Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Electrochimica Acta 50 (2005) 5384–5389

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Structure and chemical composition of supported Pt–Sn electrocatalysts for ethanol oxidation

Luhua Jiang[a,1], Gongquan Sun[a], Shiguo Sun[a],
Jianguo Liu[a], Shuihua Tang[a], Huanqiao Li[a], Bing Zhou[a,b], Qin Xin[a,c,*]

[a] *Dalian Institute of Chemical Physics, Direct Alcohol Fuel Cell Group,*
Zhongshan Road 457, Liaoning Province, Dalian 116023, China
[b] *Headwater NanoKinetix Inc., USA*
[c] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics,*
Graduate School of the Chinese Academy of Sciences, CAS, China

Received 22 December 2004; received in revised form 25 February 2005; accepted 4 March 2005

Abstract

Carbon supported PtSn alloy and PtSnO$_x$ particles with nominal Pt:Sn ratios of 3:1 were prepared by a modified polyol method. High resolution transmission electron microscopy (HRTEM) and X-ray microchemical analysis were used to characterize the composition, size, distribution, and morphology of PtSn particles. The particles are predominantly single nanocrystals with diameters in the order of 2.0–3.0 nm. According to the XRD results, the lattice constant of Pt in the PtSn alloy is dilated due to Sn atoms penetrating into the Pt crystalline lattice. While for PtSnO$_x$ nanoparticles, the lattice constant of Pt only changed a little. HRTEM micrograph of PtSnO$_x$ clearly shows that the change of the spacing of Pt (1 1 1) plane is neglectable, meanwhile, SnO$_2$ nanoparticles, characterized with the nominal 0.264 nm spacing of SnO$_2$ (1 0 1) plane, were found in the vicinity of Pt particles. In contrast, the HRTEM micrograph of PtSn alloy shows that the spacing of Pt (1 1 1) plane extends to 0.234 nm from the original 0.226 nm. High resolution energy dispersive X-ray spectroscopy (HR-EDS) analyses show that all investigated particles in the two PtSn catalysts represent uniform Pt/Sn compositions very close to the nominal one. Cyclic voltammograms (CV) in sulfuric acid show that the hydrogen ad/desorption was inhibited on the surface of PtSn alloy compared to that on the surface of the PtSnO$_x$ catalyst. PtSnO$_x$ catalyst showed higher catalytic activity for ethanol electro-oxidation than PtSn alloy from the results of chronoamperometry (CA) analysis and the performance of direct ethanol fuel cells (DEFCs). It is deduced that the unchanged lattice parameter of Pt in the PtSnO$_x$ catalyst is favorable to ethanol adsorption and meanwhile, tin oxide in the vicinity of Pt nanoparticles could offer oxygen species conveniently to remove the CO-like species of ethanolic residues to free Pt active sites.

Keywords: Direct ethanol fuel cell; Electrocatalyst; Pt–Sn; Ethanol electro-oxidation

---

1. Introduction

Bimetallic nanoparticles supported on high surface area carbon find widespread application as electrode materials. Of particular interest is Pt–Sn bimetallic particles used for the electro-oxidation of ethanol at the anode of low temperature fuel cells [1–9]. Supported Pt–Sn with low loadings (<5%) has been studied well as a catalyst for ethanol or gasoline reforming at high temperature in the past decades [10–13]. However, to the best of our knowledge, few studies on the microchemistry of high loading supported Pt–Sn catalysts employed in low temperature direct ethanol fuel cells has been reported. Preparation procedure strongly affects the dispersion and the compositional homogeneity of the bimetallic clusters, both of which are important factors in determining their electrocatalytic activity toward ethanol oxidation. In the previous work [7], we have shown that the carbon supported

---

[*] Corresponding author. Tel.: +86 411 84379071; fax: +86 411 84379071.
E-mail addresses: sunshine@dicp.ac.cn (L. Jiang), xinqin@dicp.ac.cn (Q. Xin).
[1] Tel.: +86 411 4379668; fax: +86 411 4379071.

doi:10.1016/j.electacta.2005.03.018

Pt–Sn catalyst synthesized by a modified polyol method possessed much higher catalytic activity for ethanol electro-oxidation than pure Pt. Lamy and co-workers [2–5] also found PtSn catalysts prepared by impregnation–reduction method showed superior performance for ethanol electro-oxidation. However, the active component and the preferred microstructure of PtSn catalysts were still undiscovered till now. Therefore, it is clearly of importance to verify the desired composition and microstructure of the supported bimetallic particles. Here our focus is to prepare two kinds of PtSn catalysts with different tin chemical states and examine the supported bimetallic catalysts in terms of particle size and the components using HRTEM, XRD, and microchemical analysis by HR-EDS. Furthermore, CV and CA experiments were carried out to study the effects of the chemical state of tin and the microstructure of PtSn/C catalysts on the ethanol electro-oxidation and the performance of DEFCs.

2. Experimental section

2.1. Catalyst and electrode preparation

$H_2PtCl_6{\cdot}6H_2O$ and $SnCl_2{\cdot}2H_2O$ were used as precursors of PtSn catalysts. Vulcan XC-72R carbon black (Cabot Corp., $S_{BET} = 236.8\,m^2\,g^{-1}$) was used as a support for all samples. Two PtSn/C catalysts prepared by successive reduction and co-reduction, respectively, were prepared for comparison. PtSn-1 was prepared by the successive reduction via the following procedure: calculated $SnCl_2{\cdot}2H_2O$ was first added to the EG solution to form a clear solution with a concentration of $0.5\,mg\,Sn\,mL^{-1}$ solution, and then the solution was heated to 190 °C at a rate of $10\,°C\,min^{-1}$ and kept at this temperature until the solution changed to slight yellow colloid (the TEM image is shown in Fig. 1). After the colloid cooled down to room temperature, the needed amount of $H_2PtCl_6{\cdot}6H_2O$ was added and stirred for half hour. Then the pH value of the solution was justified to above 13 with sodium hydroxide and the solution was heated to 160 °C and kept at this temperature for 2 h to obtain brown–black sol. The calculated amount of carbon was added to the above sol and stirred for another 2 h. The obtained black product was filtered, washed and dried. In this process, the pre-formed SnO_2 nanoparticles could be covered by Pt skin. PtSn-2 was prepared by co-reduction method according to literature [8]. The required amount of Pt and Sn precursors were added to EG to obtain a mixture with 2 mg metal/ml solvent. The mixture was stirred for half-an-hour at room temperature to obtain a homogeneous solution. Suitable amount of sodium hydroxide was added to modify the pH value of the solution to above 13. Then the mixture was heated to 160 °C at a rate of $10\,°C\,min^{-1}$ in an oil bath and kept at this temperature for 3 h. The needed amount of vulcan XC-72 was then added and stirred for another 2 h to deposit metal particles completely. In this process, Pt and Sn ions could be reduced together to form PtSn alloy whether according to thermodynamic calculation [14] or experimental data [7]. After the black mixture cooled down to room temperature it were filtered, washed, and dried at 80 °C for 10 h in a vacuum oven. The Pt nominal loading of the two catalysts was all 20 wt.% (the nominal atomic ratio of Pt to Sn is 3:1).

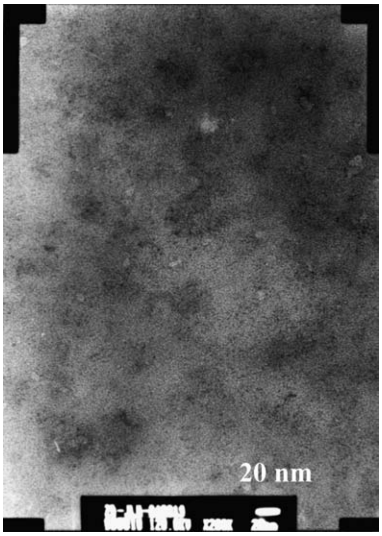

Fig. 1. TEM image of the colloid from $SnCl_2$.

Three-layer (substrate/diffusive/catalyst layer) gas diffusion electrodes were prepared according to literature [15–17]. The backing layers were loaded with $4\,mg\,cm^{-2}$ of a mixture of carbon (Vulcan XC-72) and 10% PTFE. The noble metal loading of the electrodes was $1.5\,mg\,cm^{-2}$ on the anode and $1.0\,mg\,cm^{-2}$ on the cathode. The MEAs were prepared by hot-pressing the cathode and the anode on both sides of the Nafion® 115 membrane at 130 °C for 90 s.

2.2. Physical chemical characterization

XRD patterns were recorded with a Rigaku Rotalflex (RU-200B) X-ray diffractometer using Cu Kα radiation with a Ni filter. The tube current was 100 mA with a tube voltage of 40 kV. The 2θ angular regions between 15 and 85° were explored at a scan rate of $5°\,min^{-1}$.

Transmission electron microscopy (TEM) investigations were carried out using a JEOL JEM-2000EX microscope operating at 100 kV. HRTEM images were taken on JEOL JEM-2010F with resolution of 0.102 nm operating at 200 KV.

2.3. Electrochemical characterization

Electroactivities towards ethanol oxidation of PtSn/C electrodes were measured by CV and CA experiments using an EG&G model 273A potentiostat/galvanostat and a three-electrode test cell at room temperature. The working electrode was a thin layer of Nafion impregnated PtSn/C composite cast on a vitreous carbon disk electrode. The detailed preparation method was described in literature [8,9]. A 5.0 mg catalyst sample were suspended in 1.0 mL of ethanol,