



Carbon-supported PdSn nanoparticles as catalysts for formic acid oxidation

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ABSTRACT

Pd and PdSn nanoparticles supported on Vulcan XC-72 carbon are prepared by a microwave-assisted polyol process. The catalysts are characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), linear sweeping voltammetry, and chronoamperometry. The results show that the Pd and PdSn nanoparticles, which are uniformly dispersed on carbon, are 2–10 nm in diameters. All Pd/C and PdSn/C catalysts display the characteristic diffraction peaks of a Pd face-centered cubic (fcc) crystal structure. It is found that the addition of Sn to Pd can increase the lattice parameter of Pd (fcc) crystal. The PdSn/C catalysts have higher electrocatalytic activity for formic acid oxidation than a comparative Pd/C catalyst and show great potential as less expensive electrocatalyst for formic acid electrooxidation in DFAFCs.

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1. Introduction

During the past 20 years, direct methanol fuel cells (DMFCs) have been widely studied and considered as possible power sources for the portable electronic devices and electric vehicles. These fuel cells offer a variety of benefits such as high specific energy and the ready availability and portability of methanol. On the other hand, the problem of methanol ‘crossover’ from the anode to the cathode through membrane leads to low system efficiency. Methanol crossover prevents utilization of high concentration of methanol; the limits generally less than 2 M. The feasibility of direct formic acid fuel cells (DFAFCs) based on proton exchange membranes has been demonstrated by Masel and co workers [1,2]. Hsing and co workers [3] have also reported that the rate of fuel crossover can be reduced by a factor of 5 and thus a higher performance can be obtained when formic acid is used in place of methanol under the same conditions.

Carbon-supported Pt catalysts for electrooxidation of formic acid are poisoned severely by the adsorbed CO intermediate of the reaction [4,5]. It has been demonstrated [6,7] that PtRu and PtPd alloys can diminish this CO poisoning effect to some extent, but it still limits significantly the catalytic activity for formic acid oxidation. Recently, Masel co workers [8] have disclosed that unsupported Pd and Pd/C catalysts can overcome CO poisoning effect and thereby yield high performances in the DFAFCs. In order to further improve the electrocatalytic performance of the Pd and Pd/C catalysts, the Pd-based bimetallic catalysts, such as Pd–Ni [9], Pd–Au [10], Pd–Pt [11] and Pd–Ir [12], have been investigated.

However, to the best of our knowledge, PdSn bimetallic catalysts for formic acid electrooxidation have not been reported yet.

In this paper, PdSn nanoparticles are synthesized by a simple microwave-assisted polyol procedure and deposited on carbon to produce carbon-supported PdSn catalysts, aiming to have a less expensive electrocatalyst in the DFAFC. The physicochemical properties and electrochemical activities of the nanoparticles for formic acid oxidation are investigated. The reasons of oxidation activity enhancement for PdSn catalysts are discussed in detail.

2. Experimental

The Pd_aSn_b/carbon black (Cabot Vulcan XC-72, subscript denotes the atomic percentage of the alloying metal) catalysts were prepared by microwave heating of ethylene glycol (EG) solutions of PdCl₂ and SnCl₂·2H₂O. The Pd content in each sample was 20 wt.%. 1.46, 1.95, 2.93 and 5.85 mL of 0.02 M SnCl₂·2H₂O (Aldrich, A.C.S. Reagent) and 5.85 mL of 0.02 M PdCl₂ (Aldrich, A.C.S. Reagent) were chosen to yield Pd₄Sn₁/C, Pd₃Sn₁/C, Pd₂Sn₁/C and Pd₁Sn₁/C, respectively. A typical preparation of Pd₂Sn₁/C catalyst would consist of the following steps: 5.85 mL of 0.02 M PdCl₂ and 2.93 mL of 0.02 M SnCl₂·2H₂O was mixed with 30 ml of ethylene glycol (Mallinckrodt, AR). 0.5 mL of 0.8 M NaOH was added dropwise. About 0.05 g of Vulcan XC-72 carbon was added to the mixture and sonicated. The solution was placed in a CEM ‘Discover’ microwave reactor (CEM Corporation) with the maximum temperature set at 170 °C at atmospheric conditions for 30 s. The resulting suspension was filtered; and the residue was washed with acetone and dried at 100 °C over night in a vacuum oven. For comparison, Pd/C catalyst (20 wt.% Pd loading) was also prepared using the same method.

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To determine the actual palladium and tin contents in the PdSn alloys, inductively coupled plasma spectroscopy (ICP) was used to measure the unreacted metal ions remaining in the ethylene glycol mixtures. The PdSn alloy nanoparticles of compositions of $\text{Pd}_4\text{Sn}_{1.05}$, $\text{Pd}_3\text{Sn}_{1.09}$, $\text{Pd}_2\text{Sn}_{1.03}$, and $\text{Pd}_1\text{Sn}_{1.06}$ were obtained from precursors of Pd_4Sn_1 , Pd_3Sn_1 , Pd_2Sn_1 , and Pd_1Sn_1 . The palladium and tin contents in the PdSn alloy nanoparticles were about the same as that in the initial mixtures.

The catalysts were examined by TEM on a JEOL JEM 2010. For microscopic examinations the samples were first ultrasonicated in acetone for 1 h and then deposited on 3 mm Cu grids covered with a continuous carbon film. X-ray diffraction (XRD) patterns were recorded by a Bruker GADDS diffractometer with area detector using a $\text{CuK}\alpha$ source ($\lambda = 1.54056 \text{ \AA}$) operating at 40 kV and

40 mA. The samples were prepared by depositing carbon-supported nanoparticles on a glass slide.

An AUTOLAB potentiostat/galvanostat and a conventional three-electrode test cell were used for electrochemical measurements. The working electrode was a thin layer of Nafion-impregnated catalyst cast on a vitreous carbon disk held in a Teflon cylinder. The catalyst layer was obtained in the following way: (i) a slurry was first prepared by sonicating for 1 h a mixture of 0.5 ml of deionized water, 13 mg of Pd/C or PdSn/C catalyst, and 0.2 ml of Nafion solution (Aldrich: 5 wt.% Nafion); (ii) 4 μl of the slurry was pipetted and spread on the carbon disk; (iii) the electrode was then dried at 90 °C for 1 h and mounted on a stainless steel support. The surface area of the vitreous carbon disk was 0.25 cm^2 . Pt gauze and an Ag/AgCl electrode were used as the

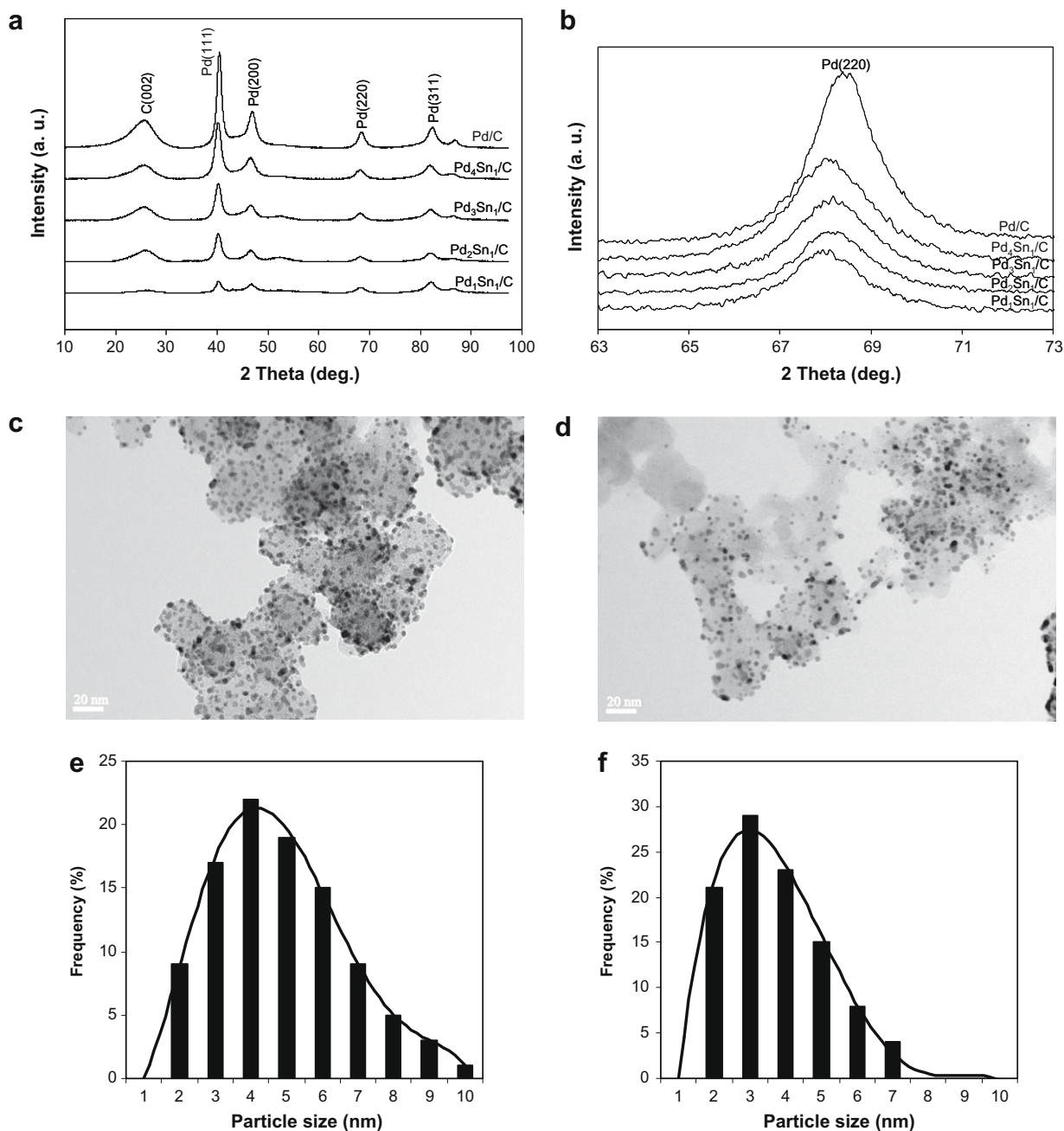


Fig. 1. (a) XRD patterns of PdSn/C catalysts, (b) an expanded view of the (2 2 0) reflections of the fcc phase, (c) TEM image of $\text{Pd}_4\text{Sn}_1/\text{C}$ catalyst, (d) TEM image of $\text{Pd}_2\text{Sn}_1/\text{C}$ catalyst, (e) particle size distribution of $\text{Pd}_4\text{Sn}_1/\text{C}$ catalyst, and (f) particle size distribution of $\text{Pd}_2\text{Sn}_1/\text{C}$ catalyst.

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