Effect of Nanoparticle Addition into Anode Electrodes for Direct Ethanol Fuel Cells

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The effect of nanoparticle addition into an anode electrode on direct ethanol fuel cells is reported. When nanopartilces such as TiO_2, SnO_2, and SiO_2 were added to the anode electrode, the short circuit current (J_{sc}) increased from 2.8 to 4.4–9.0 mA cm^{-2}. The nanoparticle and the carbon-supported PtRu (PtRu/C) were mixed merely at the ratio of 1:1. The PtRu content decreased to a half of the original electrode, but, J_{sc} increased after the nanoparticle addition. The results were explained by the increase in the fuel diffusion and the catalyst activity. These effects of the nanoparticle addition were not observed for direct methanol fuel cells.

Direct methanol fuel cells (DMFC) have attracted interests because of the simple cell structure.[1] On the other hand, ethanol is well known as a renewable resource. If ethanol is used instead of methanol for the direct fuel cell, it would be one of the best fuel cell systems in terms of the renewable energy.

The research effort of the direct ethanol fuel cell (DEFCs) has been focused on developing new electrocatalysts to improve the catalytic activity for ethanol oxidation reactions.[2–9] One of the problems is that the DEFC performances are less than that of DMFC, which is associated with less ethanol oxidation reactions by the carbon-supported PtRu catalyst (PtRu/C).[10,11] The PtRu/C catalyst is poisoned by the oxidation products of ethanol.[12–16] In order to avoid the poisoning, the composite catalysts (metal alloy) such as PtSn/C and $PtSnO_2$/C have been reported,[17–26] where Pt is alloyed with Sn or is on the SnO_2 directly. It has been reported that the surface Sn–OH groups act as the remover.[26] In the course of the study on dye-sensitized solar cells consisting of nanoparticles, we handled variety of TiO_2 and SnO_2 nanoparticles and the surface OH groups show interesting properties.[27] This prompted us to use these nanoparticles as the scavenger of the adsorbed oxidation product. We report the effect of the nanoparticle addition to the anode electrode in terms of the catalyst activity and the mechanism. The difference from the previous report on $PtSnO_2$/C[26] is that the nanopartilces such as SnO_2 are merely mixed with PtRu/C in this experiment and this should be abbreviated as PtRu/C-*n*SnO_2. On the contrary, Pt was directly bonded on SnO_2 or Sn for the $PtSnO_2$/C catalyst previously reported.[26] Beside the simplicity, we report the effect of the other nanoparticle addition which is not expected from the previous report.

The following nanoparticles were used for this experiment. TiO_2 (AEROXIDE TiO_2 P 25, diameter: 21 nm, Degussa Japan), SnO_2 (NanoTek Tin Oxide, diameter: 21 nm, C. I. Kasei Co., LTD), and SiO_2 (AEROSIL 200, diameter: 12 nm, Degussa Japan, and AEROSIL 380, diameter: 7 nm, Degussa Japan). A counter electrode (a cathode electrode) consisting of Pt/C (TEC10E50E) was purchased from Tanaka Kikinzoku Group. The anode catalyst paste (PtRu/C paste) was prepared by mixing 0.2 g of PtRu/C (Pt:Ru:C = 30:24:46 wt %, Tanaka Kikinzoku Group) and 1 g of Nafion solution (5 wt %). The anode catalyst layer was made by printing the PtRu/C paste on the carbon paper (TPG-H-120, Toray) by using a 0.05-mm thick film as the spacer, followed by drying in an air at room temperature for 30 min. The supported catalyst on the carbon paper was about 1 mg cm^{-2}. The composite anode catalyst pastes (PtRu/C-*n*SnO_2, PtRu/C-*n*SiO_2, and PtRu/C-*n*TiO_2) were prepared by mixing 0.2 g of PtRu/C, 0.2 g of the nanoparticle, and 1 g of Nafion solution (5 wt %). The anode electrode was prepared

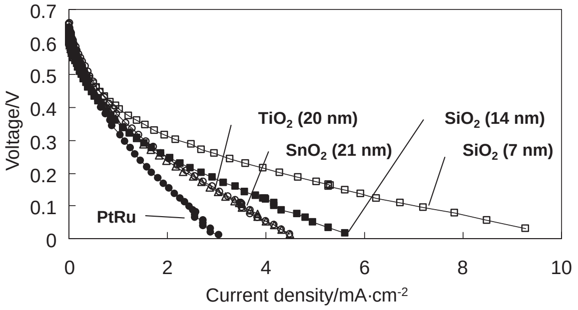

Figure 1. *I–V* curves for DEFC cells consisting of nanoparticles. PtRu: PtRu/C, SnO_2: PtRu/C-*n*SnO_2, TiO_2: PtRu/C-*n*TiO_2, SiO_2: PtRu/C*n*SiO_2 Operation temperature: 25 °C, 1 M ethanol in water for fuel.

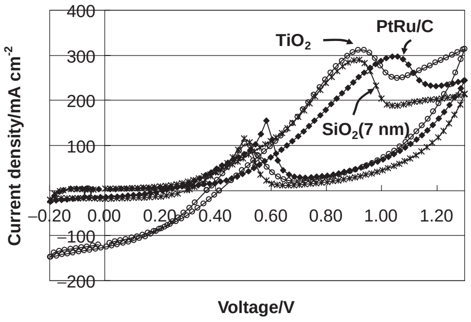

Figure 2. CV curves for anodes consisting of nanoparticles. See experimental section. Abbreviation: see Figure 1.

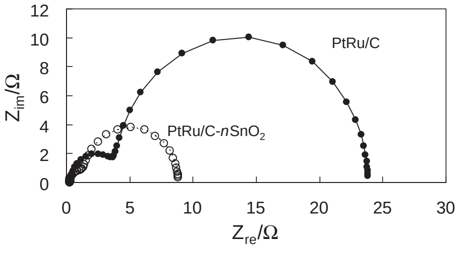

Figure 3. Cole–Cole plot for cells before and after SnO_2 nanoparticles.

in the same way as the PtRu/C electrode described above. Nafion 117 membrane was pretreated by 3 wt % H_2O_2 solution and 0.5 M H_2SO_4 as is described in the previous paper.[15] The membrane-electrode assembly (MEA) was fabricated by sandwiching the Nafion 117 membrane between the cathode and the anode electrodes by hot pressing at $100\,kg\,cm^{-2}$ and 130 °C for 5 min.

Single DEFC tests were performed on the MEA with an active electrode of 2.2×2.2 cm. The DEFC cell outer frame was purchased from ElectroChem (EFC05). The flow fields consisting of machined two-pass serpentine grooves on graphite blocks were identical for both the anode and the cathode. The MEA was inserted into the compartment. Aqueous ethanol solution was supplied through the anode compartment by a peristaltic pump (Masterflex, Model 7518-00) at a flow rate of $1.0\,mL\,min^{-1}$. The flow rate of nonpreheated dry air was controlled by a pressure controller (AS ONE, Compact Air Pump), and the cell temperature was controlled by a digital temperature controller (Iuchi, Model T-550). The polarization curves were obtained at 40 °C in a fuel cell testing system using a dc electric load (Fujitsu Access, Model EUL-150XL). 1 M aqueous solution of ethanol was used as the fuel. The cyclic voltametric (CV) experiments were carried by employing a potentiostat/galvanostat (Hokuto Denko, Model HSV-100) coupled with a personal computer and a three-electrode test cell at room temperature. The working electrode was a thin layer of a Nafion solution (5 wt %) impregnated catalyst composite on a carbon paper electrode. An aqueous solution containing 0.5 M H_2SO_4 and 1 M ethanol was used as the electrolyte. A saturated calomel electrode (SCE) was used as the reference electrode, and a platinum wire as the counter electrode.

Figure 1 shows I–V curves for cells containing various nanoparticles. The open-circuit voltage (V_{oc}) of the cell (PtRu/C) was 0.68 V and did not vary when the various nanoparticles were added in the PtRu/C electrode. Short-circuit current (J_{sc}) of the cell (PtRu/C) was $2.8\,mA\,cm^{-2}$. When the nanoparticle was added in the (PtRu/C) electrode, the J_{sc} increased to $4.4\,mA\,cm^{-2}$ for PtRu/C-$n$$TiO_2$, $4.4\,mA\,cm^{-2}$ for PtRu/C-$n$$SnO_2$, and $5.8\,mA\,cm^{-2}$ for PtRu/C-$n$$SiO_2$ (14 nm) and more than $9.0\,mA\,cm^{-2}$ for PtRu/C-$n$$SiO_2$ (7 nm). Surprisingly, SiO_2 nanoparticle showed the best results. The nanopartilce and the carbon-supported PtRu (PtRu/C) were mixed at the ratio of 1:1. The PtRu content decreased to a half of the original electrode, but, J_{sc} increased inversely after the nanoparticle addition. CV curves for the cells containing nanoparticles were measured. The peak associated with ethanol oxidation was observed at 1.06 V (SCE) for the PtRu/C cell. The peak shifted to 0.92–0.94 V (SCE) when these nanoparticles were added in the electrode, as shown in Figure 2. This suggests that the ethanol oxidation occurred at more negative potential when these nanoparticles were added to the electrodes.

Figure 3 shows the Cole–Cole plot for the cells before and after the SnO_2 nanoparticle addition. It has been reported that the left circle is associated with the resistance for the reaction on the electrode and that the right circle is associated with the resistance for the material diffusion.[28] When the SnO_2 nanoparticle was added in the PtRu/C electrode, the right semicircule reduced from 20 to 7 Ω and the left semicircle reduced from 4 to 1 Ω. This suggests that both the catalyst activity and the fuel diffusion were improved when the SnO_2 nanoparticle was added in the PtRu/C electrode. The same phenomena were observed for the addition of the other nanoparticles. The increase in the J_{sc} after the nanopartilce addition was not observed for DMFC. This suggests that the addition of the nanoparticles may be useful for bigger molecules than methanol.

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