Characterization of nanostructured PbO$_2$–PANi composite materials synthesized by combining electrochemical and chemical methods

Thi Binh Phan, Thi Tot Pham and Thi Thanh Thuy Mai

Institute of Chemistry, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Road, Cau Giay, Hanoi, Vietnam
E-mail: ptbinh@ich.vast.ac.vn

Received 5 September 2012
Accepted for publication 14 January 2013
Published 7 February 2013
Online at stacks.iop.org/ANSN/4/015015

Abstract
Nanostructured PbO$_2$–PANi composite materials were prepared by combining electrochemical and chemical methods. Firstly, PbO$_2$ was deposited on a stainless steel substrate by pulsed current method and then obtained PbO$_2$ electrode was immersed into acidic aniline solution to form nanostructured PbO$_2$–PANi composites. The synthesized samples were characterized by infrared (IR) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and x-ray diffraction (XRD). The electrocatalytic oxidation of methanol on those composites was evaluated by potentiodynamic polarization from 1.4 to 2.2 V versus Ag/AgCl/saturated KCl electrode. The adsorption of N–H group as well as the presence of benzoid and quinoid ring vibrations on IR-spectrum asserts that PANi coexisted with β-PbO$_2$ which is evidenced by x-ray analysis. With increasing immersion times of the PbO$_2$ electrode in the acidic aniline solution the electrocatalytic performance of the obtained PbO$_2$–PANi composites for methanol oxidation was improved due to the formation of less closely knitted nano-sized PANi fibers, which was confirmed by surface morphology analysis.

Keywords: PbO$_2$–PANi composite, combining method, immersion method, nanostructure, electrocatalytic

Classification number: 5.00

1. Introduction

It is known that PbO$_2$ material has good electrical conductivity that is similar to metal and PbO$_2$ is an excellent electrical catalyst and catalyst carrier [1, 2]. Polyaniline (PANI) is non-toxic, inexpensive and a stable conducting polymer, which can be synthesized by simple chemical and electrochemical routes [3–5]. Currently, it is hybridized with oxides of some metals like titanium, lead and manganese to form composites as materials for energy storage and conversion as well as electrocatalysis [6–9]. Among them, there is a lack of publications about PbO$_2$–PANi which may be obtained by combining chemical and electrochemical methods resulting in a better catalyst. Hence, it is of significance in this research to prepare PbO$_2$–PANi catalyst by this method and investigate its electrocatalytic performance for oxidation of a small organic molecule such as methanol.

2. Experimental

2.1. Material and methods

Analytical grade nitric acid, Cu(NO$_3$)$_2$, Pb(NO$_3$)$_2$, ethylenglycol (Merck) and methanol were used without any purification. Aniline (Merck) was freshly distilled under vacuum condition at about 120 °C before use. The pulsed current method was applied to electrosynthesize PbO$_2$ (the height of pulse: 30 mA cm$^{-2}$, the width of pulse: 3 s, $Q = 9$ A s cm$^{-2}$). For each time, the obtained PbO$_2$ electrode was immersed 60 s into acidic aniline solution (0.1 M),
Figure 1. SEM images of PbO$_2$ formed by electrochemical method (a), PbO$_2$–PANI composites formed by combining electrochemical and chemical methods: immersion of PbO$_2$ into acidic aniline solution twice (b) and five times (c).

Figure 2. TEM images of PbO$_2$–PANI composites formed by combining electrochemical and chemical methods based on immersion of PbO$_2$ into acidic aniline solution (a) two times and (b) five times.

washed by distilled water, immersed in acetone to remove the excess of aniline and after that dried for half an hour at room temperature. This procedure was used for preparing samples of two kinds. The first one was immersed twice and the second one five times.

2.2. Detection method

The structure of the film layer was carried out by infrared spectrum on IMPACT 410-Nicolet unit. The surface morphology of coatings was examined by SEM on an FE-SEM Hitachi S-4800 (Japan) and TEM on a Jeol 200CX (Japan). The analysis of crystalline structure of those layers was performed by using an x-ray diffractometer D5000, Siemens (Germany). The electrocatalytic oxidation of methanol was measured by electrochemical workstation unit IM6 (Zahner-Elektrik, Germany).

3. Results and discussions

3.1. SEM images

The image in figure 1(a) showed that non-uniform tetragonal $\beta$-PbO$_2$ crystals were formed on the surface of stainless steel substrate under pulsed current method. However, its surface morphology was changed completely after immersing into
aniline solution (figures 1(b) and (c)). It can be explained that aniline was chemically polymerized on the surface of an electrode owing to the presence of PbO₂ layer as an oxidation agent by the following reaction [10]:

\[
Pb^{4+} + 2C_6H_5NH_2 \rightarrow Pb^{2+} + 2C_6H_5NH^-_2.
\]

Aniline has converted to anilinium cation radical which can begin the polymerization reaction leading to PANi product, while Pb²⁺ in the PANi lattice can be solved because we used 0.1 M HNO₃ as an electrolyte. The surface of PANi–PbO₂ composite electrode in case (b) was more closely knitted by PANi fibers than that in case (c). Reasonably, this can be explained as follows: the more time the electrode was immersed in the above solution, the less aniline was oxidized on its surface because a conductive prelayer like a barrier reduces the following polymerization process of aniline resulting in a spongy surface.

3.2. TEM images

The TEM images in figure 2 evidence convincingly that among two clearly different colors, the light one belongs to PANi enclosing the dark one belongs to PbO₂. Both of them had size in the nano range. The gained results from SEM and TEM analysis explained that nanostructured PbO₂–PANi composites were successfully prepared by combining electrochemical and chemical methods.
Figure 5. Potentiodynamic diagrams of PANi–PbO$_2$ composites in 0.5 M H$_2$SO$_4$ containing different methanol concentrations. Sample prepared by immersing twice (a) and five times (b).

Figure 6. Relation of $\Delta i$ and applied potential. Conditions: measuring PANi–PbO$_2$ composites in 0.5 M H$_2$SO$_4$ containing different methanol concentrations; sample prepared by immersion of PbO$_2$ into acidic aniline solution twice (a) and five times (b).

Figure 7. The effect of methanol concentration on electrocatalytic ability of PANi–PbO$_2$ composites. Sample prepared by immersion of PbO$_2$ twice (blue line) and five times (green line).
3.3. X-ray diffraction

X-ray diffraction (XRD) was used to determine the structure of the electrode before and after immersion into acidic monomer solution following the above-mentioned procedures, as shown in figure 3. For all cases the first peak was found to be located at 2θ degree of 30° and the second peak strongly oriented at 2θ of over 62° indicated β-PbO$_2$ as reported in [11]. This explains that β-PbO$_2$ existed in our prepared composites. This is evidence to prove that only a part of the surface of PbO$_2$ layer was reduced by aniline to Pb$^{2+}$ which might be moving into electrolyte, and the rest of it remains in composite matrix.

3.4. Infrared spectrum analysis

Figure 4 shows the spectrum of the PbO$_2$–PANI composite prepared by procedure 2 (immersion of PbO$_2$ into acidic aniline solution five times). The band from 3447 to 3206 cm$^{-1}$ is assigned to the N–H stretching mode, from 3043 to 2916 cm$^{-1}$ (aromatic C–H), from 1447 to 1353 cm$^{-1}$ (–N = quinoid = N–). It exhibits clearly the presence of benzoid and quinoid ring vibrations at 1652 and 1533 cm$^{-1}$, respectively. The signals at 1182 and 1096 cm$^{-1}$ were determined due to the C–N$^+$ group, at 905 and 825 cm$^{-1}$ confirmed due to the absorption of the N–H group, at 650 and 592 cm$^{-1}$ explaining the adsorption of NO$_3^-$ ion. These vibration signals were similar to those reported in the literature [12, 13] which showed that PANI co-existed in composite matrix in emeraldine salt form (PANI$^{+}$NO$_3^-$) because of using HNO$_3$ as an electrolyte.

3.5. Electrocatalytic oxidation of methanol

The electro-oxidation of methanol on the surface of anodic PbO$_2$–PANI composites can occur by the following reaction:

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 6\text{H}^+ + 6\text{e}^- + \text{CO}_2.$$  \hspace{1cm} (2)

From data given in figure 5, the electro-oxidation current $\Delta i$ of methanol can be calculated by equation

$$\Delta i = i - i_{\text{base line}},$$  \hspace{1cm} (3)

where $i$ is corresponding current measured in acidic methanol solution and $i_{\text{base line}}$ is that measured in acidic solution without methanol (base line).

The results given in figure 6 showed that only one oxidation peak ($\Delta i_p$) of methanol in the potential range of 2.05–2.10 V (versus Ag/AgCl/saturated KCl electrode) was found. Additionally, the height of $\Delta i_p$ linearly increased with increasing methanol concentration in solution, among which the composite prepared by increasing immersion times into acidic aniline solution could electrocatalyse better for oxidation of methanol because its $\Delta i_p$ shift is higher (green line in figure 7). The $\Delta i_p$ values in this research were very high (up to 30 mA cm$^{-2}$) in comparison with those reported in our previous report (less than 8 mA cm$^{-2}$), which resulted from only the electrochemical pulsed current method [14]. It can be said that methanol oxidation could be positively catalysed on the surface of PANI–PbO$_2$ composites prepared by combining chemical and electrochemical methods.

4. Conclusions

From the above results we conclude that nanostructured PbO$_2$–PANI composite prepared by combining electro-chemical and chemical methods improved its electrocatalytic ability for methanol oxidation in comparison with that prepared by the pulsed current method (only by the electrochemical way).

By increasing immersion time of PbO$_2$ electrode in acidic aniline solution, the surface morphology was obtained with less closely knitted PANI fibers resulting in nanostructured PbO$_2$–PANI composite on which electrocatalytic ability for methanol oxidation improved positively.

Acknowledgments

This study was financially supported by the NAFOSTED of Vietnam under code number 104.05.58.09. The authors would like to thank the Humboldt-Fellowship for the support of the IM6 equipment.

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