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RESEARCH PAPER

Pt-Ir-SnO_2/C Electrocatalysts for Ethanol Oxidation in Acidic Media

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Abstract: A series of Pt-Ir-SnO_2 catalysts supported on carbon were synthesized by a modified Bönnemann method. An electrochemical study showed that the Pt-$Ir_{0.07}$-SnO_2/C catalyst had a three times higher ethanol oxidation current and a two times higher CO_2 formation selectivity compared with the Pt/C catalyst under an application voltage of 0.5 V vs the RHE at 25 °C. This demonstrates that the Pt-$Ir_{0.07}$-SnO_2/C catalyst is a potentially ideal ethanol oxidation catalyst for direct ethanol fuel cells.

Key words: platinum; iridium; tin oxide; carbon; supported catalyst; ethanol electro-oxidation; direct ethanol fuel cell

Direct ethanol fuel cells (DEFCs) have attracted great interest as a power source in numerous applications because ethanol is a nontoxic and high density energy carrier, which is widely available from the reformation of various kinds of biomass [1,2]. However, the complete electro-oxidation of ethanol is a complicated reaction because it involves the transfer of twelve electrons, C–C bond breaking, relatively slow reaction rate on Pt, and the production of partially/incompletely oxidized acetaldehyde and acetic acid as the main products in acidic media instead of completely oxidized CO_2 [3,4]. Therefore, the development of novel catalysts with high catalytic activity for the complete oxidation of ethanol, especially anode electrocatalysts, is an important and challenging research topic for the eventual use of ethanol as a fuel for DEFCs.

A comparison of the ethanol total oxidation level together with the selectivity of the complete oxidation of ethanol to CO_2 is a general method to evaluate the performance of catalysts for DEFCs. The addition of a secondary element such as Ru or Sn to Pt can enhance the ethanol oxidation reaction [5–8]. However, these kinds of alloys usually show relatively low selectivity for CO_2 formation compared with Pt alone [5,6]. The catalyst composed of Pt and SnO_x showed slightly higher selectivity compared with Pt-Sn alloys, but the product is still acetaldehyde and selectivity toward CO_2 is even lower than on Pt [5,6]. De Souza [9] studied the electrochemical behavior of ethanol on Pt, Rh, and Pt-Rh electrodes. Rh was found to have relatively low electrocatalytic activity toward ethanol oxidation. Pure Pt electrodes show similar electric current density compared with $Pt_{73}Rh_{10}$, but the latter has a high CO_2 production activity. Recently, Li et al. [10] found that the addition of Rh to Pt-SnO_2/C enhanced the catalyst capacity to break C–C bonds while enhancing the electric current for ethanol oxidation. In this work, Ir was used as the third metal to replace the Rh that was incorporated into Pt-SnO_2 based catalysts. Many reports describe the use of Ir in catalysts for ethanol electro-oxidation. For example, Cao et al. [11] found that Ir based catalysts such as Ir_3Sn/C gave improved catalytic performance for the ethanol oxidation reaction (EOR) compared with Pt_3Sn/C. This might be due to the formation of IrO_2 on Pt since Pt-IrO_2 has been reported to be a good catalyst for the EOR [12]. Ir and Sn co-doped $Pt_{68}Sn_9Ir_{23}$/C has also been reported to be an excellent EOR promoter [13]. Fatih et al. [14] synthesized a series of quaternary PtRuIrSn/C catalysts and found that the $Pt_{30}Ru_{30}Ir_{10}Sn_{30}$/C catalyst gave the best performance for the complete oxidation of ethanol as well as excellent long-term stability. These results demonstrate that the addition of Ir can enhance EOR activity [12–14] and promote the oxi-

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dation of CO_{ads} species adsorbed on active metal sites [15]. However, the role of each element in this catalytic activity has not been well addressed because of the complexity of the catalytic system. In this paper, a series of Pt-Ir-SnO_2/C electrocatalysts were prepared by the modified Bönnemann method [16,17].

1 Experimental

1.1 Catalyst preparation

$N(Oct)_4(BEt_3H)$ was prepared according to a report in the literature [16]. $N(Oct)_4(BEt_3H)$ dissolved in tetrahydrofuran (> 99.5%, 100 ml) was added to a tetrahydrofuran solution containing $PtCl_2$ (0.1027 g), $SnCl_2$ (0.0758 g), and $IrCl_3$ (0.0398 g) under vigorous stirring at 50 °C under a nitrogen atmosphere. After a 2 h reaction, the reaction mixture turned into a colloidal suspension, and high surface area carbon (Vulcan XC-72, 0.0588 g) was added. After filtration and air drying at room temperature, the powder was further calcined at 330 °C in air. Three Pt-Ir-SnO_2/C catalysts with a Pt:Ir:Sn atomic ratio of 1:0.2:1, 1:0.3:1, and 1:0.75:1, respectively, were obtained. For comparison, Pt/C and Pt-SnO_2/C samples were prepared following the same procedure. To study the effect of Ir addition to Pt-Sn on the catalytic activity, the atomic ratio of Pt:Sn was fixed at 1:1.

1.2 Catalyst characterization

The morphologies of the nanoparticles that were deposited on the high surface area carbon were studied by transmission electron microscopy (TEM, JEM-2100F, JEOL). The amount of metal loading was determined by inductively coupled plasma-mass spectrometry (ICP-MS, 7500a, Agilent) and thermogravimetric analysis (TGA, Perkin Elmer). Crystallographic phase analysis was carried out using X-ray diffraction (XRD, RINT 2500, Rigaku) and the spectrometer was equipped with a Cu K_α radiation source. The lattice parameters were obtained by fitting the Pt (220) XRD diffraction peak with the pseudo-Voigt function assuming that the Pt (220) surface is free from the impact of carbon and the SnO_2 crystal face. X-ray photoelectron spectroscopy (XPS, ESCALAB MK) data were used to determine the oxidation states of Pt, Sn, and Ir on the surface layers of the samples.

1.3 Electrochemical measurements

Electrochemical experiments were conducted on an HZ3000 electrochemical measurement system (Hokuto Denko, Japan) using a conventional three-electrode measurement system. A spiral Pt wire was used as a counter electrode, a reversible standard hydrogen electrode (RHE) in H_2SO_4 solution was used as the reference electrode, and Pt-Ir-SnO_2/C was used as the working electrode. The procedure for the preparation of the working electrode was as reported in Ref. [18].

The gas products evolved during the electrochemical measurements were analyzed by gas chromatography (GC, Shimadzu GC-14B). The current efficiency (η) of the products such as CO_2, acetic acid, and acetaldehyde was calculated based on Faraday's law [5]:

$$\eta(\%) = \frac{n \times F \times z}{Q} \times 100\%$$

where n is the amount of substance (mole), F is the Faraday constant (96485 C), z represents the number of electrons transferred per molecule of products (6 for CO_2; 2 for acetaldehyde; 4 for acetic acid), and Q is the total electric charge during electrolysis (C).

2 Results and discussion

2.1 TEM and HRTEM characterization

Figure 1 shows TEM images and histograms of the particle size distribution. Both the particle size and the size distribution increase upon the addition of Ir to Pt-SnO_2. The Pt-$Ir_{0.07}$-SnO_2/C catalyst gave the best size distribution although it has a similar particle size to Pt/C. The Pt:Sn ratios were approximately 1:1 for all of the prepared samples per ICP-MS analysis, which is consistent with the Pt:Sn ratio in the initial reaction mixture. However, the Ir content in Pt-Ir_x-SnO_2/C (x = 0.04, 0.07, 0.1) is lower than the nominal values, indicating a loss of Ir because of the incomplete reduction of Ir precursors during the synthetic process, or the Ir precursor was not completely loaded onto the active carbon.

Figure 2 shows TEM and HRTEM images of the Pt-$Ir_{0.07}$-SnO_2/C sample. The pixel intensity profile of the brighter cluster reveals that the distance between the adjacent fringes is 0.3363 nm, which agrees well with the SnO_2 d_{110} of 0.3353 nm that was calculated using the XRD patterns [19]. For the darker colored cluster, the average distance between the adjacent fringes is 0.2222 nm, which is close to the interplanar distance of fcc Pt-Ir(111), d_{111}= 0.2265 nm [19].

In the ICP analysis, the Pt content in the sample is more than ten times the Ir content, and because Pt is usually considered one of the best catalysts for ethanol adsorption, it is likely that the ethanol molecules are mainly adsorbed on Pt although there might be a minor amount of ethanol molecules adsorbed onto Ir and SnO_2. Therefore, it is relatively important to investigate the Pt structure for ethanol electro-oxidation.

From XRD, only the changes of Pt(220) surface are observed, and this is probably due to small amounts of Ir loading leading to a low impact on electronic structure changes for Pt. Figure 3 shows the dependence of the fcc lattice parameters of the catalysts on the Ir content, which corresponds to the Pt(220)