



Lead paste recycling based on conversion into battery grade oxides. Electrochemical tests and industrial production of new batteries[☆]

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HIGHLIGHTS

- Recycling of lead acid batteries based on hydrometallurgical processes.
- Procedure ensuring low environmental impact.
- Treatments requiring limited energy consumption.
- Methods involving safe or low hazard industrial treatments.
- Processes suitable for application to medium-sized battery production facilities.

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ABSTRACT

We present the preparation and characterization of pure lead monoxide obtained through recycling of the lead paste recovered from exhausted lead acid batteries. The recycling is based on a hydrometallurgical procedure reported in a STC Patent, that includes simple chemical operations (desulphurisation, leaching, precipitation, filtration) and a final thermal conversion. Materials obtained by treatment at 600 °C consist predominantly of β -PbO. The electrochemical behaviour of Positive Active Mass (PAM) prepared from different materials (or mixtures) is then investigated and compared. An optimized oxide material, obtained by prolonged (8 h) thermal treatment at 600 °C, consists of pure β -PbO and appears suitable for preparation of battery elements, alone or in mixture with a small fraction (10%–30%) of traditional industrial lead oxide. The resulting battery performances are similar to those obtained from pure lead oxide. In comparison with traditional recycling processes, the proposed method guarantees lower energy consumption, limited environmental impact and reduced operating risk for industry workers.

1. Introduction

Power storage is a subject of increasing interest, boosted by the advent of inconstant renewable energy sources, interconnected grids and electric vehicles [1–4]. Most of the current research is focused on development of high energy density systems like Li-Ion batteries [4], that pose still important challenges in terms of safety and long term reliability [5,6]. The Lead-Acid Battery (LAB), despite the intrinsic limit of low specific energy (Wh kg^{-1}), remains a battle horse in many applications [7] due to its great advantages: high power, reliable performances, low self-discharge rates, low cost, ease of production and

recycling. The LAB still occupies an important market position in automobile applications [7] and there are many studies on the possible improvements in production and recycling of its materials, especially the toxic active species (lead and lead oxide/sulphate).

The secondary lead industry is today the main source of raw material for LABs production. The traditional recycling technology is based on pyrometallurgical processes, and produces considerable amounts of wastes: for each ton of metallic lead produced, 100–350 kg of slag are generated that contain approximately 5% of lead compounds [8,9] and a minor part of trace elements [10,11]. Moreover, these processes are energy consuming and may produce large amounts of SO_x and lead dust

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[8,12], or require costly additional treatments.

The lead materials for batteries produced in industrial plants (Barton-pot or ball-mill processes) consist invariably of mixtures of metal lead (Pb) and lead monoxide (PbO) called “leady oxide” [7]. Composition and physico-chemical properties of these materials depend on details of the preparation procedure, e.g. the operating temperature of the plants. This variability will affect the treatment required for full activation and the device performances [13,14]. Concerning the critical positive plates, certain authors have proposed the use of pure lead monoxide [15], and the use of additives to increase their performances [16,17]. Furthermore, β -PbO showed to have the same or better behaviour compared to leady oxide despite showing apparently lower features, e.g. low acid absorption [18].

In this context, we have investigated a possible application of pure lead monoxide such as β -PbO, in the preparation of Positive Active Mass (PAM) used in lead-acid batteries. The scope is the conversion of exhausted LAB paste into pure β -PbO suitable for the preparation of new batteries, and the verification of the procedure at an industrial scale: about 1000 batteries with a nominal capacity of 70 Ah were produced and representative samples were tested. The recycling consists of a series of simple chemical steps (desulphurisation, leaching, precipitation, filtration) according to an STC Patent [19]. A final thermal treatment converts the lead material into pure lead oxide, mostly β -PbO. This technology (from now on “the STC method”) has important advantages in comparison with traditional processes based on pyrometallurgical steps: less hazardous synthesis, efficient use of energy and limited production of wastes, in harmony with the green chemistry guidelines [20]. It is shown that the lead monoxide resulting from this treatment may directly be used, alone or mixed with a small fraction of ordinary leady oxide, in the preparation of positive plates, the most important and critical for battery performances and service life.

2. Experimental

2.1. Chemicals. Industrial preparation of leady oxide

All reagents used for laboratory tests and low scale industrial plant production were Sigma Aldrich, Analytical Grade. S.I.A. S.p.A. (henceforth SIA) provided the samples of Pb-Ca alloy grids for the electrochemical experiments. Leady oxide was produced at SIA through a conventional ball-mill apparatus (model CAM MOP8). The leady oxide material was prepared starting from ingots of pure soft lead (Pb 99.97%). The preparation was made with standard process parameters and warm mill. The freshly prepared material contained $30\% \pm 2\%$ of free Pb, estimated by a method involving dissolution of lead oxide in acetic acid, and a complexometric titration using EDTA [21].

2.2. The recycling process

The innovative STC method followed procedures reported in an STC Patent [19] and summarized in the synthetic flow sheet in Fig. 1. The main steps were the following: i) *desulphurisation* of lead paste in an aqueous carbonate solution; ii) *calcination* of desulphurised lead paste at about 600 °C, producing low purity lead monoxide, followed by grinding; iii) *leaching* of the impure lead monoxide by an aqueous solution of acetic acid followed by filtration in order to separate solid residues; iv) *precipitation* of lead hydrate by treatment with hydroxide, followed by filtration of the precipitate; v) eventually, after drying, a final *thermal conversion*, necessary to remove residual carbonate resulting from the hydrometallurgical processes. Depending on temperature and duration of the last thermal treatment, various products were obtained (Table 1). During laboratory experiments, an additional treatment was tested: the partial reduction of pure lead monoxide. Using a reducing agent stream, lead oxide was partially reduced to metallic Pb. For the sake of brevity, we report and discuss data of only a

few samples. The code numbers (Table 1) are those used during the experiments.

Preliminary preparation runs were performed at laboratory scale to produce small amounts of products (typically 1 Kg) for characterization; synthesis parameters were varied and composition, structure and electrochemical properties of the resulting materials were tested. After identification of the procedure leading to the best electrochemical performances, a relatively large amount (about 10 tons) of recycled oxide was prepared accordingly. The preparation, intended for 1000 batteries, was made in an STC's pre-industrial plant installed in a lead recycling factory (MECA S.p.A., Italy).

2.3. Materials characterization

SEM images and EDS analyses were obtained with a FEI Quanta 200 FEG ESEM instrument, equipped with a field emission gun, operating at an accelerating voltage variable in the range of 20–30 kV. X-Ray Diffraction (XRD) patterns were obtained using a Philips X-PERT PW3710 diffractometer with a Bragg-Brentano geometry, employing a $\text{CuK}\alpha$ source (40 kV, 30 mA). The relative phase abundances were estimated by Rietveld analysis, using the MAUD software [22].

For ICP analyses, 4 g samples were grinded using a RETSCH MM200 ball mill; after treatment with concentrated acids (HNO_3 , HCl, HF), the material was mineralized in a MLS 1200 MEGA Milestone microwave oven. The samples were then analyzed with a ICP Emission Spectrometer Thermo Scientific iCAP 6000 DUO, equipped with: a CID (Charge Injection Device) solid-state detector, which allows the simultaneous reading of wavelengths in the range of 166–847 nm; a DUAL VIEW device (axial view + radial view); an RF generator with software-controlled power-adjustable at 4 values: 750, 950, 1150, 1350 W. Calibration solutions were prepared from Carlo Erba mono-elemental standard solutions ($1000 \mu\text{g ml}^{-1}$). Five solutions with concentrations of 0, 1, 3, 6 e $10 \mu\text{g ml}^{-1}$ (ppm) for each element (six solutions of 0, 4, 15, 30, 50, $80 \mu\text{g ml}^{-1}$ for Sulfur) were used for calibration curves. The same reagents used for samples mineralization were added in order to minimize the matrix effect. When appropriate, samples were diluted prior to determination. Results are reported in Table 2. The electrical resistivity of oxide mixtures was measured at room temperature. Pellet samples were prepared with a Perkin Elmer hydraulic press (applied pressure ca 10000 kg cm^{-2}). Measurements were performed with the four-probe technique using a Keithley 220 programmable current source and a Keithley 195A digital multimeter.

2.4. Electrochemical laboratory measurements

Two series of experiments consisted in cycling the materials described in Table 1.

In a first series, deep cycling (extensive charge-and-discharge) was imposed by two common potentiostats-galvanostats, Autolab PGSTAT 302N and Biologic SP300. During potentiostatic control the reference electrode was a saturated mercurous sulfate electrode $\text{Hg}/\text{Hg}_2\text{SO}_4$ ($E = 0.640$ vs NHE), and all potentials reported in the following are accordingly referred. We shall indicate henceforth with I_n the current that allows discharging a battery element in n hours [23]. Charging of positive elements was performed using limits of current ($I \leq I_s$) and potential ($E \leq 1.37$ V) to avoid local depletion of reagents and onset of electrolyte discharge, respectively. The discharge was obtained extracting current at a constant rate around I_{20} , with the limit $E_{\min} = 0.85$ V at which the total charge was recorded. Charging of negative elements was obtained in a similar way with similar/symmetrical limits ($I \leq I_s$, $E \geq -1.40$ V). The discharge was obtained extracting current at a constant rate around I_{20} , with the limit $E_{\max} = -0.95$ V at which the total charge was recorded.

Additional experiments - consisting of prolonged cycling with total re-charge and partial discharge - were performed in a test cell with two negative electrodes coupled on both faces of a positive electrode. In this

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