Surface Analysis of Ti/Sb-SnO$_2$/PbO$_2$ Electrode after Long Time Electrolysis

Xu Hao$^1$, Yan Wei$^1$, Yang Honghui$^2$

$^1$ Department of Environmental Science and Engineering, Xi’an Jiaotong University, Xi’an 710049, China; $^2$ The State Key Laboratory of Multiphase Flow in Power Engineering, Xi’an Jiaotong University, Xi’an 710049, China

Abstract: The surface morphology is significant on the stability of electrode. In this study, the surface morphology of a target electrode, Ti/Sb-SnO$_2$/PbO$_2$, was analyzed after long time electrolysis under constant current density conditions in Na$_2$SO$_4$ solution. SEM, EDS, XRD and ICP-OES were used to characterize the change of its surface morphology and the metal content in the electrolyte solution. The SEM images show that the dissolution and detachment phenomenon occur on the surface of Ti/Sb-SnO$_2$/PbO$_2$ electrode after long time electrolysis. Pb element is detected in the electrolytes after electrolysis, which uncovers the dissolution of PbO$_2$. The XRD patterns indicate that the surface layer is still PbO$_2$ but the intensity of diffraction peaks is decreased. It is speculated that the mechanisms of the Ti/Sb-SnO$_2$/PbO$_2$ electrode deactivation are the oxide layer dissolution, detachment and the substrate passivation.

Key words: PbO$_2$; long time electrolysis; surface analysis; deactivation

In recent years, the electrochemical oxidation treatment has attracted more and more attention for its potential application in degradation of refractory pollutants$^{[1-3]}$. In the electrochemical oxidation treatment, one of the most crucial components is the anode where the decomposition reactions of pollution take place.

Currently, the most typical electrodes are dimensionally stable anodes (DSA) which is used widely due to the easy preparation and high cost-efficiency. Among the reported DSA electrodes, PbO$_2$ electrode is considered as an excellent metal oxide electrode because of its high chemical stability in corrosive media, relatively high over-potential for the oxygen evolution reaction and low price compared with noble metal electrodes$^{[4]}$. Therefore, the PbO$_2$ material has attracted more and more attention in the field of electrochemical oxidation treatment$^{[5-10]}$. Many recent literatures addressed the two goals of developing PbO$_2$ electrode that allow high current densities and efficiencies for particular electrode reactions and enhanced stability of the coating$^{[11-17]}$. However, there is little literature focused on the deactivation mechanism of PbO$_2$ electrode. Long time stability is a critical issue of PbO$_2$ electrodes since the unstable property will limit its application and the corrosion of the coating will lead to contamination of the product/effluent with toxic Pb(II). Thus it is necessary to find out the possible deactivation mechanism of PbO$_2$ electrode in the electrolysis, which can be helpful for the future enhancement of the PbO$_2$ electrode stability.

The electrode surface is the main place for the electrochemical reaction. The change of the surface morphology is directly related to the stability of the electrode. Consequently, the surface analysis is significant on revealing the electrode’s deactivation phenomena. A small amount of works related to the surface analysis of PbO$_2$ electrode. Duan et al.$^{[18]}$ reported that the edges and apexes of lead dioxide particles on the modified PbO$_2$ electrode disappeared, and many holes and nano-sized amorphous particles that were far smaller than those of the fresh electrodes emerged on the surfaces of electrodes. The similar phenomena were observed on the...
surface of the cerium-doped lead dioxide anode fabricated by Li et al. [19], Tong et al. [20] reported that the polymer film generated on the surface of the PTFE-modified PbO2 electrode during the electrochemical oxidation was the main reason for the electrode deactivation. Cao et al. [21] inferred that partial active oxygen atoms produced as intermediate diffused toward titanium substrate and oxidized Pb\textsuperscript{5+} to Pb\textsuperscript{4+} in the PbO2 coating to occupy the oxygen vacancies gradually. This resulted in the decrease of conductivity and the change of intrinsic stressed from tensile stresses to compressive stresses, which led to the electrode deactivation.

All the above results were obtained under the accelerated electrolysis condition (high current density and high acidic solution). To the best of our knowledge, there is few work focused on the surface analysis of PbO2 electrode under a moderate electrolysis condition which is similar to the practical condition. In this study, the Ti/Sb-SnO\textsubscript{2}/PbO\textsubscript{2} was used as the target electrode for electrolysis under constant current density for both accelerated life test and long time electrolysis. After that, SEM, EDS, XRD and ICP-OES were employed to determine the surface morphology and the metal content in the electrolytic solution. Then the possible reason for the deactivation of Ti/Sb-SnO\textsubscript{2}/PbO\textsubscript{2} electrode after accelerated life test and long time electrolysis was proposed.

1 Experiment

All chemicals used in this study were analytical reagents or higher and were used as received without further purification. Titanium (Ti) plate (purity: 99.6%, BaoTi Co. Ltd, China) with 0.5 mm-thickness was used in this study. Deionized water prepared from an EPET-40TF system (EPET Co. Ltd, Nanjing, China) was used for aqueous solution preparation and Ti plate washing.

Prior to the electrode preparation process, Ti plates with the size of 2.5 cm×4 cm×0.5 mm were mechanically polished with 1000-grid abrasive papers, and then rinsed with deionized water. The plates were subsequently immersed into a mixture of acetone and 1 mol·L\textsuperscript{-1} NaOH (1:1 volume ratio) in an ultrasonic bath (KQ2200DB, Kunshan Ultra Co. Ltd, China) for removing organic residues from the surface, followed by etching in 10 wt\% oxalic acid at 98 °C for 2 h, and then the products were rinsed thoroughly with deionized water.

The Ti/Sb-SnO\textsubscript{2}/PbO\textsubscript{2} electrode was prepared via two steps: (1) deposit the inner coating layer (Sn-SnO\textsubscript{2}) through thermal decomposition; (2) electrochemical deposition of the outer layer of PbO\textsubscript{2}.

In the first step, the precursor solution was freshly prepared by dissolving SnCl\textsubscript{2}·6H\textsubscript{2}O and SbCl\textsubscript{3} in a mixed solution composed of n-butanol, iso-propanol, ethanol and hydrochloric acid (37%). The salts were mixed in stoichiometrically according to the experimental setting.

The titanium surface was brushed with the precursor solution, and subsequently calcined in an oven at 450 °C for 15 min, for the thermal deposition of expected metal oxide. This procedure was repeated for 10 times before a final annealing step at 450 °C for 1 h. The average oxide loading amount by the brush coating method is 1.10 mg·cm\textsuperscript{-2}.

In the second step, the PbO\textsubscript{2} layer was coated on the as-prepared Ti/Sb-SnO\textsubscript{2}/PbO\textsubscript{2} electrode through electrochemical deposition. The electrochemical deposition process was carried out at 10 mA·cm\textsuperscript{-2} for 120 min in a (65±1) °C water bath, and powered by an DC electricity source (WYK-303B, China). The electrolyte was composed of 0.5 mol·L\textsuperscript{-1} Pb(NO\textsubscript{3})\textsubscript{2}, 0.1 mol·L\textsuperscript{-1} Cu(NO\textsubscript{3})\textsubscript{2}, 0.01 mol·L\textsuperscript{-1} NaF, and 10 mg·L\textsuperscript{-1} dodecyl sodium sulfonate (pH adjusted to 2 using HNO\textsubscript{3}). Finally, the as-prepared Ti/Sb-SnO\textsubscript{2}/PbO\textsubscript{2} electrode was rinsed by doubly-distilled water.

The long time electrolysis of the electrodes was tested in a conventional two-electrode cell at room temperature, using the as-prepared PbO\textsubscript{2} as the working electrode and platinum sheet as the counter electrode. It was conducted on an electrochemical system (LK3200A, Lanlike, China), and carried out at 5 mA·cm\textsuperscript{-2} in a 0.1 mol·L\textsuperscript{-1} Na\textsubscript{2}SO\textsubscript{4} solution for 300 h.

The morphology of the metal oxide coating film was characterized by SEM (JEOL, JSM-6700A). The crystal structure of the as-prepared electrodes was characterized by a Rigaku D/MAX-2400X X-Ray Diffractometer with CuK\textsubscript{α} radiation. The concentration of metal element in the solution after electrolysis was determined by ICP-OES (ICP-9000SHIMADZU).

2 Results and Discussion

2.1 Surface morphology

The SEM images of Ti/SnO\textsubscript{2}-Sb/PbO\textsubscript{2} electrodes before and after electrolysis are shown in Fig.1. Form the images, one can see that pronounced change of surface morphology takes place when the PbO\textsubscript{2} electrodes is used under a constant current density for a long time.

PbO\textsubscript{2} electrodes before electrolysis have uneven deposits, as shown in Fig.1a, which provide larger surface areas and potentially increase the electrode efficiency. However, there are fractions of the surface (i.e. black spots) that are not fully covered by PbO\textsubscript{2}, which is similar to the earlier reports [19,22].

It is presumed that cracks between these particles may lead to the chemical instability of electrodes after application for a long time. After 300 h electrolysis, most of the electrode surface is still covered by the PbO\textsubscript{2} layer, as shown in Fig.1b. But there are some distinct broken regions on the surface caused by the detachment of PbO\textsubscript{2}. From microscopic point of view, this PbO\textsubscript{2} layer damage is more obvious in Fig.1c and 1d. A part of PbO\textsubscript{2} particles lose their apex angle of the tetrahedron by dissolution, as shown in the white square area in Fig.1c. The similar phenomena are observed on the surface of the carbon nanotube modified PbO\textsubscript{2} electrodes [18] and
cerium-doped PbO$_2$ electrodes \[19\] after the accelerated life test, even on the long life fluorine resin modified PbO$_2$ electrode after 320 h of use with a low current density of 4 mA·cm$^{-2}$ \[11\]. This may be caused by the higher local current density on the top of tetrahedron particle than the average current density.

Meanwhile, the number of cracked tetrahedral PbO$_2$ particles increases. Fig.1d shows that part of the local tetrahedral PbO$_2$ particles detach from the titanium substrate, as shown in the white square. In Fig.1e, the big crack in the surface of PbO$_2$ layer can be clearly seen. Such crack may be due to the high pressure of oxygen produced during the electrolysis reaction. The direct consequence of this crack is the detachment of PbO$_2$ layer from the substrate. In Fig.1f, the left side of the white line (the bright part) is PbO$_2$ layer, the right side of the white line (the dark part) is the substrate area where PbO$_2$ layer detaches from. Some researchers \[14,17\] reported the similar detachment during the accelerated life test of the unmodified PbO$_2$ electrode. The appearance of these detachments may be associated not only with the presence of mechanical stress in the PbO$_2$ film acquired during the electro-deposition process, but also with the thermal stress related to the possible extreme conditions during electrolysis \[22\].

### 2.2 Element distribution

The results of EDS analysis on Ti/SnO$_2$-Sb/PbO$_2$ electrode before and after long time electrolysis (Fig.1a and 1b) are listed in Table 1. Before long time electrolysis, the elements in the electrode surface are Pb, O and C, indicating that its surface is well covered by PbO$_2$ layer. After electrolysis, five elements are detected on electrode surface including Pb, O, C, Sn and Ti. This result indicates that the electrode surface is broken and leads to the exposure of Sn and Ti which are originally covered by the PbO$_2$ layer. This conclusion can be clearly proofed by Fig.1d–1f.

<table>
<thead>
<tr>
<th>Pb</th>
<th>Sn</th>
<th>Ti</th>
<th>C</th>
<th>O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.77</td>
<td>-</td>
<td>-</td>
<td>25.13</td>
<td>57.11</td>
<td>100</td>
</tr>
<tr>
<td>9.36</td>
<td>3.95</td>
<td>8.41</td>
<td>16.92</td>
<td>61.36</td>
<td>100</td>
</tr>
</tbody>
</table>

Meanwhile, the concentration of lead ion in the solution after 300-h electrolysis is 0.301 mg·L$^{-1}$ determined by ICP-OES. Liu et al. \[23\] measured the residual concentration of lead ion in solution after 2 h electrolysis, and the value was 0.052 mg·L$^{-1}$. Both of our work and the literature report confirm that the surface PbO$_2$ layer dissolves into the electrolyte during the electrolysis process.

### 2.3 XRD analysis

The XRD patterns of the Ti/SnO$_2$-Sb/PbO$_2$ electrodes before and after electrolysis are shown in Fig.2. For the unused PbO$_2$ electrode (Fig.2a), two types of PbO$_2$ crystallites can be distinguished. The diffraction peaks at 25.4°, 31.9°, 49.0°, 52.2°, 62.5°, 74.4°, 76.8° and 78.5° correspond to the (110), (101), (211), (220), (301), (321), (400) and (222) crystal surfaces of $\beta$-PbO$_2$, respectively, and the diffraction peaks at 36.2° and 58.9° correspond to the (200) and (222) crystal surface of $\alpha$-PbO$_2$, respectively.

It can be seen from Fig.2 that there is little apparent change of crystal structure in PbO$_2$ electrodes before and after electrolysis. The major diffraction peaks are almost identical and still correspond to $\beta$-PbO$_2$, which is consistent with the result obtained by Duan et al. \[16,18\]. However, the intensity of the peaks decreases which may be attributed to the dissolution...
2.4 Analysis of the PbO2 deactivation phenomena

Based on the above results, the instability of PbO2 anode can be described as follows: When electrolysis begins, the gas reaction will occur at the interface of the anode and electrolyte, as shown in Eqs. (1) and (2)[24].

$$2H_2O \rightarrow 2H^+ + O_2 + 2e^- \text{ (Acid)}$$
$$4OH^- + 4e^- \rightarrow O_2 + 2H_2O \text{ (Neutral and basic)}$$ (2)

SEM images show that there are some defective areas on the surface of PbO2 anode (in Fig.1a) and some cracks on the PbO2 tetrahedron particles (in Fig.1c). The electrolyte and the active oxidative species will diffuse into the titanium substrate through the electrode surface cracks[25,26]. The reactions in Eqs. (1) and (2) would occur not only on the coating surface, but also on these defective area and cracks. From Fig.1, it can be found that the size of the cracks is in micron level, or even in nanometer level. It is very difficult for the mass transfer in such hole-in-the-wall place. The pressure inside the metal oxide layer (both PbO2 layer and SnO2-Sn layer) is increased by oxygen evolution[19,27]. And then, the generated oxygen gas strokes the surface layer. Long-playing strike will lead to the mechanical rupture of the surface layer, as shown in Fig.1d-1f.

According to the formula (1) and (2), the pH value of electrolyte in the interface region would decrease to form a strongly acidic region after the occurrence of the electrolysis reaction. In this acidic region, the dissolving process of PbO2 would occur as shown in formula (3).

$$PbO_2 + 4H^+ \rightarrow Pb^{4+} + 2H_2O$$ (3)

This process would induce the dissolution of the PbO2 layer as shown in Fig.1c. Meanwhile, due to poor mass transfer rate, the pH value of the solution in the cracks and crevices would be much lower than that of the bulk solution. This would inevitably result in accelerated dissolution of the coating oxide.

Part of the titanium substrate would be uncovered and contacted with the electrolyte directly due to the effect of electrochemical dissolution and mechanical detachment as shown in Fig.1b, 1d, 1f and Table 1. The exposed titanium base could be oxidized to TiO2 easily under the electrolysis condition, which leads to the increase of the resistance of the PbO2 electrode. At the same time, some of the electrochemical-generated oxygen would be released and the other part would adsorb on the electrode surface. These new generated oxygen atoms would diffuse to the substrate direction due to the effect of electric field. During the migration process, the oxygen will fill the oxygen vacancies in the PbO2 lattice and then reduce the conductivity of PbO2 electrode[4]. Both of the above results are harmful to the electrochemical property of the PbO2 electrode. It would lead to the increase of the electrolysis cell voltage until it reaches the specified failure criteria. Zheng et al. [14] pointed out that the titanium substrate passivation was the main mechanism leading to the failure of an oxide coated electrode without total consumption of the active oxide layer. The schematic diagram of surface change on the Ti/SnO2-Sb/PbO2 electrode during the long time electrolysis process is shown in Fig.3.

2.5 Possible mechanisms for the deactivation of electrode

Based on the above results, the possible mechanisms of the deactivation of PbO2 electrode are proposed as follows.

1. (1) The dissolution of PbO2 coating

When the electrolysis starts, the PbO2 coating would slowly dissolve into the solution due to the electrochemical reactions occurring at the electrode/solution interface (strongly acidic and high current density condition). This is proved by ICP-OES test results and SEM images of the electrode surface after electrolysis.

2. (2) The detachment of PbO2 coating

Gas evolution in the cracks and the interface between the outer layer and the inner layer may detach part of PbO2 coating. The low mass transfer rate increases the gas pressure and enlarges the detachment. This is proved by EDS test results and SEM images of the electrode surface after electrolysis. This also indicates that the electrode surface morphology plays a significant impact on the electrode stability. Further improvement of the electrode surface morphology to reduce the presence of cracks and crevices would greatly improve the electrode stability.

3. (3) Passivation

The oxygen evolution between the metal oxide layer and the titanium layer promotes the generation of the insulated TiO2 layer, which increases the electrode resistance and blocks the electrochemical reaction.

![Fig.3: Surface change of Ti/SnO2-Sb/PbO2 electrode during the long time electrolysis process](image-url)
3 Conclusions

1) Ti/Sb-SnO<sub>2</sub>/PbO<sub>2</sub> is electrolyzed under constant current density conditions for long time electrolysis in Na<sub>2</sub>SO<sub>4</sub> solution.

2) The dissolving and detachment phenomenon are found out on the surface of PbO<sub>2</sub> electrode after electrolysis. Meanwhile, the Pb element is detected in the solution and its concentration is 0.301 mg L<sup>-1</sup>. This result further proved the PbO<sub>2</sub> dissolution during the electrolysis.

3) The dissolution and detachment process increase the explosion opportunity of the titanium substrate, which can be easily oxidized to isolative TiO<sub>2</sub> layer. Therefore, it is speculated that the possible reasons for the Ti/Sb-SnO<sub>2</sub>/PbO<sub>2</sub> electrode deactivation are the oxide layer dissolution, detachment and the substrate’s passivation, respectively. And the electrode surface morphology plays a large impact on the electrode stability.

References

7 Han W, Chen Y, Wang L et al. Desalination[J], 2011, 276: 82
12 Song Y, Wei G, Xiong R. Electrochim Acta[J], 2007, 52: 7022
18 Duan X, Ma F, Yuan Z et al. Electrochim Acta[J], 2012, 76: 333
19 Li Q, Zhang Q, Cui H et al. Chem Eng J[J], 2013, 228: 806
22 Saez V, Esclapez M D, Frias-Ferrer A J et al. Ultrasonics Sonochemistry[J], 2011, 18: 873

**Ti/Sb-SnO<sub>2</sub>/PbO<sub>2</sub>**


1984 黔029-82664731 E-mail: xuhao@mail.xjtu.edu.cn