Fabrication of a Nano-structured PbO₂ Electrode by Using Printing Technology: Surface Characterization and Application

K. Kannan, G. Muthuraman, G. Cho and I. S. Moon

Department of Chemical Engineering, Sunchon National University, Suncheon 540-742, Korea

(Received 14 January 2014, in final form 4 March 2014)

This investigation aimed to introduce printing technology for the first time to prepare a nano-structured PbO₂ electrode and its application to a cerium redox transfer process. The new method of nano-size PbO₂ preparation demonstrated that nano-PbO₂ could be obtained in less time and at less cost at room temperature. The prepared nano-PbO₂ screen printed on a Ti electrode by three different compositions under similar conditions showed through surface and electrochemical analyses no adherence on Ti and no contact with other nano-PbO₂ particles. Gravure printing of nano-PbO₂ on a PET (poly ethylene thin) film at high pressure was done with two different compositions for the first time. The selective composition of 57.14 % nano-PbO₂ powder with 4.28 % carbon black and 38.58 % ECA (ethyl carbitol acetate) produced a film with a nanoporous structure with an electron transfer ability. Finally, the optimized gravure-printed nano-PbO₂ electrode was applied to the oxidation of Ce(III) to Ce(IV) by using cyclic voltammetry. The gravure-printed nano-PbO₂ should pave the way to promising applications in electrochemical and sensor fields.

PACS numbers: 14.80.-j
Keywords: Nano-PbO₂, Screen printing, Gravure printing, Nano-structure electrode
DOI: 10.3938/jkps.65.372

I. INTRODUCTION

Fabricating metal oxides on thin films with thicknesses in about the nanometer to micrometer range for both crystalline and amorphous films has immense importance in the age of high technology for microelectronic devices, magnetic thin films in recording devices, magnetic sensors, gas sensors, solar cells, decorative coatings, etc. Initially, electrochemical deposition was used to fabricate metal oxides, and still this method is crucial in some fields of interest. This method, particularly for deposition on a nonconducting surface, fails, disadvantage of this method are poor thickness, poor uniformity on complex components, the need for acidic plating baths, etc.

Additional coating techniques, like screen printing, inkjet printing, chemical vapor deposition, spray coating, spin coating, dip coating, gravure printing, sputter coating with a thick deposition of metal oxide at an elevated temperature have emerged in many fields of interest. Through screen-printing techniques, carbon, gold, platinum, silver or carbon nano-tube materials, which are widely used in electrochemical analysis and for clinical purpose due to their low cost and one time use have been coated [1]. Similarly, gravure printing has been adapted for nano-carbon, etc. As evidenced by past studies, semiconducting metal-oxide thin-film materials such as ZnO [1], In₂O₃ [2], SnO₂ [3], WO₃ [4], SiO₂ [5], and MnO₂ [6] have a wide range of applications such as gas sensors, solar cells, catalysts, and pH sensors. Metal-oxide electrodes that have been developed by using printing technology have recently started to appear and a few reports have been published. Comparable to other semiconductive materials, lead dioxide has a wide range of applications apart from its use in lead acid batteries. For example, it is applied as anode for electrochemical oxidation of organic pollutants [7], for sensors [8], for direct oxidation of NOₓ and SOₓ [9], for corrosion resistances, for low cost syntheses, for high oxygen over potentials and for chemical stabilities.

Recently, PbO₂ has been coated, along with other compounds, by using screen-printing technology for glucose sensors [10]. Herein, we wish to adopt both screen and gravure printing for nano-PbO₂ on different supports. First nano-PbO₂ was chemically prepared using a new method. Then, the prepared nano-PbO₂ particles were coated on a conducting surface (Ti) and a non-conducting surface (PET film). Similarly, gravure printing was adapted to print nano-PbO₂ on both Ti and PET under different conditions, such as the composition ratio, solvents, and additives. The prepared electrodes were then characterized by using SEM (scanning electron microscope), EDX (energy dispersive x-ray), and cyclic voltammetry analyses. Finally, the prepared thin-film electrodes were applied for cerium oxidation.
Fabrication of a Nano-structured PbO$_2$ Electrode by Using Printing – K. KANNAN et al.

II. EXPERIMENTS AND DISCUSSION

1. Synthesis of the nano-PbO$_2$ Powder

First, 33.12 g of lead nitrate was dissolved in 100 ml of deionized (DI) water. Then, 1 ml of Triton-X-100 was added to make a 1% surfactant solution and to ensure that the solution became clear under a magnetic stirrer was used at room temperature ($25 \pm 1 ^\circ C$). An aqueous solution of 3.78 g of NaBH$_4$ (highly hygroscopic) was slowly injected into the bath with dissolved lead nitrate and triton-100. During addition, the clear solution turned black in color, and soon black particles started to appear as nano-lead metal (Pb). Immediately, 50 ml of 12% NaClO was added to the nano-Pb-containing solution until the solution color changed to a brown color. Then, 5 min was allowed for the mixture to react, after which the mixture was filtered using sub-micro-porous filter paper. The collected precipitate was washed several times in ethanol and water and finally dried at 60 $^\circ C$. The collected particles were analyzed by using SEM and XRD, and the obtained results are depicted in Fig. 1. Figure 1(a) presents on SEM image of the nano-PbO$_2$ powder, where the prepared particle has a spherical shape with an approximately 30-nm in diameter. The XRD data (Fig. 1(b)) for the nano-PbO$_2$ powder with a tetragonal phase of $\beta$-PbO$_2$ at the 110 and the 101 planes at $2\theta$ values of about 25$^\circ$ and 32$^\circ$ confirmed that the prepared powder was nano-PbO$_2$.

2. Screen Printing and Its Characterization

Screen printing was done using the usual method reported elsewhere [11]. The mesh that we used was 250 $\mu$m in pore size with a working area of about 5 $\times$ 5 cm$^2$. Before printing on the Ti surface, the Ti was polished with sandpaper and was then cleaned using ultrasonication for 10 min to remove any sand particles.