Journal of Power Sources 252 (2014) 156–163

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Platinum catalysts promoted by In doped SnO_2 support for methanol electrooxidation in alkaline electrolyte

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HIGHLIGHTS

- Composite metal oxides In_xSnO_2 are prepared with a simple hydrothermal process.
- In_xSnO_2 is used as functionalized support of Pt catalyst toward MOR.
- A small amount of In doped in SnO_2 exhibits much higher promoting effect to Pt.
- The increase in activity arises from the changes in the Pt electronic structure.

ARTICLE INFO

Article history:
Received 7 September 2013
Received in revised form
22 November 2013
Accepted 2 December 2013
Available online 11 December 2013

Keywords:
Indium
Tin
Oxide
Platinum
Methanol electro-oxidation

ABSTRACT

Composite metal oxides In_xSnO_2 are prepared with a simple hydrothermal process and used as functionalized support of Pt catalyst toward methanol electrooxidation reaction (MOR). The catalytic activity of Pt is strongly dependent on the composition of the support. Introduction of a small amount of In into SnO_2 support exhibits much higher promoting effect to the Pt catalytic properties as compared with Pt/SnO_2 and commercial Pt/C catalysts. The mass-specific activity (MSA) and intrinsic activity (IA) of Pt in Pt/$In_{0.1}SnO_2$ is 3.0 and 4.3 times that of Pt/C, respectively. Changes in Pt electronic structure arising from the interaction between Pt and the support are responsible for this improvement. Our findings clearly suggest that the composite metal oxides In_xSnO_2 can not only act as the catalyst support but also act as an effective promoter to Pt toward MOR, which would be promising in designing new catalysts that can replace the traditional catalytic nanostructure.

1. Introduction

Direct methanol fuel cells (DMFCs) are one of the very promising power sources for portable electronic devices and vehicles. It has been reported that the kinetics of both methanol anodic oxidation and oxygen cathodic reduction in alkaline electrolyte are more facile than in acidic electrolyte [1,2]. In addition, the electrode materials show much higher stability in alkaline electrolyte in comparison with that in acidic media. The above advantages make the alkaline direct methanol fuel cells exhibit a growing interest in recent years. To date, Pt is the most active catalyst toward methanol electro-oxidation reaction (MOR), nevertheless, it is easily poisoned by the CO-like intermediates formed in the MOR process, which strongly depresses the catalytic properties of Pt [3].

Recently, many researches focused on introducing a second metal into Pt to form bimetallic PtM catalysts (PtNi, PtRu, PtAu, PtAg, etc.) or Pt-on-M nanostructures (Pt-on-Ru, Pt-on-Co, etc.) [4–11] so as to improve the poison tolerance of Pt. The enhanced catalytic activity of Pt comes from the ligand effect [4,8–11] or bifunctional mechanism [5–7]. The ligand effect arises from the presence of other metals which change the electronic environment of Pt, giving rise to the modifications of the Pt electronic structure and consequently, the catalytic performance. The d-band center theory proposed by Nørskov and co-workers has been widely accepted and regarded as an indicator to determine the surface reactivity of Pt [12]. A downshift of d-band center would weaken the interaction between Pt and some simple adsorbates such as H, O, CO and thus improve the poison tolerance of Pt in the bimetallic PtM or Pt-on-M catalysts as compared with

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http://dx.doi.org/10.1016/j.jpowsour.2013.12.008

pure Pt [12,13]. Difference in the work function between pure Pt and the Pt-based catalysts may play an important role for this improvement [14]. In addition, the promoter M can activate water at lower potentials than Pt, the adsorbed OH species on M can oxidize the −CO adsorbed on the surface of the neighboring Pt atoms to CO_2 and thus increase the CO tolerance of Pt [15], which is usually called synergistic effect or bifunctional mechanism. Besides the metal promoter, some metal oxides such as CeO_2, NiO and V_2O_5 are also investigated as the promoter to Pt toward MOR in alkaline electrolyte [16–21]. Shen et al. have reported that the addition of CeO_2 into Pt catalysts could significantly improve the catalytic activity and poisoning resistance of Pt toward alcohol electrooxidation due to the synergistic effect [19–21].

Supported catalysts are of special interest, for they allow for the fine dispersion and stabilization of small metal nanoparticles (NPs). Traditional DMFC catalysts use carbon material as the support because it has sufficient electronic conductivity, large surface area (e.g. 250 $m^2\ g^{-1}$ for XC-72 carbon black) and well-developed pore structure. The carbon materials can not only make the charge transport to/from the catalyst easily but also exhibit a high dispersion state of Pt on their surface [22]. However, during the repeated power-on and -off processes of fuel cells, the high potential often accelerates the carbon corrosion, which would make the Pt metal NPs be prone to agglomerating and thus lead to a decrease in their electrochemically active surface area (EAS) and activity [23,24]. In order to solve these problems, other support materials such as metal oxides are investigated [23,25–28]. It has been reported that the TiO_2-supported Pt catalyst show ultrahigh stability as compared with carbon-supported catalyst [23]. The $NbRu_yO_z$-supported Pt catalyst can facilitate the C–C scission and exhibit a much higher catalytic performance toward ethanol oxidation [26]. Recently, a nanostructured $Ti_{0.7}Mo_{0.3}O_2$ material was prepared and used as the support for Pt catalyst [27], the electron transferring from $Ti_{0.7}Mo_{0.3}O_2$ to Pt induces changes in the surface electronic structure of Pt, the catalytic activity of Pt toward oxygen reduction reaction (ORR) is then improved remarkably.

Although some metal oxides have been identified as good promoters to Pt, a small fraction of them can be used as catalyst support because of their poor electrical conductivity. Tin dioxide is electrically conductive, and the Pt or Pd-based electrocatalysts that are promoted by SnO_x have shown high catalytic properties for the electrooxidation of small organic molecules due to the high CO-poisoning tolerance [29,30]. In addition, Sn-containing multicomponent metal oxides such as In-doped SnO_2 or Sn-doped In_2O_3 (ITO) have been used as a perfect conductive material in many fields, such as the liquid crystal displays, touch panels, plastic electroluminescent lamp and catalyst supports [31–33]. Inspired by the high electrical conductivity of ITO and the good promoting effect of SnO_x to Pt toward the electrooxidation of small organic molecules [29], in the present work, we prepared the In-doped SnO_2 material through a traditional hydrothermal method. The multicomponent metal oxide materials are used as the catalyst support to carry Pt NPs toward the MOR in alkaline electrolyte. The promoting effect of the multicomponent In-doped SnO_2 materials arises from the ligand effects, which are related to the modification of the electronic structure of Pt [34] and vital for the enhancement of the Pt catalytic properties. Compared with the conventional carbon-supported Pt catalyst, small amount of In doping in SnO_2 support show much higher promoting effect to Pt catalytic activity and stability for MOR. These results are of fundamental importance to the in-depth understanding or the MOR mechanism and also exhibit potential applications in the design of fuel cell catalysts.

2. Experimental section

2.1. Synthesis of the In_xSnO_2 metal oxide supports

Traditional hydrothermal method was used to prepare the In_xSnO_2 nanostructures. Take the $In_{0.1}SnO_2$ for example: 2 mL $InCl_3$ (50 mM) and 20 mL $SnCl_4$ (50 mM) solution was stirred for 30 min and then transferred into a Teflon-lined autoclave with a stainless steel shell and heated to 200 °C in the oven. The sample was kept at 200 °C for 3 h and then cooled to room temperature. The as-prepared sample was washed with deionized water and centrifugated for several times. The precipitates were dried at 80 °C oven overnight. The $In_{0.8}SnO_2$ and SnO_2 samples were prepared through the same method only the ratio of the added metal precursors was different.

2.2. Preparation of the In_xSnO_2-supported Pt samples (Pt/In_xSnO_2)

Platinum NPs were prepared through the polyols method. 0.65 mL H_2PtCl_4 (0.04 M) and 20 mg sodium citrate were added into 15 mL ethylene glycol. After stirring for 30 min, sodium hydroxide solution was added dropwise to adjust the pH = 8.5–9.0. 20 mg In_xSnO_2 was added and continued stirring for 30 min. The mixed solution was heated at 130 °C in an oil bath for 4 h to ensure the complete reduction of Pt. During this process, a flow of N_2 kept passing through the solution to remove the dissolved oxygen. Then, the as-prepared sample was cooled to room temperature, washed with deionized water and centrifugated for several times. The precipitates were dried at 80 °C in a vacuum oven overnight. For all the samples, the Pt loading was kept at approximately 20 wt. %.

2.3. Physico-chemical characterizations of the samples

The morphology of the as-prepared samples was investigated using JEM-2100 transmission electron microscope (TEM) operating at 120 kV. X-ray diffraction (XRD) patterns were measured with a D8-Advance Bruker diffractometer at a scan rate of 4 deg/min ($30° < 2\theta < 85°$) and the wavelength of the incident radiation was 1.5406 Å (Cu Kα). X-ray photoelectron spectroscopy (XPS) measurements were taken on a Thermo ESCALAB 250 instrument with Al Ka radiation (h = 1486.6 eV). The actual loading amount of Pt in the as-prepared catalysts was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin Elmer Optima-4300DV Spectrometer).

2.4. Electrochemical characterizations

A glassy carbon (GC) electrode of 5 mm diameter (surface area: 0.1963 cm^2) embedded in a Teflon holder was used as the working electrode. Prior to each use, the electrode was polished with 0.5 and 0.05 μm alumina suspensions followed by washed ultrasonically with HNO_3 (1:1), ethanol, acetone and deionized water, sequentially. The catalyst ink was prepared by sonicating a suspension of the In_xSnO_2-supported catalyst (5.0 mg) in isopropanol (1.0 mL). 10 μL of the suspension was firstly transferred onto the disk electrode, after the solvent evaporation at room temperature, 10 μL 0.05 wt. % Nafion solution (Dupont) was then pipetted onto the catalyst layer and air-dried. Since the actual Pt loading is slightly different for all of the catalysts, the MOR current normalized by the mass of Pt on the electrode was used for the comparison of the Pt catalytic activity in this study.

Electrochemical measurements were carried out on a CHI 660D (Shanghai Chenhua Apparatus, China). A conventional three-electrode cell was used for cyclic voltammetry (CV), CO-stripping and chronoamperometry (CA). A Pt foil (1.0 cm × 1.0 cm) and a