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Short Communication

Electrospun Pt/SnO_2 nanofibers as an excellent electrocatalysts for hydrogen oxidation reaction with ORR-blocking characteristic

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ABSTRACT

Pt/SnO_2 nanofibers were synthesized via electrospinning. The unique electrochemical properties were in evidence based on the activity that allowed a hydrogen oxidation reaction and inhibit an oxygen reduction reaction. A high electrochemically active surface area value of 81.17 m^2/g-Pt was achieved with ultra-low Pt loading (4.03 wt.%). The kinetics of a hydrogen oxidation reaction was investigated using a linear sweep voltammetry technique under a hydrogen atmosphere. A diffusion-limited current was achieved at 0.07 V and was stable at a high potential. This preparation technique shows great promise for the design of anode electrocatalyst material for fuel cells.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are of great scientific interest as future energy sources owing to their advantages such as high energy conversion efficiency, a wide operation temperature, and low/zero emissions [1–3]. A couple of reactions are necessary to continuously generate electric current during the operations of PEMFCs: a hydrogen oxidation reaction (HOR) at the anode, and an oxygen reduction reaction (ORR) at the cathode. Platinum-based nanoparticles supported on high surface area carbon are widely used to catalyze both HOR and ORR [1,2]. Research on electrocatalyst materials has been focused on cathode ORR catalyst development due to sluggish reactions that result in a voltage drop in fuel cells. However, over-potential at the anode during shutdown and startup causes an undesired ORR and significantly contributes to an overall fuel cell voltage drop. Therefore, a design of electrocatalyst materials that tolerant to an ORR without sacrificing HOR activity is extremely challenging [4–6]. Prior study has shown that the surface modification of Pt by an organic molecules effectively block an ORR [4,5]. However, the HOR activity of modified Pt catalyst was sacrificed.

Pt nanoparticles dispersed on the metal oxide support materials are considered to be an effective strategy to increase the activity and the stability of electrocatalyst [7,8]. Presumably, a strong interaction between Pt and a metal oxide could result in unique properties, including ORR-blocking. In recent years, various metal oxides have been investigated as catalyst support materials [7,8]. Among these oxides, SnO_2 is very promising due to its characteristics such as a high electron mobility, reasonable electric conductivity, and corrosion resistance [9–11]. Previous studies have reported that Pt nanoparticles grown *ex situ* on the surface of SnO_2 via an impregnation method exhibited significant tolerance against potential cycling of up to 10,000 cycles [9]. However, the HOR activity in Pt/SnO_2 with tolerance to ORR activity has never been elucidated, and its electrocatalytic activity remains unsatisfactory.

The structural engineering of Pt/SnO_2 into nanofiber morphology would enhance the performance of PEMFCs, due to the fact that nanofiber morphology provides an easy access to electron transport along an alignment that is contrary to that of nanoparticles where there is a significant interface between particles that may add resistance to the system [12]. Herein, we present a novel *in situ* method to grow Pt nanoparticles on SnO_2 nanofiber matrix via electrospinning. The processing technique and the electrochemical activities are reported herein.

2. Experimental

Raw materials used in the experiment were polyacrylonitrile (PAN, $M_W = 150{,}000$ gr/mol, Sigma Aldrich, USA), tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, Nacalai Tesque, Japan) hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, Mitsuwa Chemical, Japan), and *N,N*-dimethylformamide (C_3H_7NO, DMF, Sigma Aldrich, USA). SnO_2 and Pt/SnO_2 nanofibers were synthesized in order to investigate the effect of Pt deposition on SnO_2 nanofibers to the electrocatalytic activity. A precursor containing of PAN (1.422 g), $SnCl_4 \cdot 5H_2O$ (1 g), and DMF (12.8 g) was electrospun to produce SnO_2 nanofibers. In another experiment, $H_2PtCl_6 \cdot 6H_2O$ (0.05 g) was added to produce Pt/SnO_2 nanofibers. The general setup

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for electrospinning was similar to that of previously reported work [13]. The voltage, distance between needle and electrode, precursor flow rate, and rotation drum velocity were 14 kV, 23 cm, 20 μl/min, and 450 rpm, respectively. The electrospun composite nanofibers were then heated at 500 °C at a heating rate of 2 °C/min for 4 h under an ambient air atmosphere.

The morphology of nanofibers was examined using a transmission electron microscope (TEM; Topcon EM-002BF) and a field emission scanning electron microscope (FE-SEM; Hitachi S-5000). The crystalline structures were examined using X-ray diffraction (XRD) measurement (Rigaku RINT2000 X-ray diffractometer with nickel filtered Cu-K_α ($\lambda = 0.154$ nm) radiation at 40 kV and 30 mA with a scanning rate of 0.02°/2θ). Inductively coupled plasma measurement (ICP, SII, S6000) was applied to determine the amount of Pt loading on the Pt/SnO_2 nanofibers.

A potentiostat (Hokuto Denko, HR-301) was used for electrochemical measurement. Catalyst inks were prepared following a procedure reported previously [2]. A known amount of catalyst was mixed with 6 mL isopropanol (Cica-reagent, Kanto Chemical Co. Inc., Japan) and 19 mL ultrapure water, followed by the addition of 100 μL of a Nafion® dispersion solution (5 wt.%, Wako Pure Chemical Industries, Ltd., Japan). The catalyst ink was then placed in an ice bath and ultrasonicated for 30 min. For the electrode preparation, 10 μL of catalyst ink contained 3.39 μg of Pt, was transferred onto the polished glassy carbon disk (area 0.196 cm^2) and dried to produce a thin film of the catalyst layer. The measurement setup was a typical three-electrode system, which consisted of a working electrode, a Pt wire as the counter electrode, and a reversible hydrogen electrode (RHE) as the reference electrode. All measurements were performed at (25 ± 0.5) °C using an aqueous electrolyte solution of 0.1 M $HClO_4$. The electrolyte solution was saturated with nitrogen gas for 30 min before cyclic voltammetry (CV) measurements. The CV measurements were scanned between 0 and 1.2 V vs. RHE with a sweep rate of 100 mV/s. The HOR activity was measured by linear sweep voltammetry (LSV) method. The saturation gas was switched to hydrogen for 30 min prior to LSV measurement. Rotation rate was controlled at 400, 900, 1600, 2500, and 3600 rpm. Measurements were carried out at 10 mVs^{-1} sweep rates and scanned between 0 and 1.2 V vs. RHE. The electrochemical properties of commercial Pt/C catalyst (46 wt.% Pt, purchased from Tanaka Kikinzoku Kogyo, TKK, Japan) were also measured.

3. Results and discussions

The XRD patterns of SnO_2 and Pt/SnO_2 nanofibers are shown in Fig. 1. Both diffraction patterns were consistent with references, with no formation of any other crystal phase (e.g., PtO). This observation revealed that Pt nanoparticles can be grown *in situ* simultaneously with metal oxide formation only by heat treatment under an air atmosphere. Presumably, Sn atoms are more attractive than Pt atoms on making a bounding with O atoms during the crystal growth, so that SnO_2 formation was more favorable. The diffraction peaks of SnO_2 and Pt can be indexed to the tetragonal rutile and face-centered cubic (fcc) structure according to the JCPDS Cards Nos. 41-1445 and 04-0802, respectively. The crystallite sizes of SnO_2 were calculated following the Scherer law and were 21.48 and 23.74 nm for SnO_2 and Pt/SnO_2 nanofibers, respectively. Meanwhile, the crystallite size of Pt was calculated to be 19.50 nm for Pt/SnO_2 nanofibers. The optimum size of Pt particles for electrocatalytic activity was reported to be below 5 nm [14]. This fact indicates that the electrocatalytic activity of the present Pt/SnO_2 nanofibers might not be optimum. It is a great challenge to reduce the Pt size on Pt/SnO_2 nanofibers to below 5 nm under the present processing conditions.

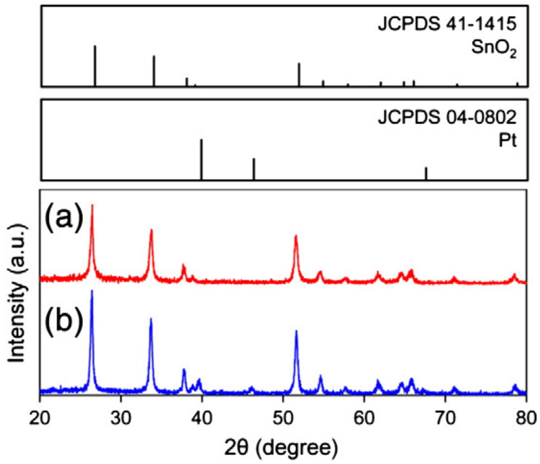

Fig. 1. XRD patterns of (a) SnO_2 nanofibers and (b) Pt/SnO_2 nanofibers.

Fig. 2 shows the FE-SEM, TEM, HR-TEM, and elemental mapping of Pt/SnO_2 nanofibers. The morphology of SnO_2 nanofibers was found similar to that of Pt/SnO_2 nanofibers. It was found that the average diameter of prepared nanofibers was ~400 nm. The as-prepared nanofibers were very flexible and smooth with a length up to several centimeters prior to the heat treatment. After calcination, the surface of the nanofibers became rough, porous, and grainy. The lengths of the nanofibers were reduced to several micrometers, as shown in Fig. 2(a). The existence of Pt nanoparticles on the tin oxide matrix was clearly visible, as shown by TEM and HR-TEM images (Fig. 2(b), (c)). The actual Pt loading on the prepared Pt/SnO_2 nanofibers was measured as 4.03 wt.% according to the ICP measurement. Elemental mapping of Pt/SnO_2 nanofibers was conducted to verify the elemental composition of the nanofibers (Fig. 2(d)). Sn, O and Pt atoms were confirmed as existing to be well-distributed on the nanofiber matrix. In addition, C and N atoms were also detected in the nanofiber. They may derive as a byproduct of polyacrylonitrile.

The cyclic voltammogram, recorded at 200th cycle, are presented in Fig. 3(a). The voltammogram are necessary to determine the electrochemically active surface area (ECSA). The CV-curve of Pt/SnO_2 nanofibers was very stable up to 200th cycle (see Supporting Information). SnO_2 nanofibers had a very small ECSA indicated by its CV-curve that almost formed a straight line. On the other hand, the presence of Pt nanoparticles on SnO_2 nanofibers significantly increased the ECSA. Typically, there are three regions in a CV-curve that correspond to hydrogen adsorption-desorption, double-layer charging, and Pt oxidation-reduction activities that could be clearly seen on CV-curve of Pt/C TKK [4,5]. However, the CV-curve of Pt/SnO_2 nanofibers shows a unique characteristic. It shows the features of hydrogen adsorption-desorption at $E < 0.4$ V, however it does not show the Pt oxidation–reduction activity, indicated by its CV-curve that significantly suppressed at $E > 0.6$ V. Based on this phenomenon, we assume that Pt/SnO_2 nanofibers had an ORR-blocking characteristic (see Supporting Information). It is a great challenge to develop this kind of electrocatalyst with high ORR activity. The unique activity of prepared Pt/SnO_2 nanofibers was probably due to the presence of organic nitrile-group molecules on nanofibers as shown by elemental mapping. Previous study showed that PAN-based nanofibers had nitrile molecules derived from polyacrylonitrile, and this molecules are known to be easily adsorbed by hydroxyl molecules [13,15]. Pt nanoparticles are typical of conductive material for hydroxyl molecules. It makes hydroxyl molecules easily transferred to near Pt nanoparticles site and finally cover the surface of Pt nanoparticles and introduce nitrile group to the Pt/SnO_2 nanofibers simultaneously. It has been shown that high hydroxyl coverage on Pt nanoparticle inhibits ORR activity [16].

The ECSA values were then calculated using the following equation:

$$\mathrm{ECSA} = \frac{Q_H}{Q_0 \times m_{Pt}} = \frac{v^{-1} \int I dE}{Q_0 \times m_{Pt}}, \qquad (1)$$