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Preparation of leady oxide for lead–acid battery by cementation reaction

Joon-Ho Shin, Ki-Won Kim *, Hyo-Jun Ahn

Department of Metallurgical and Material Engineering, Advanced Materials Research Institute, Gyeongsang National University, Chinju, 660-701, South Korea

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Abstract

The aim of this research is to prepare leady oxide with high specific area for lead–acid batteries by a new production process. Leady oxide is produced by a cementation reaction in 1.0 wt% HCl solution using a pure aluminum or a magnesium rod as the reductant. Leady oxide prepared in this process is much superior to Barton-pot or ball-mill oxide in terms of physical characteristics. The particle-size distribution of the leady oxide produced by this new process is similar to that of ball-mill oxide. Its acid absorption, however, is much higher because of the different particle shape with respect to ball-mill oxide. Ball-mill oxide is composed of particles of non-uniform plate shape, whereas the new leady oxide is composed of particles of perfect flat (flake) shape. The former oxide has higher specific surface area and greater acid absorption than ball-mill or Barton-pot oxide. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ball mill; Barton pot; Cementation; Leady oxide; Lead–acid battery; Surface area

1. Introduction

Many ingenious ways to make lead oxide have been explored and evaluated, especially with respect to leady oxide for lead–acid battery manufacture, and, as a result, nearly 50 different oxide-manufacturing procedures have been evaluated during the past 95 years. Over the past two decades or so, three basic ways of making battery leady oxide have been established as a proven commercial success, viz., (i) Shimadzu ball mill, (ii) Hardinge cone ball mill, (iii) Barton-pot. Today, nearly all battery leady oxide is made in either a ball mill or a Barton-pot [1–4]. Other processes for the production of lead dust, for example, spraying molten lead under gas pressure or ultrasonics, are not in use at this time. The purely chemical processes, which include the reduction of plumbous salts with zinc, the decomposition of lead carbonate, preparations based on lead amalgam or lead–sodium alloy, as well as lead sulfate and lead dioxide, and the precipitated lead oxyhydrates or hydroxides, have not yet become acceptable for battery use. Lead dust produced by processes that require additional chemicals is less economical than the ball-mill or Barton-pot processes [5].

In the Barton-pot approach to making battery oxide, lead is melted, forced into a spray of droplets, and then oxidized by air at a regulated temperature (330°C to 400°C). Any accumulated bulk molten lead is broken up again into droplets by a revolving paddle that directs the lead against a fixed baffle arrangement attached to the side of the pot. By careful control of the pot temperature, paddle rotation speed, rate of air flow and size of operating load, battery oxide of the desired polymorph and particle-size distribution can be obtained. Some manufacturers, however, pass the Barton-pot oxide through an additional milling stage, which aims to produce finer particles with greater reactivity. The ball-mill process, which is the alternative means for preparing battery oxide, involves tumbling lead balls, cylinders, billets or entire ingots in a rotating steel drum through which a stream of air is passed. The heat generated by friction between the lead pieces is sufficient to start oxide formation. This reaction generates more heat and thus allows the lead particles that are rubbed off by the abrasion to be converted to leady oxide of the required composition. As with the Barton-pot method, the relative amounts of the oxide constituents can be controlled by manipulation of the operational parameters which govern the oxide-making process, namely: mill temperature, mill speed, flow rate and temperature of the air stream, amount of mill charge [1,2,6].

* Corresponding author. Fax: +82-591-795-1745.

The ball-mill drum is usually cooled either with water or by forced air flow and, as a result, the oxidation takes place at a much lower temperature than in a Barton-pot. This difference in operation causes corresponding differences in the relative amounts of free-lead, α -PbO and β -PbO that are produced by the two processes. In general, the conversion of lead to oxide is lower for the ball-mill process, i.e., the material has a higher free-lead content than the Barton-pot variety. The transition temperature at which α -PbO converts to β -PbO is around 480°C; therefore, the latter will be formed in appreciable amounts only when using the Barton-pot method [6]. Moreover, Barton-pot and ball-mill oxides also exhibit dissimilarities in particle size and morphology. The free-lead particles are elongated (or flaky) in ball-mill oxide, but roughly spherical in Barton-pot material. The greater surface area of the free-lead particles in ball-mill material increases the rate of secondary oxidation during storage. Ball-mill oxide provides plates with greater mechanical strength and higher initial electrical capacity. The Barton-pot process produces the larger oxide particles. As a consequence, Barton-pot oxide is less prone to aggregation and, therefore, is easier to handle.

Barton-pot oxide particles are usually round or spherical in shape, and are all less than 60 μm in size with a mean diameter of 3 to 4 μm . By contrast, ball-mill oxide particles are flat and non-uniform in shape, and are smaller in size [7]. Thus, the surface area and acid absorption of ball-mill oxide are much higher than those of Barton-pot oxide. Therefore, the active material utilization of ball-mill oxide is greater than that of Barton-pot oxide. On the other hand, the active-material utilization of Barton-pot and ball-mill oxides is relatively low (around 35–40%) compared with that of the active material in other batteries, e.g., nickel/metal-hydride and lithium-ion. This is due to the regulated particle morphology and limited surface area of the lead oxides. Lam et al. [8] have reported that active-material utilization can be increased to 50% by an improvement in electrical conductivity caused by the addition of a proprietary particulate that consists of glass-flakes coated with a thin (< 5 μm) layer of tin dioxide.

The objective of this study is to prepare a lead oxide that has much superior physical and chemical characteristics. This has been achieved through the oxidation and ball milling of sponge lead that has a dendrite phase prepared by a purely chemical cementation reaction in acidic solution.

2. Experimental

2.1. Preparation of lead oxide

A 1.0-wt.% HCl solution containing Pb^{+2} and Cl^- was heated to 90(\pm 5)°C, and then sponge lead was prepared via a cementation reaction by using a pure aluminum or a

magnesium rod as the reductant. The sponge lead was cleaned with warm distilled water. The cleaned sponge lead was placed in a crucible (diameter 60 mm, height 55 mm), and then subsequently oxidized in air in an electric furnace at 300°C or 400°C. Finally, the oxidized sponge lead was converted in lead oxide by ball milling for 1 h.

2.2. Characterization of lead oxide

The free-lead content which is contained in the lead oxide was measured by differential scanning calorimetry (DSC) and chemical analysis. The DSC measurements were carried out using a DSC2010 (TA Instrument) instrument. Calibration was achieved by placing the cell in the detection area and measuring the enthalpy of fusion of a 10-mg sample of high-purity lead (99.9999%), as follows. The lead oxide sample was put in an aluminum boat, and, then, heated under a stream of argon at 65 ml min^{-1} . The DSC instrument was programmed to heat the sample quickly to 310°C, then to 342°C at 1°C min^{-1} . The experimental conditions for the determination of the free-lead content of lead oxides by the well-known acetic acid method [9] were optimized by conducting tests on pure lead and on lead oxide samples of known free-lead content by DSC. A mixture of 2 ml glacial acetic acid and 20 ml 15 wt.% ammonium acetate water was heated to a temperature of 75°C to 80°C. The heated solution was poured into a flask containing 3 g of the oxide sample and the solution was stirred with gentle heating. The coagulated free-lead residue was washed with warm water, recovered by filtration, dried in a vacuum desiccator at 75°C for 24 h, and weighed. New acid absorption gives an approximate guide to the wetted surface area of the oxide. The test consists of weighing a 50-g sample of the oxide into sulfuric acid a 500 cm^3 flask which is shaken vigorously for 10 min and then stood for 5 min. The clear liquid is decanted to a dry filter. From the filtrate, solution of 25 g is titrated with 1 M KOH. The difference is the degree of absorption. The acid absorption is expressed as the change in weight (mg) of sulfuric acid per gram of oxide. New particle-size distribution measurements of the lead oxide were carried out using a Fritsch Particle Sizer Analysette 22 instrument. Distilled water was used as dispersion solvent. New the surface area of lead oxides was measured using krypton adsorption at the temperature of liquid nitrogen. The samples were outgassed at 150°C overnight, or until the pressure was less than 1.3 mPa. The adsorption measurements were carried out using a Carlo Erba Model 1820 instrument.

3. Results and discussion

3.1. Morphology of sponge lead

The sponge lead was prepared for morphology observation by washing with distilled water, cleaning with ethyl

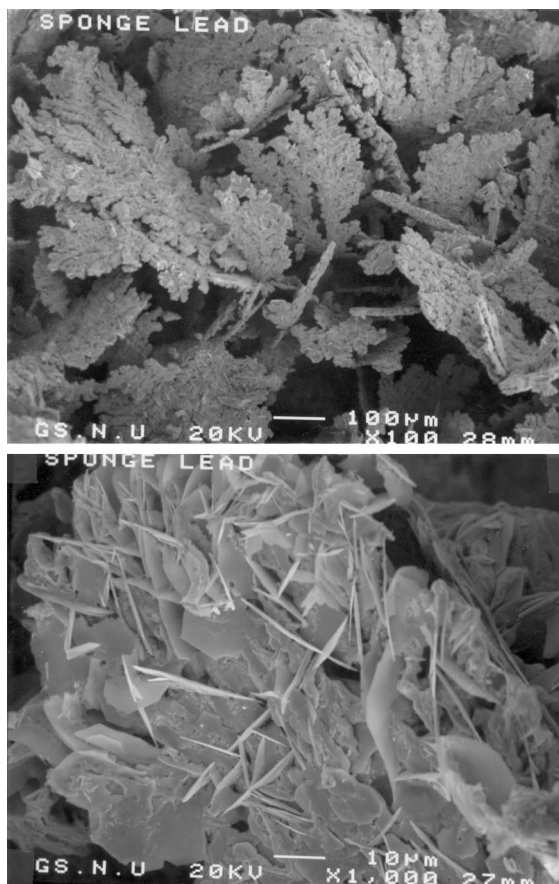


Fig. 1. SEM morphologies of sponge lead samples prepared by cementation. (a) low magnification 100 \times ; (b) high magnification of 1000 \times .

alcohol, and then drying in a vacuum desiccator at 75 $^{\circ}$ C for 24 h. The morphology of leady oxide prepared in a 1.0 wt.% HCl solution is presented in Fig. 1. The macroscopic morphology observed at a low-magnification of 100 \times is shown in Fig. 1(a). The obtained sponge lead consists of a dendritic phase of leaf shape and growth with a preferred orientation. The microscopic morphology for the sponge lead of Fig. 1(a) is shown in Fig. 1(b) at higher magnification (1000 \times). The sponge lead has a geometrical structure which is composed of lead products of plate shape with a thickness around 1 μ m, a length of 10 to 30 μ m, and a width of 10 to 30 μ m. The sponge lead formed at random shows a typical dendritic growth.

3.2. Morphology of leady oxide

Visual observation of the spatial relationships between the component phases in leady oxides is of particular importance in attempts to rationalize measurements of their surface area, particle and pore-size distributions, and chemical and/or electrochemical reactivity. The general trend in recent years has been to use scanning electron microscopy (SEM) for studies of this kind since this technique allows very high magnifications to be achieved

simultaneously with a good focal depth-of-field [10]. Leady oxide powder was prepared for SEM observation by drying a droplet of weak mixture solution which consisted of leady oxide and ethyl alcohol. Gold coating was then carried out with a 10 mA current in an ion-sputtering device instrument for 300 s. The morphology of the coated samples was observed with a JSM-6400 SEM instrument at magnifications of 500 \times and 1000 \times .

Leady oxide oxidized at 400 $^{\circ}$ C for 1 h and pulverized by ball milling for 1 h after preparation of sponge lead in 1.0 wt.% HCl solution is shown in Fig. 2. In general, Barton-pot leady oxide has a spherical shape and ball-mill oxide has a non-uniform platelike shape. Leady oxide prepared in this work has mainly a perfect flat-plate shape of around 3 to 5 μ m in size, as shown in Fig. 2(a). The large particles above approximately 10 μ m are agglomerates of sub-microscopic size particles, but still retained the flat plate shape.

3.3. Cross-section of leady oxide

Leady oxide was prepared for cross-sectional observation by laying a small quantity of the oxide on a flat glass plate, mounting this in a cavity in an epoxy mould,

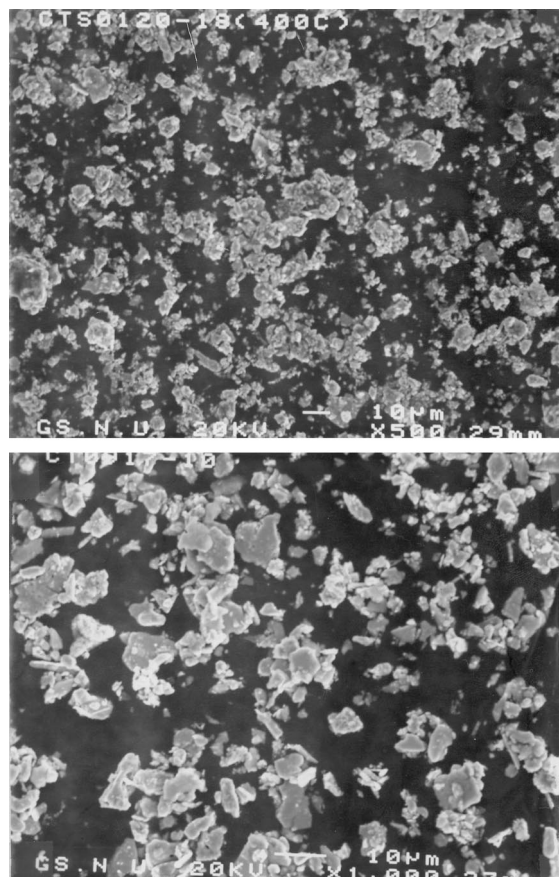


Fig. 2. SEM morphologies of leady oxide samples. (a) low magnification 500 \times ; (b) high magnification 1000 \times .

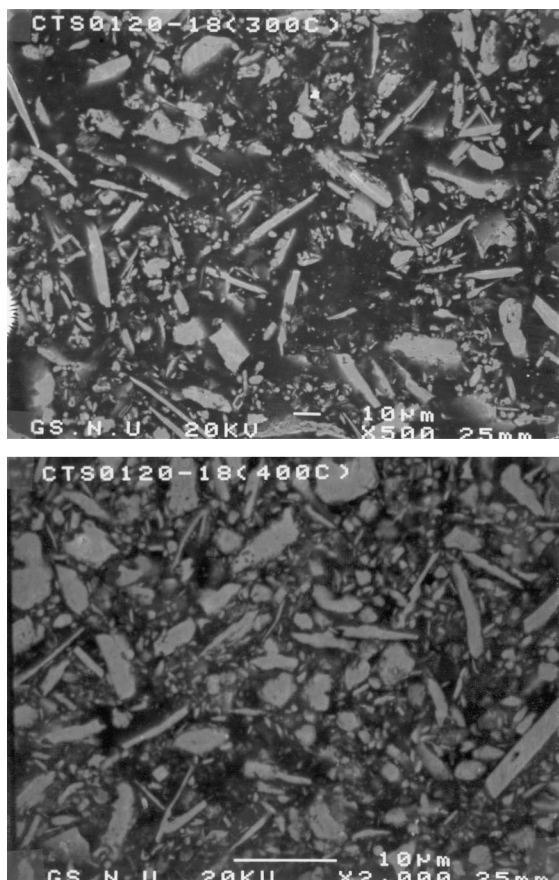


Fig. 3. Cross-sectional SEM micrographs of polished mount of leady oxide samples oxidized at (a) 300°C and (b) 400°C.

allowing it to set, and then polishing the surface with 1200 grade SiC paper, followed by successive polishing with 3 and 1 μm alumina powders. The polished mounts were then observed in a JSM-6400 SEM instrument at a magnification of 500 \times .

The cross-section of leady oxide oxidized at 300 or 400°C for 1 h and pulverized by ball milling for 1 h after preparation of sponge lead in 1.0 wt.% HCl solution is shown in Fig. 3. The polished PbO particles show a different shape compared with the electron micrographs in Fig. 2 at the same magnification. The explanation is as follows. A large 'stick' form shows whether the plate

particle is tilted to one side or set up perpendicularly to the cross-sectional area, while a round form shows that the plate particle is located horizontally. These results correspond with the SEM morphology shown Fig. 2.

3.4. Physical and chemical characteristics of leady oxide

The surface area, mean particle size, acid absorption and free-lead content for Barton-pot, ball mill and leady oxide samples prepared in this work are presented in Table 1. The surface area of leady oxide is highly dependent upon the PbO content, shape and size of the particles. There is a general belief that flat particles are preferable to those of a spherical shape. This is one of the reasons why some manufacturers pass leady oxide through a hammer mill prior to paste-mixing. In general, Barton-pot and ball-mill oxides have mean particle sizes of 3 to 5 μm , but the surface area is somewhat low due to the limited particle shape [1]. The leady oxide powder prepared in this work has a mean particle size of 3.15 and 5.92 μm , but the specific surface area is 3.878 and 5.847 $\text{m}^2 \text{g}^{-1}$, which are approximately twice that of conventional leady oxide powder, as shown in Table 1. It is considered that the surface area is increased markedly because of rather perfect flat plate shape as shown in Fig. 2.

The value of the acid absorption provides an approximate measure of the wettable surface area of the oxide powder. This property essentially depends on the number of particles and their individual surface area [4]. The acid absorption values of Barton-pot and ball-mill oxides are about 140 to 160 and 230 to 250 $\text{mg H}_2\text{SO}_4/\text{g oxide}$. The acid absorption values of the leady oxide powder prepared in this work are 297.9 and 325.4 $\text{mg H}_2\text{SO}_4/\text{g oxide}$. These values are greatly higher than those of conventional leady oxide powder.

In an ideal particle-size distribution, the particles would all be close to the average size, i.e., with very few fine or coarse particles. This is very difficult to achieve. In reality, the particle-size distribution covers a relatively wide spectrum. The oxide powder should not be composed of too great a proportion of very fine particles balanced by very

Table 1

Surface area, particle-size distribution, acid absorption and free-lead content data for Barton-pot and ball-mill oxides and leady oxide prepared in this work

Oxide sample	SSA ^a ($\text{m}^2 \text{g}^{-1}$)	MPS ^b (μm)	AA ^c ($\text{mgH}_2\text{SO}_4/\text{g oxide}$)	Free-lead (wt.%)		Color
				DSC ^d	CA ^e	
300°C oxidation	3.878	5.92	297.9	22.7	27.0	Yellow-green
400°C oxidation	5.847	3.15	325.4	17.2	21.3	Yellow
Barton-pot	0.4–1.8	2–10	140–160	20–30		Yellow
Ball mill	2.4–2.8	2–10	230–250	20–30		Yellow-green

^aSSA = specific surface area.

^bMPS = mean particle size.

^cAA = acid absorption.

^dDSC = differential scanning calorimetry.

^eCA = chemical analysis.

coarse particles to give an average size within specification.

Lead oxide powders prepared in this work show a relatively wide spectrum from sub-micron size to tens of microns ($< 25 \mu\text{m}$), as shown in Fig. 4(a) and (b), but have a few very fine particles and an average size of 3–5 μm . There are few large particles of about 10 μm , but most of them are agglomerated with very fine particles, as shown in Fig. 2(b).

Plots of the variation of the DSC heat flow as function of sample temperature for pure lead and two lead oxide powders are given in Fig. 5(a) to (c). The size of the DSC peak varies directly with the amount of free-lead in the samples. The shape of the DSC peak obtained from pure lead is quite different from that observed for the lead oxide powder. This is due to the different thermal responses of the lead oxide particles. Moreover, the DSC peak profile varies considerably between the different oxides, reflecting differences in the shape, size and degree of encapsulation of the lead particles in these samples. The melting point of the lead varies by less than 0.5% between the two samples however, and this demonstrates the reliability of the DSC method for free-lead determination [10].

The fusion enthalpy and melting point for pure lead are shown in Fig. 5(a). The observed enthalpy of fusion is $-22.82(\pm 0.05) \text{ J g}^{-1}$ and the melting point is $327.6(\pm 0.1)^\circ\text{C}$. The corresponding critically assessed values are $-23.16(\pm 0.02) \text{ J g}^{-1}$ and 327.4°C , respectively.

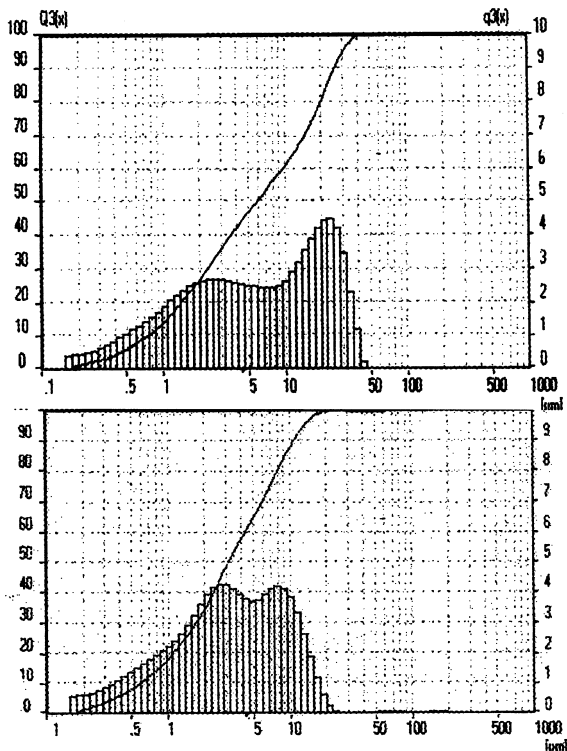


Fig. 4. Particle-size distribution of lead oxide samples oxidized at (a) 300°C and (b) 400°C .

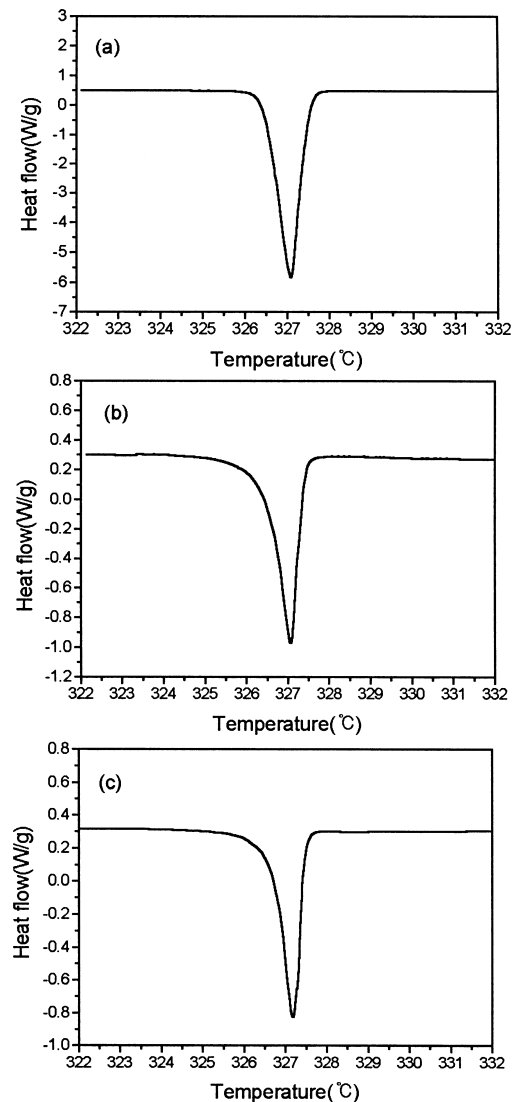


Fig. 5. Variation of heat flow with temperature in vicinity of melting point of lead in samples of (a, top) pure lead 99.9999% Pb, lead oxide oxidized at (b, middle) 400°C and (c, bottom) 300°C .

Comparison of these values with those observed experimentally demonstrates that the DSC calibration is accurate to within $\pm 0.015\%$. The enthalpy value used to calculate the lead contents is $-22.82(\pm 0.05) \text{ J g}^{-1}$. The fusion enthalpy and melting point for the two lead oxide powders are shown in Fig. 5(b,c). The free-lead content, which is calculated from the fusion enthalpy of Fig. 5(a,b,c) is 22.7 and 17.2 wt.%. There is a difference of about 4 to 5 wt.% compared with the value obtained by chemical analysis, as shown in Table 1.

3.5. X-ray diffraction analysis of lead oxide

The X-ray diffraction results for lead oxide are presented in Fig. 6. In general, lead oxide is composed of $\alpha\text{-PbO}$, $\beta\text{-PbO}$ and free-lead. The preferential formation of

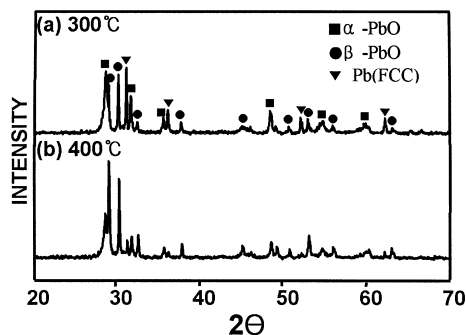


Fig. 6. X-ray diffraction patterns for leady oxide oxidized at (a) 300°C and (b) 400°C.

β -PbO in the Barton-pot is expected since this is the high-temperature polymorph and the Barton-pot process operates at high temperatures. Thus, ball-mill oxide contains significantly less β -PbO than Barton-pot oxide. The phase analysis results reveal significant differences between the chemical compositions of ball-mill and Barton-pot leady oxides. The α -PbO and Pb_3O_4 contents of both types of oxide are about the same [10]. Pb_3O_4 is formed when lead monoxide is heated in a stream of air at around 540°C. Sometimes, it is used in battery manufacture due to its ability to assist in plate formation (about one-third of the oxide effectively exists as PbO_2 before the formation charge). Recently, however, the application of Pb_3O_4 has slowly declined because of its extra cost and handling problems [1].

Leady oxide powder prepared in this work is composed of α -PbO, β -PbO and free-lead, as shown in Fig. 6. The two XRD results clearly demonstrate the large difference in β -PbO and free-lead content of the two leady oxides. After oxidation at 300°C, leady oxide powder is mainly composed of α -PbO and β -PbO. After oxidation at 400°C, the β -PbO content increases.

4. Conclusions

In this study, the physical and chemical characteristics of leady oxide powders prepared by a cementation reaction in HCl aqueous solution using pure aluminum or magnesium as a reducing agent have been investigated. The results show that the powders have better physical and chemical characteristics than conventional Barton-pot or ball-mill leady oxide. The powders have a flat-plate shape and a dendritic structure. The specific surface area and acid absorption capability, which is critical for the performance of the lead acid battery, are superior to those of conventional leady oxide powders. Moreover, it was found that these properties can be easily controlled during subsequent ball milling and oxidation. The values of the major characteristics obtained in this work are summarised as follows: mean particle size: 3–5 μm ; acid absorption about 300 mg H_2SO_4/g oxide or higher; specific surface area: 4 to 6 $\text{m}^2 \text{g}^{-1}$.

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