Nanostructured PbO$_2$-PANi composite materials for electrocatalytic oxidation of methanol in acidic sulfuric medium

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Abstract
Hybrid materials based on PbO$_2$ and PANi were prepared by cyclic voltammetry combined with chemical method. Firstly, PbO$_2$ and PbO$_2$-PANI were deposited on stainless steel by cyclic voltammetry (CV) at a scan rate of 100 mV s$^{-1}$. Next, they were immersed in acidic aniline solution (0.1 M) to form new fresh PbO$_2$-PANI composites. The properties of materials were characterized by x-ray diffraction, IR-spectroscopy, scanning electron microscopy and transmission electron microscopy. The electrocatalytic oxidation for methanol of all PbO$_2$-PANI layers was investigated in acidic medium by potentiodynamic measure at a scan rate of 100 mV s$^{-1}$ in the range of 1.4 V to 2.2 V versus Ag/AgCl/saturated KCl electrode. The obtained results indicated that the composites prepared by above combined method could significantly enhance the electrocatalysis for oxidation of methanol.

Keywords: PbO$_2$-PANI composite, cyclic voltammetry, combining method, nanostructure, methanol electrocatalytic oxidation
Classification numbers: 5.06, 5.11

1. Introduction
Lead dioxide is known as a material which has excellent chemical stability, high conductivity and chemical inertness for electrolysis in an acidic medium. Therefore, lead dioxide is an excellent electrocatalyst and catalyst carrier [1, 2]. Polyaniline (PANI) as a conducting polymer has been widely used because of its interesting mechanical and electrical properties as well as high environmental stability without any toxicity. Additionally, PANi is easily synthesized by chemical and electrochemical methods with low price, so it is probably the most important conducting polymer today [3, 4].

Recently, the preparation of new organic/inorganic composites has rapidly developed due to a wide range of their potential use. The hybrid composites from polyaniline (PANI) and different metal oxides like as TiO$_2$, SnO$_2$, MnO$_2$ were investigated for the applications to sensor, electrocatalysis [5–7]. In the previous paper [8] we have prepared PbO$_2$-PANI composite by chemical und pulsed current method, however, methanol oxidation current density was limited only until 30 mA cm$^{-2}$. To improve the electrocatalytic ability of this composite for methanol, another combining method based on chemistry and cyclic voltammetry must be used. In this paper, we report the characterization of composites obtained by this combined method and their electrocatalytic ability for methanol oxidation.

2. Experimental
2.1. Materials and methods
All chemicals used in this study were provided by Merck (Germany). Aniline was fresh distilled under vacuum before
use. The stainless steel electrode was polished by sandpaper with 2000 grit. Firstly, PbO₂-PANI and PbO₂ as prelayers were deposited on stainless steel by CV at a scan rate of 100 mV s⁻¹ from solution of 0.5 M Pb(NO₃)₂ + 0.05 M Cu(NO₃)₂ + 0.1 M HNO₃ + 0.1 M ethylene glycol with and without aniline, respectively. Then they were immersed five times into acidic aniline solution (0.1 M) during 60 s for each time.

2.2. Detection method

The structure study of materials was carried out by infrared spectra on IMPACT 410-Nicolet unit. The surface morphology of coatings was examined by scanning electron microscopy (SEM) on an FE-SEM Hitachi S-4800 (Japan) and transmission electron microscopy (TEM) on a Jeol 200CX (Japan). The x-ray diffraction (XRD) of samples was obtained by x-ray diffractometer D5000-Siemens (Germany). The electrocatalytic oxidation of methanol was measured by potentiodynamic method on the electrochemical workstation unit IM6 (Zahner-Elektrik, Germany).

3. Results and discussion

3.1. SEM images

The SEM image of PbO₂ (figure 1(a)) demonstrated that lead dioxide existed in tetragonal β-modification. However, after it...
was immersed into acidic aniline solution to form composite of PbO$_2$-PANi (figure 1(c)) we could observe only spongy surface owing to knitted nano PANi fibres formed from the following oxidation reaction [9]

\[
Pb^{2+} + 2C_6H_4NH_2 \rightarrow Pb^{2+} + C_6H_4NH_2^+. \tag{1}
\]

It can be explained that aniline has converted to anilineum cation radical which can begin polymerization reaction leading to PANi product on the surface, while Pb$^{2+}$ in the PANi lattice can be solved because of using 0.1 M HNO$_3$ as an electrolyte [8]. Figure 1(b) represents PbO$_2$-PANi prepared by cyclic voltammetry showed a mix clearly of both PANi and lead dioxide in closed fine texture of uniform structure which is evidenced by TEM images in figure 2(c). Compared with image (c), image (d) showed a less spongy surface of PANi lattice due to immersion of the prelayer PbO$_2$-PANi into acidic aniline medium.

3.2. TEM-images

The TEM images on figure 2 convincingly evidenced that among two clearly different colours, the light one belongs to PANi enclosing the dark one belonging to PbO$_2$. Both of them had size in nano range. The gained results from SEM and TEM analyses explained that nanostructural PbO$_2$-PANi composites were successfully prepared not only by cyclic voltammetry but also by combining chemical and cyclic voltammetric methods.

3.3. X-ray diffraction

XRD pattern for determining structure of regarded materials is shown in figure 3. In the spectrum of CV-deposited PbO$_2$ (a) three small peaks at 2$\theta$ degree of near 30°, 32, 49° and one strong peak at over 62° indicated $\beta$-PbO$_2$ were observed. We found the first peak located at 2$\theta$ of 30° and the second strong peak at 2$\theta$ of over 62° on spectra b and c from CV-deposited composite and composite prepared by combined method, respectively, indicated $\beta$-PbO$_2$ as reported in [8, 10]. In contrast, they did not appear in the case of spectrum d on which we can see a peak at 2$\theta$ of over 32°, and another strong one of over 49° illustrated $\beta$-PbO$_2$ modification. It explains the existence of $\beta$-PbO$_2$ in our prepared composites. This is evidence to prove that only a part of the surface of PbO$_2$ layer

![Figure 3. X-ray spectra of CV-deposited layer. (a): PbO$_2$, (b): PbO$_2$-PANi) and new fresh PbO$_2$-PANi by combining method immersion of CV-deposited PbO$_2$ (c) and CV-deposited PbO$_2$-PANi (d) into acidic aniline solution.](image)

![Figure 4. IR-spectra of PbO$_2$-PANi composites. (a) CV-deposited PbO$_2$-PANi [11]; new fresh PbO$_2$-PANi by combining method immersion of (b) CV-deposited PbO$_2$ and (c) CV-deposited PbO$_2$-PANi into acidic aniline solution.](image)
reduced by aniline to \( \text{Pb}^{2+} \) which might be moved into electrolyte and the rest of it remains in composite matrix.

### 3.4. Infrared analysis

The data given on spectra from figure 4 and table 1 showed that all regarded composites contain PANi owing to vibration signals of benzoid and quinoid ring as well as some main groups similar to those reported in literature [8, 12, 13]. It explained that PANi in emeraldine salt form co-existed in composite lattice.

### 3.5. Electrocatalytic oxidation of methanol

As reported in [7, 8], the electro-oxidation of methanol on the surface of anodic \( \text{PbO}_2 \)-PANI composites can occur following the reaction:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 6\text{H}^+ + 6\text{e}^- + \text{CO}_2. \tag{2}
\]

The difference of current \( \Delta i \) representing an electro-oxidation current of methanol at those composites in figure 5 can be calculated by the formula

\[
\Delta i = i - i_{\text{base line}}, \tag{3}
\]

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).

#### Table 1. Wavenumbers of different bindings of spectra (a), (b) and (c) in figure 4.

| Signals \( \nu \) (cm\(^{-1}\)) | (a) | (b) | (c) | Binding |
|----------------------------------|-----|-----|-----|---------|
| 3460, 3112                      | 3330| 3100|     | \( \nu_{\text{N-H}} \) |
| 2934                            | 2910| 3008-2859| | \( \nu_{\text{C–H aromatic}} \) |
| 1370                            | 1400| 1358|     | \( \text{–N=quinoid = N–} \) |
| 1626                            | 1650| 1648|     | Benzoid |
| 1515                            | 1592| 1572|     | Quinoid |
| 1082                            | 1146|     |     | C–N\(^+\) group |
| 868, 808                        | 824 | 931, 785| | N-H group |
| 577, 537                        | 600 , 535| 600-521| | NO\(_3\) adsorption |

**Figure 5.** Potentiodynamic diagrams of \( \text{PbO}_2 \)-PANI composites in 0.5 M \( \text{H}_2\text{SO}_4 \) containing different methanol concentrations. Samples prepared by immersion of (a) CV-deposited \( \text{PbO}_2 \), (b) CV-deposited \( \text{PbO}_2 \)-PANI into acidic aniline solution for five times, (c) CV-deposited \( \text{PbO}_2 \)-PANI.

**Figure 6.** Relation of \( \Delta i \) and applied potential during measuring PANi-\( \text{PbO}_2 \) in 0.5 M \( \text{H}_2\text{SO}_4 \) containing different methanol concentrations. Samples prepared by immersion of CV-deposited \( \text{PbO}_2 \) (a), CV-deposited \( \text{PbO}_2 \)-PANI into acidic aniline solution for five times (b), and CV-deposited \( \text{PbO}_2 \)-PANI (c).
The data in figure 6 show that only one oxidation peak \((\Delta i_p)\) of methanol appeared in the potential range of 2.05 V to 2.15 V (versus Ag/AgCl/saturated KCl electrode), however, the peak position slightly shifted on the right side when concentration of methanol in solution increased. Additionally, in all cases the height of \(\Delta i_p\) increased linearly with methanol concentration in solution, among them the composite prepared only by cyclic voltammetry had the best electrocatalytic ability for oxidation of methanol, because its \(\Delta i_p\) line lay on the top of all (blue line on figure 7). The obtained oxidation current \(\Delta i\) for methanol in this research was until 85 mA cm\(^{-2}\) (in the case only by cyclic voltammetry), twice to three times as high as that one in our previous report \cite{8} owing to combining chemical and pulsed current methods.

4. Conclusion

From the above results we conclude that nanostructured PbO\(_2\)-PANI composite prepared by combining chemical and cyclic voltammetric methods improved its electrocatalytic ability of methanol oxidation in comparison with that prepared by combining chemical and pulsed current method.

CV-deposited PbO\(_2\)-PANI composite had the best electrocatalytic for methanol oxidation in acidic sulfuric medium because its morphology existed in uniform structure with closed fine texture.

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