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Structural effect of PtRu–WO_3 alloy nanostructures on methanol electrooxidation

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Abstract

PtRu–WO_3 alloy thin-film nanostructures for use as direct methanol fuel cells have been fabricated by co-sputtering for 20 and 40 at.% Ru. The structural and electrochemical properties of these nanostructures were characterized using transmission electron microscopy, X-ray diffraction, and electrochemical measurements. The nanostructures consist of PtRu alloy nanoparticles (4 nm in size) dispersed in the WO_3 matrix. For 20 at.% Ru, the alloy nanoparticles are face-centered cubic (fcc), but for 40 at.% Ru, the nanoparticles separate into Pt-rich fcc and Ru-rich hexagonal-close packed (hcp) phases.

Keywords: Direct methanol fuel cell; Methanol electrooxidation; Platinum catalyst; Platinum and ruthenium alloy; Nanostructure; Grazing incidence X-ray diffraction

1. Introduction

The physical, electrochemical, electronic, and optical properties of nanostructured materials are well known to be different from those of bulk materials. In particular, metallic alloy nanostructures can have significantly enhanced catalytic reaction rates over those of bulk materials. Hence, well-designed alloy nanostructures are essential for producing efficient catalysts and for the preparation of catalysts for use in fuel cells as power sources [1–5]. Since the size and structure of nanostuctures have a significant effect on catalytic reactions, well-controlled nanostructures are essential for achieving efficient catalysts and in the preparation of catalysts for use in fuel cells [6,7]. In particular, direct methanol fuel cells (DMFCs) have attracted considerable interest because of a variety of merits such as low operating temperatures, ease of handling a liquid fuel, the high energy density of methanol, and applications to micro-sized fuel cells. The excellent catalytic activity of platinum for methanol oxidation, especially, at low temperatures makes this metal electrocatalyst ideal for use as an anode in DMFCs. However, since pure platinum is readily poisoned by intermediates produced during methanol electrooxidation, at low temperatures, Pt-based alloy or nanocomposite catalysts by alloying or mixing platinum with 2nd or 3rd elements need to be designed and synthesized. In general, the CO poisoned platinum can be regenerated via the reaction of surface CO with oxygen species associated with an element such as ruthenium to yield CO_2 [8–10]. Accordingly, PtRu alloy structure is extremely essential for enhanced methanol electrooxidation. In addition, many efforts have been reported to modulate composition and structure of PtRu alloy nanoparticles and investigate methanol electrooxidation in nanoparticles. In addition, for best performance, the DMFC electrode should consist of two or

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more phases, such as a nanosized alloy and a porous material as a support for the nanoparticles [11,12].

In this paper, we describe thin-film nanostructures for excellent catalysis and high-performance electrodes in the thin-film fuel cells prepared by multi-gun co-sputtering. The structural and electrochemical properties of the alloy thin-film nanostructure were characterized using transmission electron microscopy (TEM), grazing incidence X-ray diffraction (GIXRD), and voltammetry. We show that nanostructures consisting of PtRu alloy nanoparticles dispersed in a tungsten oxide matrix can be formed over a range of PtRu compositions. For higher Ru concentrations, the alloy nanoparticles separate into fcc and hcp phases. These have good catalytic activity for methanol electrooxidation despite the phase separation.

2. Experimental

The alloy thin-film nanostructures were prepared using an RF magnetron sputtering system [4,5]. Indium tin oxide coated on transparent glass was used as substrates. In order to fabricate a PtRu–WO_3 alloy thin-film nanostructure, the RF power of the Pt, Ru, and WO_3 sputtering guns were individually manipulated and the PtRu alloy composition was controlled by the RF power of Pt and Ru targets. Sputtering was carried out under an atmosphere of inert Ar gas at 40 SCCM at room temperature (RT). The alloy composition was determined using Rutherford backscattering spectroscopy. Cu grids were also used as substrates for analysis by transmission electron microscopy (TEM). The TEM investigation was carried out using a Phillips CM20T/STEM Electron Microscope at an accelerating voltage of 200 kV.

X-ray diffraction measurements were conducted at the National Synchrotron Light Source, beamline X20C at an X-ray energy of 10.3 keV (a wavelength of 1.21 Å). The diffracted beam was analyzed with 1 milliradian (mrad) Soller slits and the acceptance perpendicular to the scattering plane was about 14 mrad. Both grazing incidence (GIXRD) and specular measurements were conducted, which probe diffracting planes perpendicular and parallel to the sample surface, respectively [13,14].

To evaluate the electrochemical performance of alloy thin-film nanostructures, current-potential curves were examined using a conventional three-electrode electrochemical system consisting of a deposited thin-film electrode, a Pt gauze, and Ag/AgCl as the working, counter, and reference electrode, respectively, at 25 °C. All potentials are reported with respect to normal hydrogen electrode (NHE). The solution of 2.0 M CH_3OH in 0.5 M H_2SO_4 was stirred constantly and purged with nitrogen gas. All chemicals used were of analytical grade.

3. Results and discussion

These alloy thin-film nanostructures were fabricated by co-sputtering using Pt, Ru, and WO_3 target materials. Here we focus on two nanostructures: Nano-1 and Nano-2 with metal compositions $Pt_{80}Ru_{20}$ and $Pt_{60}Ru_{40}$, respectively. Fig. 1 shows TEM micrographs for these nanostructures and shows that they consist of PtRu alloys of 4–5 nm in size that are well dispersed in tungsten oxide matrix. In spite of the fact that the thin-film electrodes were fabricated using sputtering, alloy nanoparticles were formed in the porous, amorphous oxide matrix. The diffraction patterns shown in

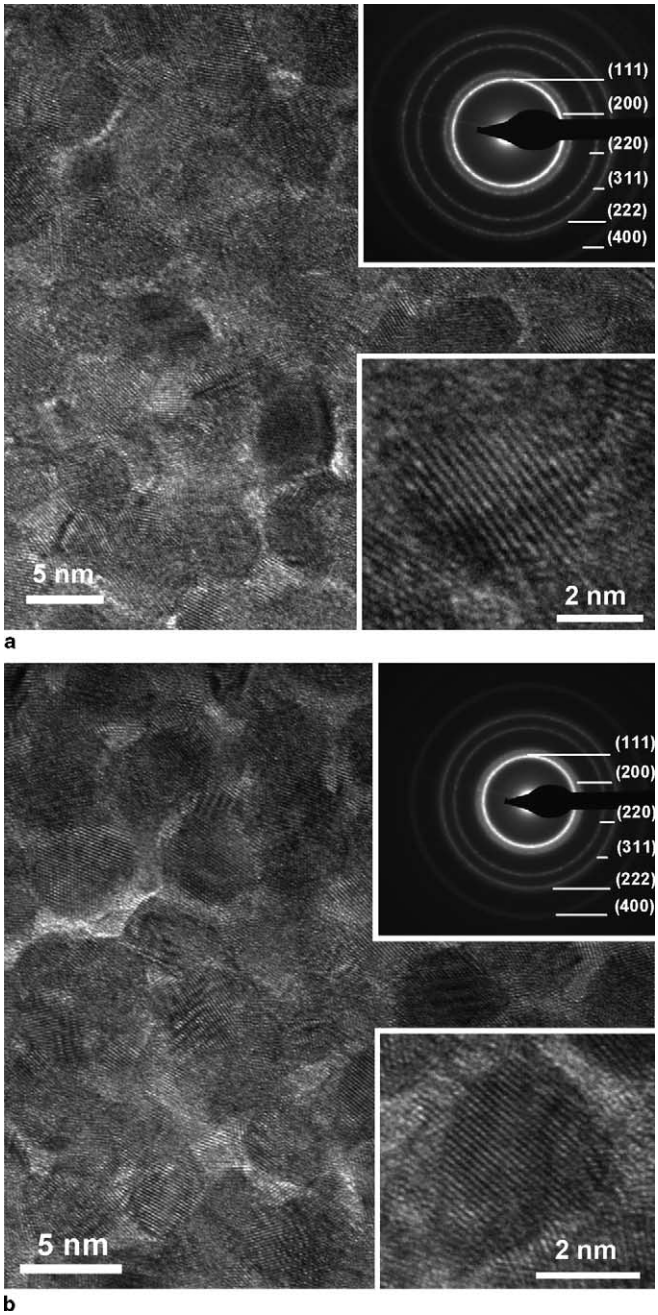

Fig. 1. Transmission electron micrograph (TEM) images of alloy thin-film nanostructures of Nano-1 (a) and Nano-2 (b). (The right top and bottom insets to Fig. 1 show the ring pattern of the electrode by transmission electron diffraction (TED) and a high-resolution TEM (HRTEM) image of the alloy thin-film nanostructure, respectively.) The rings are indexed for an fcc crystal structure. The (111) plane spacing from the high resolution TEM is the same as that obtained from the GIXRD.