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Enhanced activity of PtSn/C anodic electrocatalyst prepared by formic acid reduction for direct ethanol fuel cells

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Abstract

The Pt_3Sn/C catalyst with high electrochemical activity was synthesized under optimizing preparation conditions. The surface of carbon support pretreated by strong acid contains many O–H and C=O groups, which will increase the active sites of PtSn/C catalysts. The catalyst structure was characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and temperature programmed reduction (TPR). The co-reduction of Pt^{4+} and Sn^{2+} ions causes Sn to enter Pt crystal lattice to form PtSn alloy whose surface, however, contains tin oxides with Sn^{4+} and Sn^{2+} valences, which can promote the ethanol oxidation. The crystallinity of PtSn decreases with the reduction of the atomic ratio of Pt:Sn. By prolonging the reaction time of formic acid, the forward anodic peak current of ethanol oxidation reaches 16.2 mA on the Pt_3Sn/C catalyst with 0.025 mg Pt loading.

Keywords: Anodic catalyst; Direct ethanol fuel cell; Ethanol oxidation; Formic acid reductant; PtSn/C

1. Introduction

In the past decade, great attention has been paid to the study of directly using liquid fuels instead of hydrogen to feed fuel cells because of the difficulties associated with the handle, storage and transportation of gaseous fuels for proton exchange membrane fuel cell (PEMFC) [1]. The direct methanol fuel cell (DMFC) has a simple system design, low cost and the relatively easy transport and storage of methanol. Its anodic electrocatalysts and the methanol crossover through the proton exchange membrane have been widely investigated [2,3]. Since the methanol is a toxic product and can cause environmental problems, recent studies are focused on the direct ethanol fuel cell (DEFC) [4]. The ethanol as a liquid fuel has many advantages such as higher power density, non-toxicity, nature availability, renewability and zero greenhouse contribution to the atmosphere [5]. Therefore, ethanol is more attractive than methanol for direct alcohol fuel cells (DAFC) operating at low temperature.

The ethanol electrooxidation has a complicated multistep reaction mechanism, which involves a number of adsorbed intermediates and byproducts resulting from incompletely oxidizing ethanol. Their adsorbed intermediates are CO_{ads} and C-1 and C-2 hydrocarbon residues and the final oxidation products are mainly acetaldehyde and acetic acid. Detailed analysis for the products of ethanol oxidation on Pt indicates that acetic acid is dominant at high potentials ($E > 0.8$ V *vs.* RHE) and acetaldehyde at low potentials ($E \approx 0.6$ V *vs.* RHE). At intermediate potentials, a few CO_2, CH_4 and adsorbed intermediate species such as CO_{ads}, etc. also appear besides the two products above [5–7]. Wang et al. [8] also found that the main product is acetic acid in very dilute ethanol solution (1 mM) while it becomes acetaldehyde in the concentrated solution with 0.5 M ethanol solution. All this is due to the fact that the cleavage of the C–C bond requires higher activation energy than C–H bond breaking [9]. Incomplete oxidation of the ethanol greatly reduces the output energy density of DEFC.

Although ethanol has a low crossover rate through the Nafion® membrane, its oxidation kinetics is more sluggish on Pt catalyst, compared with methanol [10,11]. Therefore, more investigations for DEFC are concentrated on the catalyst preparation and their electrochemical activity [12–22]. Among Pt-based binary catalysts, to date, PtRu and PtSn are the most active catalysts for ethanol oxidation. So Sn can be used to replace the Ru noble metal. Different results have been reported

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with the change of atomic ratio of Pt:Sn. Zhou et al. [12] believed that Pt_3Sn_2/C has higher electrocatalytic performance at 60 °C while Pt_2Sn/C becomes better at 90 °C. Colmati et al. [13] found that PtSn alloy can promote the ethanol adsorption and C–C cleavage at elevated temperature and the electrocatalytic activity of Pt_3Sn is higher than that of PtRu for DEFC test at $T > 70$ °C. Jiang et al. [14] investigated the performance of PtSn alloy and $PtSnO_x$ particles, and believed that $PtSnO_x$ catalyst presents higher catalytic activity than PtSn alloy. Léger et al. [15] indicated that the oxidation of ethanol to acetaldehyde and acetic acid could occur through an adsorbed acetyl species at the potential higher than 0.4 V (*vs*. RHE). Colmati et al. [16] found that the increase of Sn content in PtSn/C catalyst promotes the oxidation of both CO_{ads} at low temperature and acetaldehyde to acetic acid at high temperature. Neto et al. [17] compared PtSn/C with PtRu/C and PtSnRu/C electrocatalysts for methanol and ethanol oxidation and believed that the PtSn/C has higher performance. In order to enhance activity for ethanol oxidation, other investigations still included the multi-wall carbon nanotube (MWNT) as support of PtSn catalyst [18], pretreating carbon support [19], catalyst synthesis [20–22], Pt-based catalysts without Sn [23–25] and ethanol oxidation on CuNi catalyst in alkaline solution [26].

The key for DEFC commercialization is still the electrocatalytic activity of ethanol oxidation. Although hydrogen, $NaBH_4$ and ethylene glycol, etc. are often used as reductants of Pt-based catalyst precursors, recently formic acid is also reported as a reductant of preparing PtSn/C electrocatalyst [16,20]. In practice, the activity of Pt-based catalysts is closely related not only to the chosen elements but also to synthetic route and its optimization. In present work, the formic acid was used as a reductant and the synthetic route of the PtSn/C catalysts with different atomic ratios of Pt:Sn was investigated.

2. Experimental

The active carbon support (Vulcan XC-72R) was first pretreated to remove impurities and enhance its active surface. The carbon was ground and added to 30 ∼ 40 mL 20% (v/v) HCl solution per gram carbon, followed by reflux distillation while stirring at 120 °C for 10 h. The suspended carbon was filtered, washed and dried in an oven at 150 °C for 10 h. Then the carbon was ground, treated by 20 ∼ 30 mL 5 M HNO_3 solution per gram carbon, filtered and dried again using the method above.

The pretreated carbon suspension was obtained by adding the Vulcan XC-72R carbon powder pretreated above to formic acid and ethylene glycol solution with identical volume. The stoichiometric metal precursors of H_2PtCl_6 and $SnCl_2$ with 75 at.% Pt and 25 at.% Sn was dissolved in ethylene glycol (EG), ultrasonically dispersed for 0.5 h, followed by slowly adding the precursors to the carbon suspension while stirring at 90 °C in N_2 atmosphere and reacting for 10 or 28 h. After cooling, the mixture was filtered and distilled. The filter cake was dried in a vacuum oven at 90 °C for 8 h. The Pt loading of all catalysts on Vulcan XC-72R carbon black was 20 wt.%.

Five milligram catalyst powder was added to 1 mL isopropanol, ultrasonically dispersed and then 15 μL 15 wt.% Nafion® solution was put in. After ultrasonic homogenization of the suspension, 25 μL catalyst ink was transferred with an injector to the polished glassy carbon disk electrode with the area of 0.1256 cm^2 and the solvent was evaporated under an infrared lamp. The Pt loading on glassy carbon electrode was 0.2 mg cm^{-2}. The tests of electrochemical performance were carried out in the electrolyte cell composed of three compartments with Pt foil as counter electrode and $Hg/Hg_2SO_4/0.5$ M H_2SO_4 (MMS) as reference electrode. The electrolyte was 0.5 M H_2SO_4 + 1 M CH_3CH_2OH solution. And high purity N_2 gas (99.999%) passed through it for 30 min before the experiments. The electrochemical experiments were done at 30 °C on CHI 614B potentiostat. Characterizations of the catalyst nanoparticles were carried out by Phlip X'Pert Pro MPP X-ray Powder Diffractometer (XRD) and JEOL JEM-1010 Transmission Electron Microscope (TEM). The infrared and ultraviolet spectra were performed on SP2000 Fourier Transform Infrared Spectrograph (FTIS) and T6 Ultraviolet-Visible Spectrophotometer (UVS), respectively. Temperature programmed reduction (TPR) experiments were carried out on Miromeritics AutoChem 2910 Instrument at a heating rate of 5 °C min^{-1} and a 10% H_2/Ar flow rate of 30 mL min^{-1}.

3. Results and discussion

3.1. Analysis of precursor reduction

Colloidal dispersion of metals has the adsorption band or broad adsorption range on the UV–vis spectra. In order to know the reaction mechanism of H_2PtCl_6 and $SnCl_2$ in the EG solution with formic acid as a reductant, UV–vis experiments were used to monitor the reaction processes. Fig. 1 shows the UV–vis spectra of different solutions. It can be seen that there is no peak in HCOOH/EG except the peak at around 210 nm (curve a). And there exists a prominent adsorption peak at 267 nm in H_2PtCl_6/EG (curve b) and a small shoulder at around 236 nm in $SnCl_2$/EG (curve c). The former is assigned to the absorp-

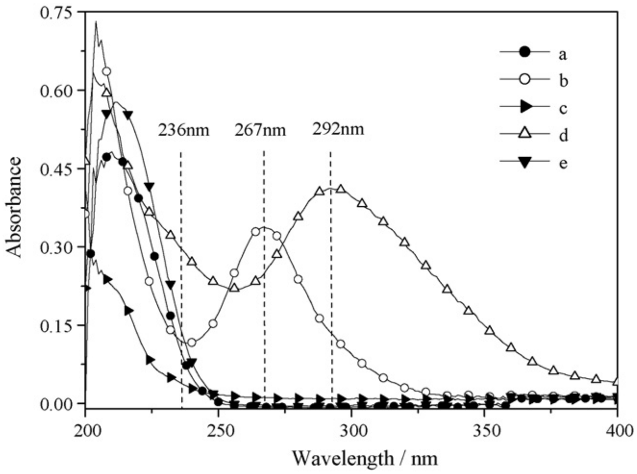

Fig. 1. UV–vis spectra of different solutions. (a) HCOOH/EG; (b) H_2PtCl_6/EG; (c) $SnCl_2$/EG; (d) $H_2PtCl_6 + SnCl_2$/EG (Pt:Sn=1:1); (e) $H_2PtCl_6 + SnCl_2$/EG + HCOOH (after 28 h at 90 °C).