Study on the Effect of the Lead Dioxide Particles on the Anodic Electrode Performance for Ozone Generation

Jingping WANG\textsuperscript{a} * and Xinli JING\textsuperscript{b}

\textsuperscript{a} Shaanxi University of Science and Technology (North Taihu Road 43\#, Xi’an, 710016, China)
\textsuperscript{b} School of Energy and Power Engineering, Xi’an Jiaotong University (Xianning Road 28\#, Xi’an, 710049, China)

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Anodic electrodes for ozone generation were prepared with lead dioxide particles of various diameters. The lead dioxide particles were characterized with X-ray diffraction analysis, and the electrodes were characterized and performed for ozone generation. It was revealed that both the diameters of the lead dioxide particles and the contents of the pore forming agent have great effect on the performance of the electrodes. With decreasing of the diameters of the lead dioxide particles from the range of 55-74 $\mu$m to the range of 15-35 $\mu$m, the performance of the electrodes improved. But no further improvement was found with further decreasing of the particle diameters to the range of 5-15 $\mu$m. However, by employing an appropriate amount of pore forming agent during the electrode preparations, the performance of the anodic electrode can be improved. The optimized weight ratio of ammonium oxalate to lead dioxide is 1.33/100.

Key Words: Ozone, Lead Dioxide, Membrane Electrode

1 Introduction

Ozone is one of the commonly known and most powerful oxidizers and has been widely used in the field of food processing,\textsuperscript{1-3} drinking water \textsuperscript{4, 5} and industrial waste water \textsuperscript{6} processing, chemical oxidizing,\textsuperscript{7} therapy \textsuperscript{8} and so on, due to not only the strong oxidizing capability and environmentally friendly nature of itself, but also the environmental compatibility of its reduced product, oxygen, which is also beneficial to mankind and other animals. For generation of ozone, the electrochemical solid polymer electrolyte (SPE) technology, mostly with a $\beta$-lead dioxide anode \textsuperscript{9, 10} and a platinum cathode,\textsuperscript{11-13} is considered as one of the novel technologies since 1980’s\textsuperscript{14, 15}. The significance of the technology covers the higher current efficiency, which can be up to 6%, as well as the no containing of NOx gases. It has been revealed that the composition and structure of the lead dioxide anode affect greatly the performance of the membrane electrodes in generating ozone.\textsuperscript{16, 17} To date, two methods are adopted in preparing the porous lead dioxide anode, i.e. either to electroplate a compact lead dioxide film on a porous matrix electrode, or to mix lead dioxide particles with poly(tetrafluoroethylene) (PTFE) latex and to prepare the porous electrode. Although tremendous works have been carried out on the former method, the electric current efficiency of the electrode for generating ozone was low at ambient temperature, generally less than 15\%\textsuperscript{,18-22} The electrodes prepared by the latter method demonstrated electric current efficiency as high as 20\% at ambient temperature,\textsuperscript{22} but little research has been focused on the area. Therefore, the effect of the composition and structure of the porous lead dioxide electrode on the performance of the electrode is discussed in this paper.

2 Experimental

2.1 Materials

Nafion solution (5 wt\%) and Nafion-117 membrane were purchased from Dupont (American). PTFE latex was purchased from Chenguang Research Institute of Chemical Industry (China). Lead nitrate, nitric acid, platinum loaded carbon (with 10 wt\% platinum), and ammonium oxalate were analytical grade from Xi’an Chemical Reagent Factory. Ammonium oxalate was purified by recrystallization in water. All other reagents were used as received and doubly distilled water was used in all experiments.

2.2 Preparation of lead dioxide particles

By using of a DJS-292 potentiostat (Leici Instrument Factory, Shanghai, China), lead dioxide was electrolyzed on the surfaces of a titanium electrode, which was polished with emery cloth (No. 600), washed with water and degreased in acetone, from an electrolyte containing 0.2 mol/dm$^3$ lead nitrate and 0.3 mol/dm$^3$ nitric acid. The electric current density was 10 mA/cm$^2$ and the temperature was kept at 65 $\pm$ 5 $^\circ$C. With 6 h’s electrolyzing, the lead dioxide was scraped off and dried at 40 $^\circ$C. After ground in a planetary ball mill (QM-1SP 2 L, Nanjing University, China) with stainless steel grinding media and screened with Taylor sieves, lead dioxide particles with specific diameters were prepared.

2.3 Preparation of the membrane electrode

Lead dioxide particles were mixed with PTFE latex with weight ratio of 100/15 and slurred with water at 70 $^\circ$C. The slurry was ground and pressed at 25-35 $^\circ$C to form a sheet of membrane with thickness of 0.15 $\pm$ 0.02 mm. The membrane was dried at 55-65 $^\circ$C and cut to the size needed to form the precursor of the anodic catalyzing membrane. With the same procedure, the precursor of the cathodic catalyzing membrane was prepared from
the mixture of platinum loaded carbon with PTFE latex with weight ratio of 1/1.5. The two precursors were glued to both sides of a Nafton-117 film, and pressed with pressure of 5.9 MPa at 165 ± 5°C for 2 min to form the sandwiched SPE membrane electrode. The effective area of the obtained electrodes was 12 cm².

2.4 Methods and instrumentations
The power supply used for characterizing the membrane electrodes was a 17303220A type potentiostat (Ningbo Zhongce Electronics Co., LTD, China), and current density of 1.5 A/cm² was always adopted. All the applied voltages and current efficiencies were averages of 6 testing data, and the results were reproducible even after tens of current stops. Scanning electron microscopy (SEM) of the lead dioxide particles was performed on a Hitachi S-2700 scanning electron microscope. X-ray diffraction (XRD) analysis was carried out using a Rigaku D/MAX-2400 XRD equipment, equipped with a CuKα source, at 40 kV and 20 mA. The electrolyzing cell is schematically illustrated in Fig. 1. For generation of ozone, the cell is performed at 25-30°C with water flow rates at anode and cathode electrodes of 0.3 L/h. The yield of the ozone gas was measured according to iodimetry as described in reference.23

3 Results and Discussion
3.1 Effect of the diameter of the lead dioxide particles
With the same loadings of lead dioxide particles in the membrane electrodes, the numbers of the catalyzing point increase with decreasing of the particle diameters. It is therefore necessary to prepare membrane electrodes by use of lead dioxide particles with various diameters and study the effect of the particle diameters on the performance of the electrodes. The morphology of the lead dioxide particles with different diameters are shown in Fig. 2 and the XRD analysis (Fig. 3) revealed the particles are mainly of β type in our studies. The loadings of the β-lead dioxide particles in the anodic electrode and that of the platinum in the cathodic electrode are fixed at 30 mg/cm² and 0.4 mg/cm², respectively, in all experiments. It is shown in Fig. 4 (A) that both the current efficiencies (χ₀) and the stabilities of the membrane electrodes increase with the diameters of the β-lead dioxide particles decreased from the range of 55-74 μm to the range of 15-35 μm, indicating the improved performance of the ozone generation with the electrodes. The reason lies in the increased specific area and, therefore, the numbers of the catalyzing points in the anodic electrodes with decreasing of the diameters of the lead dioxide particles. While with further decreasing of the particle diameters to the range of 5-15 μm, no improving of the electrode performance is observed and a small drop of the χ₀ is observed after 25 h’s running. The reason was probably owing to the decreased sizes of the gaps between the particles when lead dioxide particles with diameters of 5-15 μm were used. With further decreasing of the sizes of the gaps, both the transporta-

![Fig. 1 Schematic illustration of the electrolyzing cell.](image1)

![Fig. 2 SEM images of the lead dioxide particles with different diameters: (A) 5-15 μm; (B) 15-35 μm; (C) 35-55 μm.](image2)
tion of the reactants to the catalyzing points and the releasing of the reacted gases from the catalyzing points are hindered, and therefore either the reactants cannot be adequately catalyzed to form ozone or the ozone produced cannot be effectively released but be decomposed, resulting the poor performance of the electrode in the initial stages of running. With continuing of the running, the lead dioxides re-distributed and the gaps between the particles increased with the eroding of the water, oxygen and ozone, and therefore both the transportations of the water and the releasing of the gases improved, results to the improvement of the electrode performance. Lower cell voltages were also observed when lead dioxide particles with small diameters were used (Fig. 4 (B)). For example, cell voltage of 3.45 V is found for the membrane electrode prepared with lead

**Fig. 3** XRD spectra of the lead dioxide particles.
(The characteristic peaks for β-lead dioxide are marked with small squares.)

**Fig. 4** Effect of the diameters of the β-lead dioxide particles on the performance of ozone generation with the membrane electrode.

**Fig. 5** Effect of pore forming agent on the performance of the membrane electrodes. (Lead dioxide particles with diameters of 15-35 μm is used, and the ratios of ammonium oxalate to lead dioxide is by weight.)
dioxide particles with diameters of 5-15 µm after 25 h’s running, which is probably resulted from the compactness and therefore the increased conductivity of the catalyzing lead dioxide layer.

3.2 Effect of pore forming agents

It has been found that the diameters, lengths and distributions of the pores in porous electrodes have great effect on the performance of the electrode, and electrochemical reactions can hardly be carried out on surfaces with small pores.17, 18, 24 As mentioned above, the performance of the anodic electrode made with small lead dioxide particles (5-15 µm) is not very satisfied in the early stages of running owing to the decreased sizes of gaps between the particles. Therefore, pore forming agents are suggested in preparing the lead dioxide particles based anodic electrodes for ozone generation. Many compound like sodium chloride, sodium sulfate and ammonium oxalate25, 26 can be used as pore forming agents in electrode preparation, and ammonium oxalate was employed because it can be decomposed at 70 ºC, which is beneficial for the electrode preparations.

Note that no improving of the electrodes performance was obtained by adding of ammonium oxalate to electrodes based on lead dioxide particles with diameter range of 15-35 µm (Fig. 5), indicating that the pores in the electrode are larger enough, the effect of the pore forming agent is studied with the electrodes prepared with lead dioxide particles with diameters range of 5-15 µm. When the weight ratio of ammonium oxalate to lead dioxide was as low as 0.67/100, no difference is found between the electrode and the electrode prepared without use of pore forming agent, and a \( \alpha_0 \) of 15.3% was observed after 25 h’s running (Fig. 6 (A)). While when the ratio was as high as 2.00/100, the catalyzing layer would break off from the Nafion-117 film during handling and characterizing, and a \( \alpha_0 \) of 14.2% was observed after 25 h’s running. Therefore, an appropriate amount of the pore forming agent should be taken. The optimum weight ratio of ammonium oxalate to lead dioxide for preparing the electrode is 1.33/100, and the electrode exhibited a \( \alpha_0 \) of 18.0% after 25 h’s running, higher than the \( \alpha_0 \) of 16.9% from the electrodes made with weight ratio of ammonium oxalate to lead dioxide of either 1/100 or 1.67/100. However, no significant difference was discerned on the surfaces of the anodic electrodes with and without use of ammonium oxalate by SEM images, it was then assumed that the pores formed with help of ammonium oxalate were mainly located inside of the electrodes.

Concerning the cell voltages, no significant difference was found when the ratios of ammonium oxalate to lead dioxide are low. The higher cell voltage for the electrode made with higher ratio of 2.00/100 was resulted from the increased numbers of the pores inside the lead dioxide layer and the increased resistivity of the layer.

4 Conclusion

During preparation of the porous anodic electrodes for ozone generation, both the diameters of the lead dioxide particles and the contents of the pore forming agent have great effect on the performance of the electrodes. With decreasing of the diameters of the lead dioxide particles from the range of 55-74 µm to the range of 15-35 µm, the performance of the electrodes improved owing to the increased specific area and the numbers of the catalyzing points in the anodic electrodes. No further improvement was found with further decreasing of the particle diameters to the range of 5-15 µm. However, by employing an appropriate amount of pore forming agent in during the electrode preparations, the performance of the anodic electrode can be improved. The optimized amount of the pore forming agent, i.e. the ratio of ammonium oxalate to lead dioxide in this paper, is 1.33/100.

References