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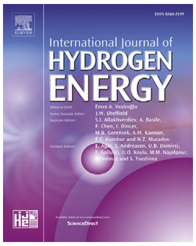

Anode catalyst with enhanced ethanol electrooxidation activity by effective interaction between Pt-Sn-SiO_2 for a direct ethanol fuel cell

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ABSTRACT

The development of active catalyst for ethanol electrooxidation is a key to improving the power output of direct ethanol fuel cells (DEFCs). In this study, Pt-Sn was supported on SiO_2 embedded carbon nanofiber as active anode catalyst for DEFC by expecting positive interactions between Pt-Sn-SiO_2. The composite catalyst, Pt_3Sn_1/SECNF, showed highest mass activity for the ethanol electrooxidation, which was 3.7 times higher than the activity of the commercial Pt/C (Pt/C_{com}). The maximum power density of DEFC single cell with the composite catalyst was 3.5 times higher than that with Pt/C_{com}.

Introduction

In recent years, compact and stand-alone power sources are required for small devices and machines. Direct ethanol fuel cells (DEFCs) have attracted attention because they are small devices without any reformer and ultimately use high volumetric energy density of ethanol, i.e., 6.3 kWh L^{-1}. Although the development of the DEFCs is currently slower than that of direct methanol fuel cells (DMFCs) [1–5], DEFCs have attracted significant attention compared to DMFCs because ethanol is not harmful and can be produced from biomass through various methods including fermentations.

A technical issue of the DEFCs is its low power output due to sluggish electrooxidation of ethanol at the anode. Pt catalysts have been used as the standard anode catalyst for the ethanol oxidation reaction (EOR) [6–9]. However, DEFCs with Pt catalysts generates much less power than DMFCs because of lower catalytic activity for the EOR. The lower activity of the Pt catalyst is attributed to poisoning by adsorbed intermediates such as CO_{ad} and $CH_{x,ad}$ [10–13]. An alternative catalyst to accelerate the EOR and increase the power output of DEFCs is required.

In order to improve the electrooxidation rate, Pt-based binary systems, such as Pt-Rh [14–19], Pt-Ru [17,19–23], and Pt-Sn (Pt-SnO_2) [19,24–30] were proposed. Especially, Pt-Sn

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(Pt-SnO_2) catalysts show a significant activity enhancement compared to the other catalysts because of OH supply from Sn to the adsorbed intermediates and ligand effect. The onset potentials of EOR and CO oxidation at Pt-Sn catalysts were lower compared to those at Pt catalyst due to the easy removal of CO_{ad} by OH supplied from Sn [24,31]. Hence, DEFC with Pt-Sn/C showed increased power density compared to that with Pt/C [24–26]. The products of EOR at Pt-Sn catalysts were still mainly CH_3COOH and CH_3CHO [25,27,29] along with a small amount of CO_2. Pt_3Sn_1 is the optimized composition of the Pt-Sn catalyst [29,31], it is believed to be one of the most promising catalysts for the DEFC anode.

It is also effective to increase the catalytic activity to utilize the interaction between metal-catalyst and support-material. Expecting such interaction, solid oxide particles were often used as a support of the metal catalysts. Reports have shown the enhanced activity of EOR or methanol oxidation reaction (MOR) by addition of TiO_2 [4,23,32–35], CeO_2 [5,36–39], and SnO_2 [35,40–44]. SiO_2 is another promising candidate for the support because SiO_2 realizes the hydrogen spillover effect from the metal-catalyst [45], has an acid resistivity [46], and might electronically interact with the metal catalyst. Pt/SiO_2 was proposed as an EOR catalyst [46], but SiO_2 itself has a low electronic conductivity, thus, an electron conductive additive such as carbon is necessary for this system. For this purpose, SiO_2 (~several tens of nanometers) embedded carbon nanofibers (SECNFs) were developed as a catalyst support for formic acid oxidation [47,48] and EOR [49,50]. The "SiO_2 embedded in carbon" structure is preferable due to the shorter electron pathway from the metal-catalyst to carbon and direct facial contact between SiO_2-carbon. In our previous study, the EOR activity of Pt/SECNF was higher than that of the commercial Pt/C, and the optimized Si/C weight ratio for SECNF was 3.1 [50]. The activity of Pt/SECNF was higher than that of Pt/CNF. The combination of the Pt_3Sn_1-catalyst with the SECNF-support is highly expected to be an active catalyst for the EOR due to the synergetic effect between the Pt_3Sn_1 and SECNF.

In the present study, Pt_3Sn_1/SECNF was prepared and its EOR activity was measured. To clarify the effect of SECNF-support, the activities of Pt_3Sn_1/SECNF and Pt_3Sn_1/CNF were compared. The chemical states of Pt and Sn were analyzed by the X-ray photoelectron spectroscopy (XPS). The performances of DEFC single cells with the different catalysts operated under atmospheric pressure with an air cathode were also evaluated.

Experimental

Catalyst preparation

The carbon nanofiber (CNF) and SECNF-support were prepared by electrospinning technique, heat treatments, and steam-activation [49,50]. First, 2.00 g of polyacrylonitrile (PAN, Sigma Aldrich Co., Ltd.), 16.4 g of dimethylformamide (DMF, 99.5%, Wako Pure Chemical Industries, Ltd. (WPCI)), and 1.00 g of 20 wt% SiO_2 in a dimethylacetamide suspension (Nissan Chemical Industries, Ltd., mean particle size: 10–15 nm) were mixed. The mixture was electrospun by applying 18 kV between a needle and a metallic collector covered with aluminum foil at a distance of 15 cm and at the precursor mixture flow rate of 50 μL min^{-1}. The obtained nanofibers in a form of a sheet were stabilized at 250 °C in air for 10 h. The nanofibers were then carbonized at 1000 °C under flowing nitrogen for 1 h. The carbonized nanofibers were then steam-activated at 850 °C for 1 h by introducing N_2 after bubbling in water at 80 °C into a tube reactor. The obtained nanofiber, SECNF, was then milled using an agate mortar for 5 min per 100 mg of the nanofibers to normalize the fiber length.

The 17 wt% Pt-Sn nanoparticles were then deposited on SECNF by a microwave-assisted polyol reduction method [3]. SECNF (100 mg) was dispersed in ethylene glycol, then 55.0 mg of $H_2PtCl_6 \cdot 6H_2O$ (98.5%, WPCI) and 6.9 mg of $SnCl_2$ (99.9%, APCI), which corresponds to the atomic ratio of Pt:Sn = 3:1, were added to the suspension. Microwaves irradiated the suspension at 600 W and a frequency of 2.45 GHz for a total of 5 min. Thereafter, the suspension was stirred overnight at room temperature, then filtered and washed several times with pure methanol and distilled water. The obtained Pt_3Sn_1/SECNF was dried overnight at 70 °C under a vacuum condition. Pt_3Sn_1/CNF and Pt/CNF were prepared by similar procedures for comparison. The commercial Pt/C (Pt/C_{com}, 19.0 wt%-Pt, TEC10E20E, Tanaka Kikinzoku Kogyo K.K.) was also tested as a reference.

Characterization

The crystal structures of the catalysts were analyzed by an X-ray diffractometer (XRD, Rint2100V/PC, Rigaku Corp.). The crystallite size of Pt-Sn or Pt was calculated using Scherrer's equation for the Pt-fcc (111) peak. The bulk catalyst composition was estimated by an energy dispersive X-ray spectrometer (EDX, SEDX-500, Shimadzu Corp.). The morphology of SECNF-support was observed by a field emission-scanning electron microscope (FE-SEM, JSM-6330F, JEOL Ltd.). The chemical states of the surface Pt and Sn were analyzed by an X-ray photoelectron spectroscope (XPS, AXIS-Nova, Kratos Analytical, Ltd.) with monochromatic Al Kα radiation, voltage of 15 kV, current of 10 mA, and C 1s calibration.

Electrochemical measurement

The electrocatalytic activity of the catalysts was measured using a glassy carbon electrode, Ag/AgCl (KCl sat.), and Pt mesh as the working, reference, and counter electrodes, respectively. Catalyst ink was prepared by mixing 5.0 mg of a catalyst, 80 μL of distilled water, 80 μL of ethanol (99.5%, WPCI), and 25 μL of a 5 wt% Nafion suspension (WPCI) under ultrasonic wave irradiation with glass beads (BZ-1, 1 mm diameter, As One Co., Ltd.) for 1 h.

The EOR activity was measured by cyclic voltammetry using a rotating disk electrode. The potential of the working electrode was scanned from 0 to 1.2 V vs. RHE at 20 mV s^{-1} in an aqueous solution of 0.5 M ethanol with 0.5 M H_2SO_4. The rotation speed of the working electrode was 1600 rpm. The electrochemically active surface area (ECSA [$m^2\ g^{-1}_{\text{-Pt}}$]) was measured by the CO stripping method [5] using 10 vol% CO. The CO adsorption was performed at 0.2 V vs. RHE.