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Effect of surface morphology of lead dioxide particles on their ozone generating performance

Jingping Wang [a,*], Xiang Li [a], Linghua Guo [a], Xiangjun Luo [b]

[a] Shaanxi University of Science and Technology, Taihua Road 43#, Xi'an 710016, China
[b] RuYuan Dongyangguang Formed Foil Ltd, Shaoguan 512721, China

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ABSTRACT

Lead dioxide is widely applied in anodic oxidation processes like the ozone generation and the degradation of various organic species in aqueous solution. In this paper, the correlation between the morphology of the lead dioxide particles and their ozone generating performance was investigated. The anode prepared by crude lead dioxide particles exhibited better performance in ozone generation than that prepared by milled lead dioxide particles. The reason lies in, probably, the higher stability of $O^{\bullet}$ on the surfaces of the crude lead dioxide particles. With 220-h running of the anode prepared with crude lead dioxide particles, the overall diameters of the lead dioxide particle decreased drastically, and many nano-scaled lead dioxide particles presented on the surfaces of the particles, which had resulted from recrystallization of the particles at high potentials. The two facts might be the main reason for the decline of the membrane electrode performance. Furthermore, a small percentage of α-lead dioxide detected in lead dioxide crystal may also decline the performance of the membrane electrode.

1. Introduction

Ozone has been widely used in the fields of water treatment, food processing, chemical oxidizing, therapy [1–4] and so on because of its strong oxidizing ability and environmental friendliness. Among the various electrochemical ozone generation technologies, solid polymer electrolyte (SPE) technology demonstrated many advantages, such as lower energy consumption, high current efficiency at room temperature, long lifetime [1,5] and so on, over the other ozone generation technologies. Lead dioxide has been used widely as anode material in SPE technology for ozone generation due to its lower cost and better stability under high positive potentials in the last several decades [6,7].

To date, two methods are generally adopted in preparing the porous lead dioxide anode. One of them is to deposit a thin lead dioxide film on a porous matrix electrode [8–11], while the other one is to mix the lead dioxide particles with a matrix substance like poly (tetrafluroethylene) (PTFE) latex first and then to prepare the porous electrode [12,13]. It has been reported that the electrocatalytic activity of the lead dioxide based anode is closely related to its morphology and structure [9,14]. In this study, we were motivated to study the effect of the surface morphology of the lead dioxide particles on their ozone generating performance. It was found that the regularity of the lead dioxide particles has great effect on the performance of the anode during ozone generation.

2. Experimental

2.1. Materials

Nafion solution (5 wt%) and Nafion-117 membrane were obtained from Dupont (American). PTFE latex was purchased from Chenguang Research Institute of Chemical Industry (China). Platinum loaded carbon (with 10 wt% platinum) was purchased from Xi'an Catalyst Chemical Ltd. All reagents were analytical grade and doubly distilled water was used in all experiments.

2.2. Preparation of lead dioxide particles

Lead dioxide was electrodeposited on the surfaces of a titanium plate electrode from an electrolyte containing 0.2 mol/dm^3 lead nitrate and 0.6 mol/dm^3 nitric acid. The electric current density was 30 mA/cm^2 and the temperature was kept at 65 ± 5 °C. With 6-h electrolyzing, the lead dioxide, which broke off naturally from the titanium plate electrode, was collected as the crude lead dioxide particles. Part of the crude lead dioxide particles were milled in a planetary ball miller to prepare the milled lead dioxide particles. Both the crude and milled lead dioxide were dried at 100 ± 5 °C and

* Corresponding author.
E-mail address: wangjplx3@yahoo.com.cn (J. Wang).

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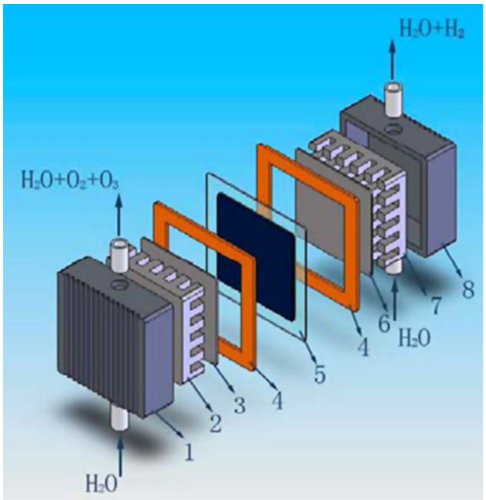

Fig. 1. Schematic illustration of the electrolyzing cell (1) anodic frame; (2) anodic transporting plank; (3) anodic current collector; (4) rubber sealing ring; (5) membrane electrode; (6) cathodic current collector; (7) cathodic transporting plank; (8) cathodic frame.

screened with Taylor sieves, respectively, to achieve the particles with diameters in the range of 25–40 micron.

2.3. Preparation of the membrane electrode

The preparation of the membrane electrode for ozone generation was described in Ref. [13]. In this study, both the loadings of the β-lead dioxide particles in the anodic electrode and that of the platinum in the cathodic electrode were fixed at 30 and 40 mg/cm^2, respectively.

2.4. Methods and instrumentations

The power supply used for characterization of the membrane electrodes was a 17303220A type potentiostat (Ningbo Zhongce Electronics Co., Ltd., China) with current density kept always at 1.5 A/cm^2. All the applied voltages and current efficiencies were averages of four testing data. Morphology of the lead dioxide particles was examined on either a JEOL JSM-6700 scanning electron microscope (SEM) or a Hitachi S-2700 SEM. X-ray diffraction (XRD) analysis was carried out on a Rigaku D/MAX-2400 XRD equipment, equipped with a Cu K® source, at 40 kV and 20 mA. The electrolyzing cell is schematically illustrated in Fig. 1. For generation of ozone, the cell was performed at 25–30 °C with water flow rates at both anode and cathode electrodes of 1 L/h. The yield of the ozone gas was measured according to iodimetry as described in Ref. [15].

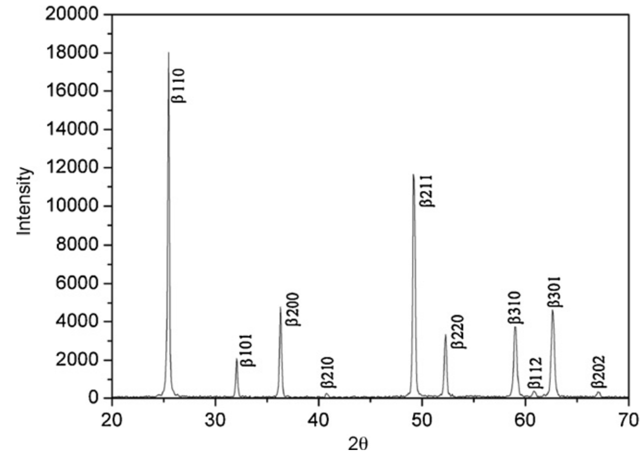

Fig. 2. X-ray diffractograms of the lead dioxide particles.

3. Results and discussion

3.1. Crude and milled lead dioxide particles

Although both the crude and milled lead dioxide particles exhibit the same crystal structure of β type (Fig. 2), anodes prepared by the two kinds of lead dioxides demonstrated completely different electrocatalytic ability in ozone generating (Fig. 3). After 7-h running, the current efficiencies (χ_{O_3}) of the two membrane electrodes reached the equilibrium (Fig. 3A). The equilibrium value (χ_{O_3}) for the milled lead dioxide particles based anode is 12.5%, which is far less than the 17.9% of the anode based on the crude lead dioxide particles. It can be concluded then that the crude lead dioxide was more effective than the milled lead dioxide for the generation of ozone. The cell voltages of the two membrane electrodes increased with running time, and equilibrium values of 3.46 and 3.6 V were observed for anodes based on crude and milled lead dioxide particles, respectively with 20-h running (Fig. 3B). The lower equilibrium cell voltage of the crude lead dioxide particles revealed that anodic catalyst layer prepared with crude lead dioxide particles had better electric conductivity than that prepared with the milled lead dioxide particles.

Morphology examinations showed that with milling of the crude lead dioxide particles, the structure of the particles changed significantly. The edges and apexes of the particles became less visible and many smaller lead dioxide particles in nano-scale were absorbed on the surfaces of the larger particles (Fig. 4) with ball milling, which is different from the relatively regular surfaces of the crude lead dioxide particles. Amadelli et al. [9] and Da Silva

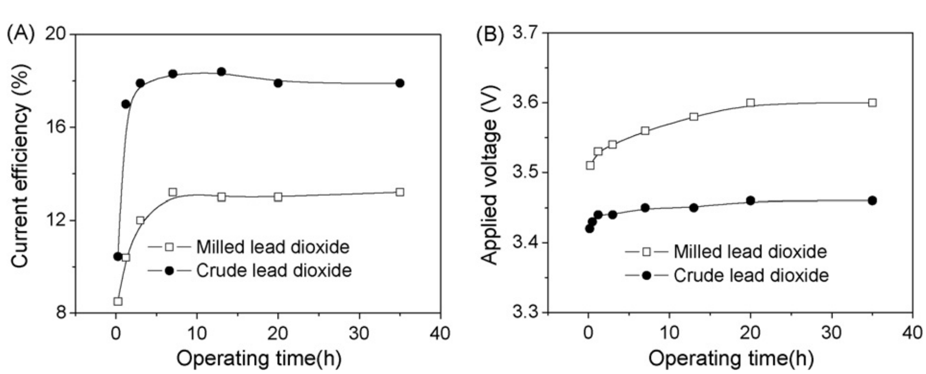

Fig. 3. Performance of the membrane electrodes prepared with crude and milled lead dioxide particles.