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Short communication

Template preparation of Pt–Ru and Pt nanowire array electrodes on a Ti/Si substrate for methanol electro-oxidation

Guang-Yu Zhao, Cai-Ling Xu, Dao-Jun Guo, Hua Li, Hu-Lin Li *

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

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Abstract

Pt and Pt–Ru nanowire array electrodes were obtained by dc (direct current) electrodeposition of Pt and Ru into the pores of an anodic aluminum oxide (AAO) template on a Ti/Si substrate. Transmission electron microscope (TEM) examination showed all the nanowires had a uniform diameter of about 30 nm. The brush shaped Pt and Pt–Ru nanowire array electrodes could be seen clearly by scanning electron microscope. Pt and Pt–Ru nanowire array electrodes gave the X-ray diffraction pattern of a face-centered cubic (fcc) crystal structure. The electro-oxidation of methanol on these electrodes was investigated at room temperature using cyclic voltammetry. The results demonstrated that the alloy nanowire array electrode was catalytically more active than a pure platinum nanowire array electrode and the Pt–Ru nanowire array electrode may have good potential for applications in portable fuel cell power sources.

Keywords: Portable power sources; AAO/Ti/Si; Pt and Pt–Ru nanowire array electrodes; Electro-catalysis; Methanol oxidation

1. Introduction

Portable power sources are critical for mobile devices such as celluller phones, lap top computers, pacemakers, and various microsystems. Direct methanol fuel cells (DMFC) are attractive as portable power sources [1–7] because they require only the introduction of methanol to generate power. They do not require the electrical charging of a traditional secondary battery. The fundamentals of the DMFC system have been studied extensively [8–12]. Several groups have made micro fuel cells using micro-fabrication technologies using C/Si plane substrates [13–18].

Research indicates that the electrochemical characteristics of the electrode materials are highly dependent on the grain size, texture, surface area and morphology. An ordered, high surface area structure of electrode materials can enhance electrochemical characteristics. Seong Ihl Woo and coworkers have demonstrated that a high surface area nanowire array electrode of the catalyst has significantly improved its capability compared with a catalyst black electrode [19]. An anodic aluminum oxide (AAO) template offers a promising route to make a high surface area, ordered nanowire electrode. Recently, PtNi nanorods for methanol electro-oxidation were prepared by the AAO template method [20]. But this method is difficult to use in practice due to the fragility of the AAO template [21–27].

In this work, AAO films were successfully grown on a Ti/Si substrate and this is the first time it was used as a template to synthesize a high surface area and ordered nanowire array electrode for methanol electro-oxidation. The electrochemical characterization of an ordered nanowire array on the Ti/Si substrate was performed by cyclic voltammetry in an 0.5 M CH_3OH + 0.5 M H_2SO_4 aqueous solution using the nanowire array as the working electrode. The electro-catalytic activity of the nanowire array electrode for methanol oxidation was investigated. The nanowire array electrode consisted of only electrochemically active material (Pt and Pt–Ru) and was fairly stable. The results demonstrate that the nanowire array electrode could have good potential applications in portable fuel cell power sources since the alloy nanowire array electrode was catalytically more active than a pure platinum nanowire array electrode.

* Corresponding author. Tel.: +86 931 891 2517; fax: +86 931 891 2582.
E-mail addresses: lihl@lzu.edu.cn, zhaogy03@st.lzu.edu.cn (H.-L. Li).

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2. Experiments

2.1. Preparation of AAO/Ti/Si

A highly pure Al film (99.999%, ~3.5 μm) was deposited on a p-type silicon substrate coated with a Ti (~300 nm) film using radio frequency (RF) sputtering. The anodization was carried out in a 0.3 M oxalic acid solution at 20 V and room temperature for 1 h for pores of ~30 nm in diameter. The resulting aluminum film was etched away in 0.4 M H_3PO_4, 0.2 M $H_2Cr_2O_4$ at 50 °C for 2 h, and the remaining aluminum was re-anodized under the same conditions until the Al film was fully oxidized. To remove the barrier layer, the anodization was continuously processed for 30–60 min.

2.2. Preparation of the nanowire array electrodes

The electrolyte used for Pt nanowires electrodeposition was 5 mM H_2PtCl_6 and 1.2 mM HCl. The electrolyte used for the Pt–Ru nanowire electrodeposition was composed of 5 mM H_2PtCl_6, 1 mM $RuCl_3$ and 1.2 mM HCl. Electrodeposition was carried out at room temperature, using a three-electrode potentiostatic control and direct current electrodeposition system with a saturated calomel electrode (SCE) as the reference electrode. A 1.0 cm × 1.0 cm platinum plate was the counter electrode and the AAO/Ti/Si structure was the working electrode. The electrodeposition was carried out at 0 V (versus SCE) for Pt and −0.2 V (versus SCE) for Pt–Ru nanowires with a CHI 660 electrochemical analyzer. The electrodeposition was continued until the deposited nanowires "overflowed" from the nanoholes. The overflowed nanowires were mechanically polished with a metallographic abrasive paper. The as-prepared samples were immersed in 1 M NaOH for 0.5 h to remove the AAO film. Then the brush shaped nanowire array was obtained. The procedure is shown in Fig. 1.

2.3. Measurements

A conventional cell with a three-electrode configuration was used throughout this work. The nanowire array electrodes were employed as the working electrodes and a saturated calomel electrode (SCE) was used as the reference electrode. The quantity of electrocatalyst on the working electrode was 1 mg cm^{-2} which was calculated from the electrodeposition charge in Coulombs. Electrochemical measurements were performed with a CHI 660 electrochemical analyzer, and the potentials were measured with respect to SCE.

The morphology of the nanowires was characterized using a Hitachi 600 transmission electro microscope (TEM). The TEM samples were prepared by scraping the Pt and Pt–Ru nanowires from the substrate and into a vessel for dispersing in ethanol. X-ray diffraction (XRD) data of the samples were collected using a Rigaku D/MAX 24,000 diffractometer with Cu Kα radiation. The morphology of the Pt and Pt–Ru nanowire array electrodes on Ti/Si substrate were examined by scanning electron microscope (FESEM, JEOL JSM-S4800).

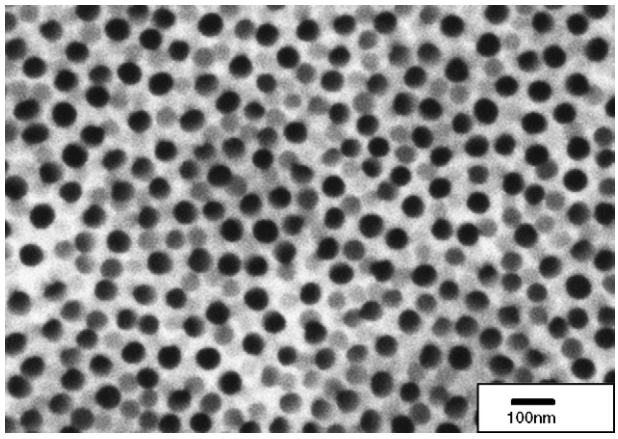

Fig. 2. FESEM images of the surface morphology of an AAO film on a Ti/Si substrate after the second anodization.

3. Results and discussion

3.1. FESEM analysis of AAO film on Ti/Si substrate

After a two-step anodization in 0.3 M oxalic acid solution at room temperature, the resulting template has parallel pores with a fairly narrow size distribution, as shown in Fig. 2. Fig. 2 shows that the porous alumina structure has an average pore diameter about 40 nm, the interspaces were about 60 nm and the pore densities about 10^{10} cm^{-2}. But their arrangement had a lower order than AAO on bulk Al probably due to the small grain size [28] and thin aluminum films [29].

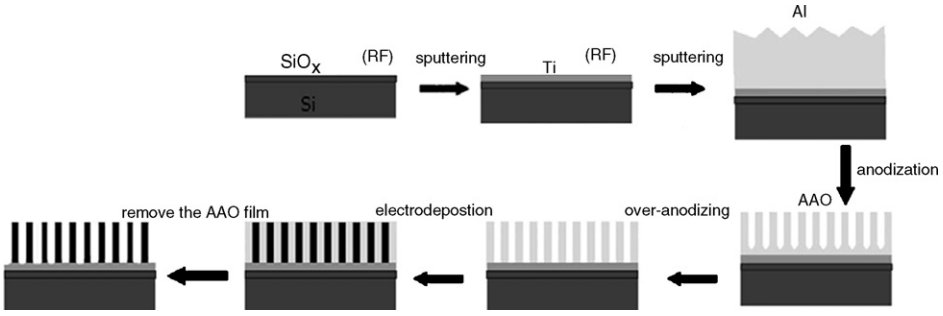

Fig. 1. Schematic of the procedure.