CYANIDE DETECTION ABILITY OF THE PbO_2 ELECTRODE SYNTHESIZED BY PULSED CURRENT METHOD

Phan Thi Binh, Mai Thi Thanh Thuy, Nguyen Van Toan and Duong Thi Doan

Institute of Chemistry –Vietnam Academy of Science and Technology

Received 22 September 2010

Abstract

Lead dioxide electrode was prepared by pulsed current method on stainless steel (pulse height: 30 mA/cm^2, pulse width: 1 s, Q = 5100 mAs) from solution of 0.5 M HNO_3 + 0.5 M $Pb(NO_3)_2$ + 0.05 M $Cu(NO_3)_2$ at room temperature. The electro-catalytic oxidation of cyanide on PbO_2 was investigated by potentiodynamic method at different scan rates in medium of 0.1 M NaOH. The result showed that PbO_2 can electrocatalyse oxidation process of CN^- which occurred at about 0.6 V versus to saturated calomel electrode. It was found a linear relationship between the height of oxidation peak and cyanide concentration, which is better than that between oxidation peak area and cyanide concentration. The both lines have R^2 equal 0.9989 and 0.9934, respectively. The electro-catalytic activity of PbO_2 layer is depended exponentially on their thickness.

Keyword: PbO_2, cyanide, electro-catalysis.

1. INTRODUCTION

The presence of cyanide ion in drinking water or waste water from electroplating is very dangerous for human or animal life due to their brain can be paralyzed with them. The most significant effects of cyanide exposure occur in the nervous system, especially in the brain. The effects are probably due to rapidly biochemical changes in the brain, such as changes in ion flux, neurotransmitter release, and possibly peroxide formation [1]. Thus, finding a simple method in detection of cyanide ion in water is important and necessary for scientists. Among metal oxides, lead dioxide (PbO_2) has a height electronic conductivity, stable in medium, height oxygen evolution over potential as well as good electrocatalytic activity, on which cyanide ion can be effectively oxidized [2, 3]. PbO_2 has been else widely used an active material on COD-sensor for environment [4, 5] and electrocatalytic electrode for electro-organic synthesis [6].

The electrocatalytic oxidation of cyanide ion depends strongly on preparing technique of PbO_2. Among electrochemical methods for getting PbO_2 layer on metal substrate, the pulsed current way can be suitable for improving not only electrochemical properties but also structural morphology of lead dioxide [7].

In this work, stainless steel (SS) was chosen as a substrate for PbO_2 pulsed anodic layer because of its inexpensive cost and good corrosive stability. The electrodeposition was carried out by the pulsed galvanostatic method in acidic solution to increase electrochemical activity and improve adhesive ability of the PbO_2 coatings on substrate. The potentiodynamic method was applied to detect cyanide ion in 0.1 M NaOH solution by varying potential scan rates and cyanide concentrations.

2. EXPERIMENTAL

2.1. Preparation of SS/PbO_2 electrode

PbO_2 was directly synthesized by the pulsed current method on the surface of SS electrode with an area of 0.33 cm^2 from solution of 0.5 M HNO_3 + 0.5 M $Pb(NO_3)_2$ + 0.05 M $Cu(NO_3)_2$. Pulse height of 30 mA/cm^2, pulse width of 1s and relaxation time of 5 s were applied at the room temperature for all samples.

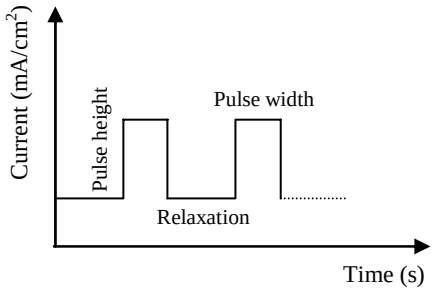

Fig. 1: Pulsed current diagram including pulse width, pulse height and relaxation

2.2. Measurements

Electrochemical measurements were performed

using an electrochemical workstation IM6 (Zahner-Elektrik). All experiments were carried out in a three electrode system. A stainless steel|PbO_2 (SS|PbO_2) was used as a working electrode for cyanide detection. The counter electrode was the platinum net. The saturated calomel electrode was employed as the reference electrode. The electrolyte was a 0.1M NaOH solution adding cyanide concentrations from 5 to 25 mg/l for investigating electro-catalytic property of SS|PbO_2 electrode in potential range from 0.4 V to 0.7 V at scan rates from 50 to 250 mV/s.

3. RESULTS AND DISCUSSION

3.1. Influence of potential scan rate

Figure 2 displays the potentiodynamic diagrams of anodic lead dioxide layer at different potential scan rates in 0.1 M NaOH solution adding cyanide (15 mg/l). In the cases of height scan rates (150 ÷ 250 mV/s), the peak potential was found at about 0.6 V corresponding to following reaction:

$$CN^- + 2OH^- \rightarrow OCN^- + H_2O + 2e^- \quad (1)$$

and shifted in left side when scan rate went down to low values (50 ÷100 mV/s). The height of current peak was depended on potential scan rate, but non-regular. There was only a small difference between the height of current peaks occurred at the ranges from 150 to 250 mV/s and from 50 to 100 mV/s as well. However, a big difference between both regarded scan rate ranges was found and the highest current peak was at scan rate of 200 mV/s at which all following experiments were carried out.

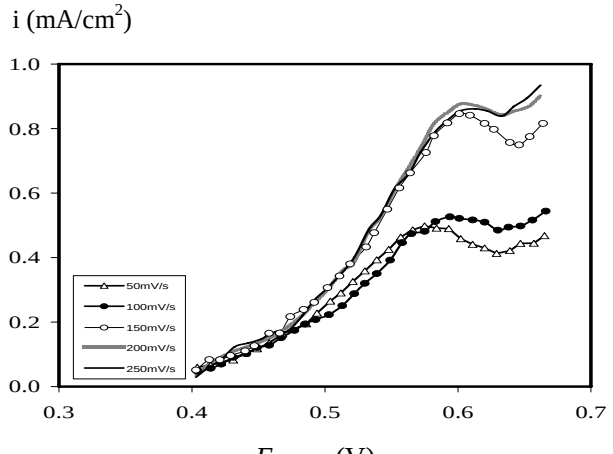

Fig. 2: Potentiodynamic diagrams of the SS/PbO_2 at different potential scan rates in 0.1M NaOH solution containing cyanide (15mg/l)
(PbO_2 prepared by 170 pulses with pulse height: 30mA/cm^2 ; pulse width: 1s ; relaxation time: 5s)

3.2. Influence of cyanide concentration

Potentiodynamic diagrams of PbO_2 electrode were taken from 0.1 M NaOH solution containing different cyanide concentrations (5 ÷ 25 mg/l) at potential scan rate of 200mV/s (figure 3). A clearly peaks corresponding to oxidation of cyanide ion

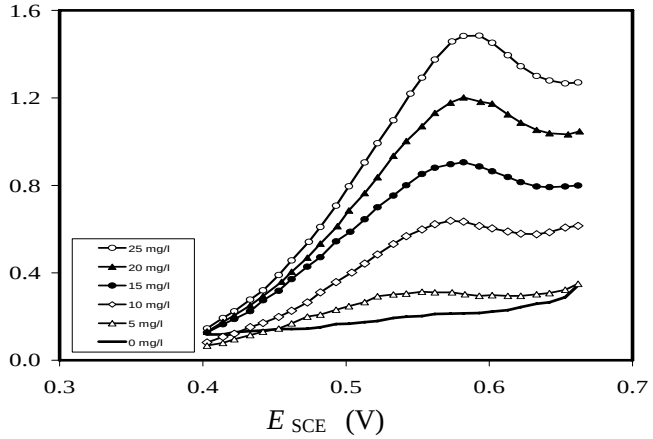

Fig. 3: Potentiodynamic diagrams of the SS/PbO_2 at potential scan rate of 200 mV/s in 0.1M NaOH solution containing cyanide
(PbO_2 prepared by 170 pulses with Pulse height: 30mA/cm^2 ; pulse width: 1s ; relaxation time: 5s)

appears at about 0.6 V versus saturated calomel electrode (reaction 1). It was found a linear dependence of oxidation current peaks (R^2 = 0.9989) on cyanide concentrations by equation *y = 0.058x + 0.03* in the range from 5 to 25mg/l (figure 3). Additionally, the oxidation peak area was also depended on CN^- concentration (Figure 4) with R^2 = 0.9934 by equation y = 4.6902x – 9.605. Note that these behaviours of both current height and area of oxidation peak show a well suitable application of SS|PbO_2 electrode for the detection of cyanide ion in solution.

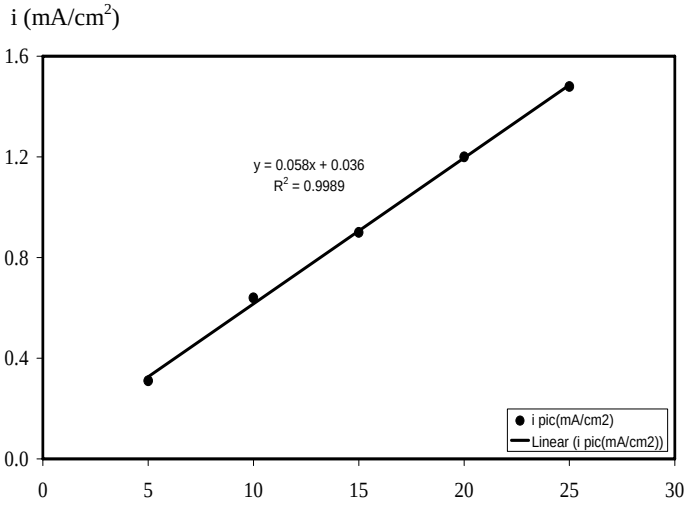

Fig. 4: Dependence of the height of oxidation current peak on cyanide concentration in 0.1M NaOH solution at potential scan rate of 200mV/s
(PbO_2 prepared by 170 pulses; Pulse height: 30mA/cm^2 ; pulse width: 1s ; relaxation time: 5s)

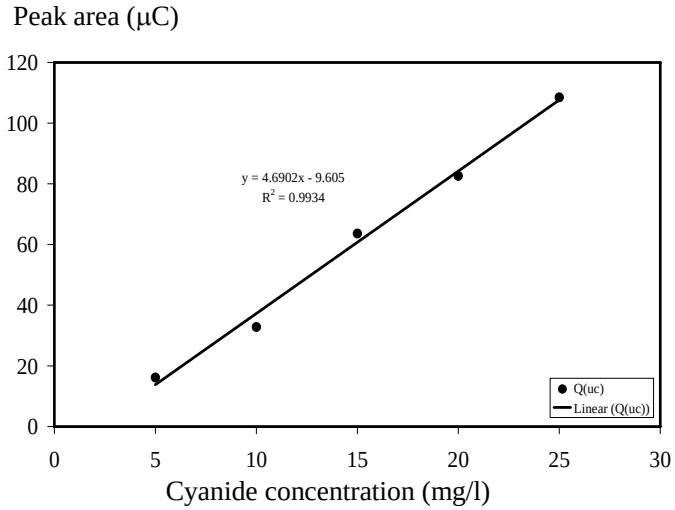

Fig. 5: Dependence of oxidation peak area on cyanide concentration in 0.1M NaOH solution at potential scan rate of 150 mV/s
(PbO_2 prepared by 170 pulses with Pulse height: 30mA/cm^2 ; pulse width: 1s ; relaxation time: 5s)

3.3. Influence of PbO_2 layer thickness

In this work the comparison of thickness of PbO_2 layers was considered under the number of current pulses used for material preparation.

Figure 6 shows the potentiodynamic diagrams of lead dioxide layers at a scan rate of 100 mV/s in 0.1M NaOH solution containing cyanide ion (15 mg/l), which prepared by different number of current pulses. There was found an exponent relationship between the height of oxidation peaks of CN^- ion and number of current pulses used for preparing of PbO_2-layer. These results demonstrated that the thickness of lead dioxide layers affected strongly on their electrocatalysis for CN^- which caused probably by the change of PbO_2-morphology.

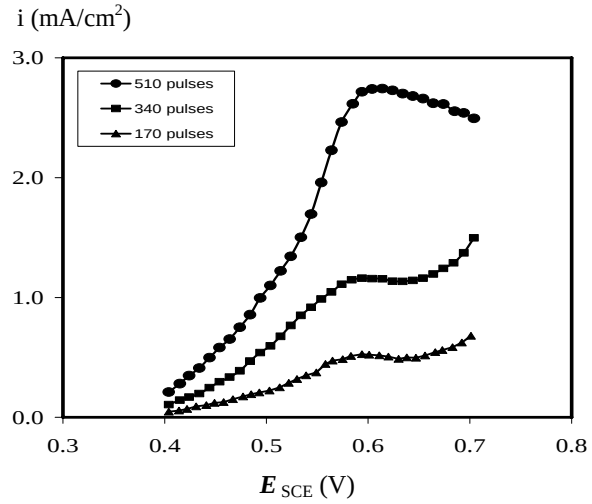

Fig. 6: Potentiodynamic diagram of the SS/PbO_2 at 100 mV/s in (0.1 M NaOH + 15 mg/l CN^-) (PbO_2 prepared with different number of pulses; pulse height: 30 mA/cm^2; pulse width: 1 s; relaxation time: 5 s)

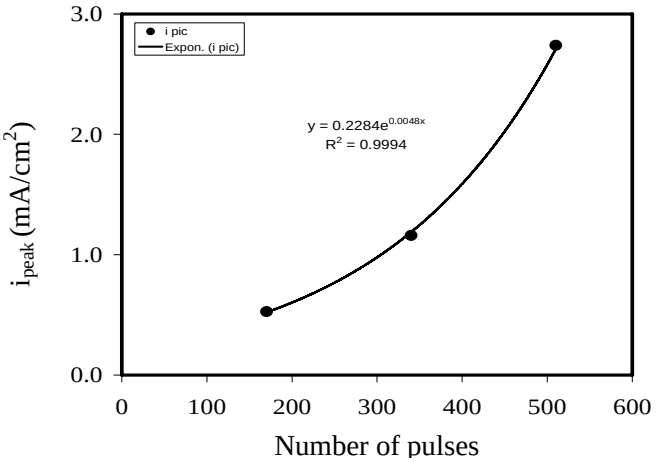

Fig. 7: Dependence of i_{peak} on number of current pulses during synthesis of PbO_2

4. CONCLUSION

PbO_2 layers were electrodeposited on stainless steel. The electro-catalytic oxidation of cyanide on SS|PbO_2 depended both on cyanide concentration in solution and potential scan rate. Linearity of the height of oxidation current peaks is much better than that of oxidation peak area on concentration of cyanide ion. It suggested that a PbO_2 layer prepared by pulsed current method can be used for detection of cyanide ion in solution. The electro-catalytic activity of PbO_2 layer depended exponentially on their thickness.

Acknowledgements. *This study was financially supported by the Institute of Chemistry-VAST. The Authors would like to thank the Humboldt-Fellowship for supporting IM6 equipment.*

REFERENCES

1. U. S. Department of Health and Human Services. Toxicological profile for cyanide, Public Health Service Agency for Toxic Substances and Disease Registry (2006).
2. A. T. Kuhn. J. Appl. Chem. Biotech., 21, 29 - 34 (1971).
3. Liu Wei, Jiang Jin-Gang, ShiI Guo-Yue, He Yan, Liu Ye, Jin Li-Tong. Chinese Journal of Chemistry, 25, 203-207 (2007).
4. Shiyun Ai, Mengnan Gao, YaYang, Jiaqing Li, Litong Jin. Electroanalysis, 16(5), 404 - 409 (2004).
5. Jiaqing Li, Lei Zheng, Luoping Li, Guoyue Shi, Yuezhong Xian, Litong Jin. Electroanalysis, 18(22), 2251 - 2256 (2006).
6. Shao-Ping Tong, Chun-An Ma, Hui Feng. Electrochimica Acta, 53, 3002 - 3006 (2008).
7. Donglan Zhou, Lijun Cao. Electrochimica Acta, 53, 2060 - 2064 (2007).

Corresponding author: **Phan Thi Binh**
Institute of Chemistry, VAST
18 Hoang Quoc Viet Road, Cau Giay District, Hanoi, Vietnam
Email: ptbinh@ich.vast.ac.vn