Journal of Power Sources 245 (2014) 892–897

Contents lists available at ScienceDirect

Journal of Power Sources

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

Short communication

Free-standing Pt@$RuO_2 \cdot xH_2O$ nanorod arrays on Si wafers as electrodes for methanol electro-oxidation

Guangyu Zhao [a], Li Zhang [a], Kening Sun [a,*], Hulin Li [b]

[a] *Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin, Heilongjiang 150080, PR China*
[b] *College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China*

HIGHLIGHTS

- Pt@$RuO_2 \cdot xH_2O$ nanorod arrays free-standing on Si wafers.
- Uniform distribution of Pt nanoparticles coated on $RuO_2 \cdot xH_2O$ nanorods.
- A practical route for fabricating micro fuel cell electrodes.

ARTICLE INFO

Article history:
Received 15 May 2013
Received in revised form
2 July 2013
Accepted 11 July 2013
Available online 20 July 2013

Keywords:
Anodic aluminum oxide template
Silicon wafer
Nanorod array
Electro-catalysis
Poisoning rate

ABSTRACT

$RuO_2 \cdot xH_2O$ nanorod arrays free-standing on Si wafers are prepared by an anodic aluminum oxide template assistant method. Pt nanograins in the size of 3–5 nm are deposited on the $RuO_2 \cdot xH_2O$ nanorod arrays uniformly by a cool sputtering approach. Electrochemical measurements indicate that, the Pt@$RuO_2 \cdot xH_2O$ nanorod arrays have larger electrochemical active areas (EAAs) and better poisoning resistant ability for methanol electro-oxidation, compared with Pt nanograins that deposited on Ti wafers directly (named Pt/Ti). The EAAs of Pt@$RuO_2 \cdot xH_2O$ and Pt/Ti electrodes are 40.6 and 31.1 $m^2\ g^{-1}$, respectively. The poisoning rate of Pt@$RuO_2 \cdot xH_2O$ arrays is 8.9×10^{-4}% per second, much smaller than that of Pt/Ti electrodes (3.4×10^{-3}% per second).

1. Introduction

Micro-electromechanical systems (MEMSs) on Si substrates arising from the integrated circuit technology have established high volume commercial markets for accelerometers and pressure sensors in the automotive industry successfully. Micro fuel cells are promising high energy density power sources for MEMSs [1]. When integrating micro fuel cells as on-chip devices into MEMSs used for sensors/actuators and other micro-devices, the processes of manufacturing electro-catalysis electrodes and the remaining fuel cell system must be post-CMOS (Complementary Metal Oxide Semiconductor) compatible [2,3]. However, it is difficult to manufacture conventional carbon-supported catalyst membranes by MEMS fabrication methods, due to the instability of carbon in the CMOS process. Therefore, a Si-based carbon-free electrode becomes necessary for micro fuel cells. Several kinds of catalyst layers deposited on Si wafers by electrodeposition [2,3], sputtering [4,5] and evaporation [6–8] have been reported. However, the researchers used self-supporting structures for the catalysts these studies, instead of proposing a new supporting material for catalyst layers. The self-supporting structures result in a low utilization of the catalysts, because of the catalyst grains accumulating on the Si substrates. These structures also fail to create fluent ion transmission channels, which are beneficial to shorten the diffusion distance in electro-catalysis processes [9,10].

$RuO_2 \cdot xH_2O$ is a good candidate for substituting carbon as the supporting material of fuel cell catalysts, since the high electron and proton conductivity [11,12], as well as the assisting oxidation of CO or CHO species by adsorption of oxygen-containing species

---

[*] Corresponding author. Tel./fax: +86 451 86412153.
E-mail address: keningsun@yahoo.com.cn (K. Sun).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.07.053

close to the poisoned Pt catalyst sites [13]. Anodic aluminum oxide (AAO) template assistant method is very helpful for preparing array structures with uniform unhindered channels. The electrodes prepared with this method exhibit prominent performances, when used as electrochemical energy storage and conversion devices [10,14]. Herein, AAO films on Si wafers are fabricated by an anodic oxidation, and used for depositing free-standing $RuO_2{\cdot}xH_2O$ nanorod arrays. A layer of Pt nanograins is deposited on the arrays by a cool sputtering approach. The free-standing $Pt@RuO_2{\cdot}xH_2O$ nanorod arrays have a large active area and prominent resistance ability to carbon oxide species poisoning.

2. Experimental

A highly pure Al film (99.999%, ~1.0 μm) and a Ti (~10 nm) layer were deposited on the p-type Si substrate by thermally evaporated deposition to form Al/Ti/Si wafers (1.0 cm × 1.0 cm). An anodic oxidation was carried out in 0.3 M oxalic acid solution at 40 V and room temperature for 10 min. The resulting alumina film was etched away in the solution of 0.4 M H_3PO_4 + 0.2 M $H_2Cr_2O_4$ at 50 °C for 0.5 h. The remaining Al was re-anodized under the same conditions until the Al film was oxidized completely. The electrolyte for electrodeposition consisted of 10 mM $RuCl_3$ and 1.2 mM HCl. The electrodeposition was carried out using a cyclic voltammogram (CV) method in a potential window of −0.8–2.0 V (vs. SCE) with a scan rate of 50 mV s^{-1} on a CHI 660 electrochemical analyzer. The as-prepared samples were immerged in 0.01 M NaOH for 1 h to remove the AAO films. Pt nanograins were deposited on $RuO_2{\cdot}xH_2O$ nanorod arrays by a Leica EM SC050 cool sputtering device at a current of 40 mA for 40 s. For comparison, Pt nanograins deposited on Ti wafers (Pt/Ti) were also prepared with the same conditions.

A conventional cell with a three-electrode configuration was used in this work. The $Pt@RuO_2{\cdot}xH_2O$ nanorod arrays and Pt/Ti were employed as the working electrodes, a 1.0 cm × 1.0 cm platinum plate as counter electrode and a SCE as the reference electrode. Electrochemical measurements were performed at room temperature with the CHI 660 electrochemical analyzer. Scanning electron microscope (SEM) images were obtained on a Hitachi Su-8100. The X-ray diffraction (XRD) patterns were obtained on a PANalytical X'pert PRO X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Transmission electron microscope (TEM) images and energy dispersive X-ray spectra (EDS) patterns were obtained on a FEI Tecnai G^2. X-ray photoelectron spectra (XPS) were tested with a Kα electron spectrometer from Thermofish Scientific Company using Al Kα (1486.6 eV) radiation. The base pressure was about 1×10^{-8} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

3. Results and discussion

The SEM images of AAOs' surface are shown in Fig. 1. The nanoholes are not very regular, compared with the AAO templates obtained on the traditional thick Al foils, because of the ultrathin Al films used in our work. It is known that the longer anodic time, the more regular nanoholes can be obtained [15]. However, these holes standing on Ti current collector vertically are competent for growing free-standing nanorod arrays. CV was employed to deposit $RuO_2{\cdot}xH_2O$ nanorods. In the CV process, the Ru^{3+} ions were reduced to metal Ru in cathodic sweeping, then the Ru metal was oxidized to $RuO_2{\cdot}xH_2O$ in the subsequent anodic sweeping [16]. The generated $RuO_2{\cdot}xH_2O$ could not be reduced in the following cathodic process. Therefore, the sequential sweeping led the nanorods growing continuously [17]. The $Pt@RuO_2{\cdot}xH_2O$ nanorod arrays were obtained by dissolving the AAO templates and sputtering Pt nanograins.

The XRD results of Pt/Ti and $Pt@RuO_2{\cdot}xH_2O$ electrodes have been presented in Fig. S1. The peaks in the pattern of Pt/Ti can be ascribed to the Ti wafer substrate (JCPDS: 65-6231). The absence of Pt diffraction peaks can be attributed to the ultra-small amount of Pt nanoparticles deposited on the substrates by the cool sputtering approach. For the same reason, the Pt diffraction peaks do not appear in the pattern of $Pt@RuO_2{\cdot}xH_2O$ electrode either. Conversely, the peaks of Ti (JCPDS: 65-5970) and RuO_2 (JCPDS: 40-1290) can be detected clearly. Additionally, the different crystal forms of Ti in the two electrodes may arise from the different preparation methods of Ti substrates.

XPS measurement was used for investigating the Pt catalyst deposited by the cool sputtering approach. The peaks of Pt can be observed clearly from the XPS survey pattern of Pt/Ti electrodes in Fig. S2. The XPS patterns of $Pt@RuO_2{\cdot}xH_2O$ arrays are shown in Fig. 2, in which, the peaks of Pt 4f, C 1s, Pt 4d, Pt 4p, Ti 2p, and O 1s present in the survey pattern. In Pt 4f of Fig. 2(b), the XPS spectra are characterized by a doublet containing a binding energy of 71.05 eV (Pt 4f7/2) and 74.4 eV (Pt 4f5/2). The two peaks have a binding energy difference of 3.35 eV and a peak area ratio of 4:3, which corresponds to the characteristics of Pt (0). The Pt 4f spectrum can be deconvoluted into two species with binding energies of 71.05–74.4 and 72–76.2 eV, corresponding to Pt (0) and Pt (II), respectively [18]. On the basis of the areas of Pt 4f7/2 and Pt 4f5/2,

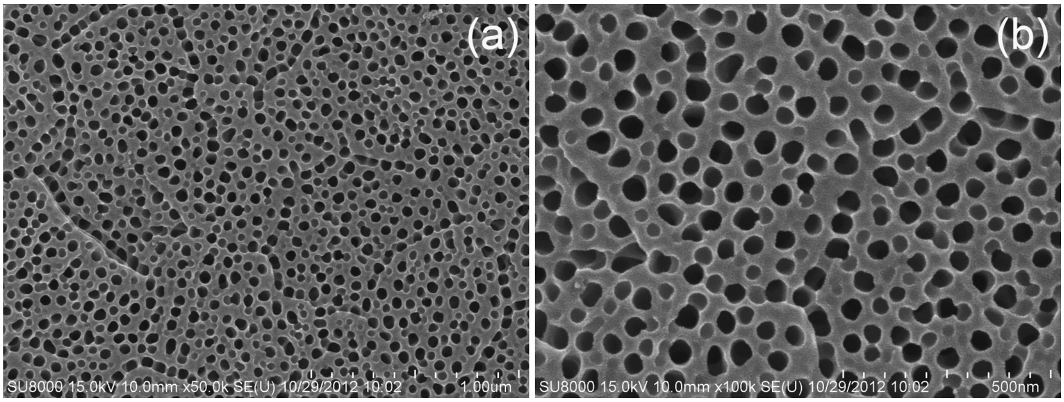

Fig. 1. SEM images of AAO templates on Si wafers.