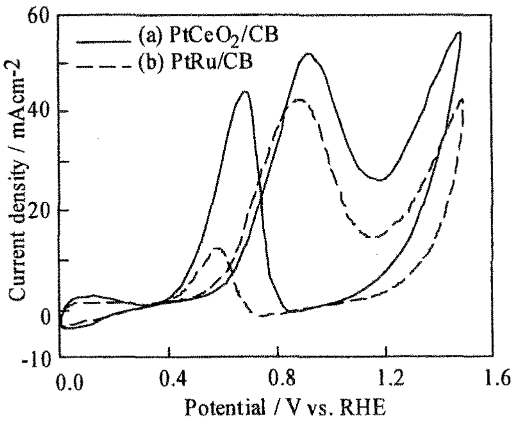

Fig. 2 Cyclic voltammograms of CH_3OH oxidation on (a) Pt-CeO_2 using CeO_2 particles prepared at 75°C for 1h supported by carbon black (CB) and (b) commercial available Pt-Ru supported by CB in 0.5M H_2SO_4 containing 0.5M CH_3OH. Scan rate: 50mV/s. Weight of Pt: 0.61g/cm^2.

Figure 4 demonstrates cyclic voltammograms of Pt anode supported by MC and CB in 0.5M H_2SO_4 aqueous solution. The voltammograms associated with hydrogen adsorption-desorption and Pt oxidation-reduction were observed. The shape of voltammograms was similar to the voltammograms recorded from the previous reported Pt anode supported CB in H_2SO_4 aqueous solution.[26] The electric double layer of Pt anode supported by MC is approximately three times bigger than that of Pt anode supported by CB. It is expected that Pt-CeO_2-MC anode material will be one of promising anode materials in DMFC.

3.4 Mechanism of anode reaction on Pt-CeO_2 -CB

In the previous study, reaction mechanism of CH_3OH oxidation on bimetallic anode material such as Pt-Ru anode material was described using both bi-functional

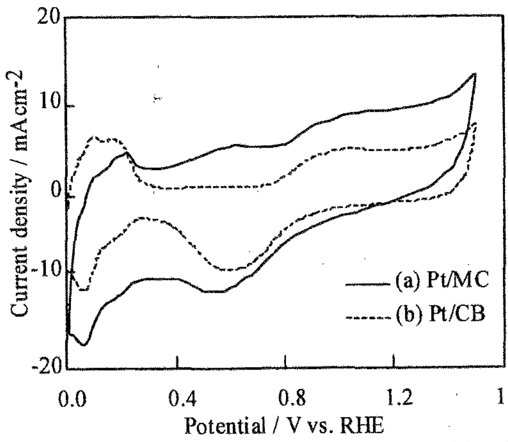

Fig. 4 Cyclic voltammograms of (a) 30wt.%Pt supported by meso-porous carbon (MC) and (b) 30wt.%Pt supported by CB in 0.5M H_2SO_4. Scan rate: 50mV/s. Weight of Pt: 0.61g/cm^2.

model[1] and ligand (electronic) model.[27] However, Pt-CeO_2 anode material consisted of metal particle (Pt) and oxide particle (CeO_2). It is difficult to explain reaction mechanism of our material using the aforementioned model. The mechanism of anodic reaction on Pt-CeO_2-CB anode materials should be discussed using a different model.

It is well known that pure CeO_2 has catalytic properties with high capacity of oxygen storage and oxygen release. In anode reaction, when pure CeO_2 particles release oxygen, oxygen vacancy is produced into CeO_2 lattice. After the creation of oxygen vacancy into CeO_2 lattice, the electron transfer from Pt surface to CeO_2 surface would become easy due to lowering of Schottky barrier in an interface of Pt particle and CeO_2 particle. The oxygen storage and oxygen release capacity in CeO_2 would be increased by this electron transfer and activated anodic performance. It is concluded that the aforementioned released oxygen from the CeO_2 lattice will contribute to the oxidation of CO molecules on Pt particles and the lowering of affection of CO poisoning on Pt particles.

4. SUMMARY

The authors proposed new anode materials usign Pt-CeO_2 particles supported by conductive carbon. The nano-sized Pt-CeO_2 particles supported on CB was prepared. The electrochemical activity of methanol oxidation reaction was investigated. Also a meso-porous carbon as a new conductive carbon was examined. To improve the anode performance, the morphology of CeO_2 particles was changed by preparation condition. The size of CeO_2 particles which were prepared at 75°C for 1h was much smaller than that of reagent CeO_2 particles or CeO_2 particles (prepared at 65°C for 1h). The average particle size of round shape particles which were prepared at 75°C for 1h was 80nm.

The nano-size Pt-CeO_2 anode materials supported by CB showed that the current density value of CH_3OH oxidation on Pt-CeO_2 anode was much bigger than that of the commercial available Pt-Ru anode material in negative sweep. It is concluded that the Pt-CeO_2 anode material has high activity of CO oxidation as compared with PtRu anode material. It is found that the MC (1,000m^2/g) as support material had high activity of anode performance using cyclic voltammetry experiment. It is expected that the anodic activity of Pt-CeO_2 will be improved by preparation of round shape nano-size CeO_2 particles and employed conductive MC as support material. Therefore, it is concluded that the nano-hetero anode Pt-CeO_2/carbon in this study is one of promising anode materials for DMFCs applications.

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