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Structural and electrochemical investigations of the electrodes obtained by recycling of lead acid batteries

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ABSTRACT

The lead acid batteries are widely used in automobile and provide spent electrodes composed of $PbO_2/PbSO_4$ and $Pb/PbSO_4$. Today, batteries are treated and recycled using the pyrometallurgical and hydrometallurgical techniques. However, these techniques have some important disadvantages: i) the small lead recovery rate (due to the rapid oxidation of the electrolytic Pb powder in the atmosphere); ii) the important amount of energy and time spent to convert oxides and sulfates into metal, which is subsequently reconverted to oxides; iii) the harmful emissions and their negative environmental impact.

In this work, we propose a method of recycling batteries by a melt quenching route in order to improve the present practice. Is the melt quenching method a new eco-innovative approach for lead recycling of spent lead acid batteries? We think that yes, since economically is more favorable (in terms of low production cost, energy and time saving) and environmentally more friendly.

Focus was addressed on both the structural characterization (by X-ray diffraction) of the samples obtained by melt quenching of spent electrodes proceeded from car batteries, as well as on their electrochemical and electrical characterization by cyclic voltammetry and electrochemical impedance spectroscopy as potential raw materials in obtaining new and more performing battery electrodes. Our results suggest that the increase of Pb concentration in the recycled electrodes implies the formation of a regulated lead sulfate layer in the oxidation process and the dissolving of $PbSO_4$ crystals followed by the hydrogen evolutions in reduction process of lead ions.

1. Introduction

1.1. Background

Recently, the energy source industry has been under intensive development. The electrochemical energy sources required for household, engineering, aerospace, medicine, and special equipment are being introduced into various fields of human activities on a large scale [1–3]. Numerous studies related to batteries, in special lithium batteries, are focused on the increase of the specific capacity, through search and creation of novel electrochemical systems for both primary and secondary batteries [4–6].

For a spent battery, the positive electrode and negative electrode as active materials are composed of $PbO_2/PbSO_4$ and $Pb/PbSO_4$. The spent batteries find themselves at recycling facility to undergo pyrometallurgical and hydrometallurgical methods [7–12].

The main problems related to the recycling of electrode materials from spent lead-acid batteries [13–21] can be summarized as follows:

- Separate recycling of anodic ($Pb/PbSO_4$) and cathodic ($PbO_2/PbSO_4$) electrodes is necessary. The metal electrode is recycled mostly by using pyro-metallurgic and hydro-electro-metallurgic methods.
- Despite the fact that pyro-metallurgic methods cover about 90% of the recycling technology, they are severally criticized especially due to: i) emissions of SO_2 and SO_3 in atmosphere as result of $PbSO_4$ decomposition above 1000 °C; ii) important energy and time spent to convert oxides and sulfates into metal which is subsequently reconverted to oxides; iii) low lead recovery rate because the electrolytic Pb powder oxidizes rapidly in the atmosphere and is volatile [16–18].
- The disadvantages of the hydro-electro-metallurgic route consisting of: i) a low solubility of lead compounds in solvents and ii) an ineffective desulfurization in aqueous solution [19,20].

The electrochemical behavior of lead electrodes in aqueous sulfuric acid has, however, been researched by many people using CV. For example, Yamamoto et al. [21] have investigated the electrochemical

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behavior of pure lead electrode in aqueous sulfuric acid solution, and they have studied almost all the peaks of the lead electrodes in the whole potential region of the positive and negative electrodes for a lead-acid cell in aqueous sulfuric acid solutions. They found that several redox peaks appeared concerning the active materials of lead electrode: the oxidation peaks are $Pb \rightarrow PbSO_4$, $PbO \rightarrow \alpha\text{-}PbO_2$, $PbSO_4 \rightarrow \beta\text{-}PbO_2$, and $H_2O \rightarrow O_2$; and the reduction peaks are $PbO_2 \rightarrow PbSO_4$, $PbO \rightarrow Pb$, and $PbSO_4 \rightarrow Pb$ [22].

Pavlov et al. [23] suggested that the oxidation of $PbSO_4$ to PbO_2 occurs when the electrode potential is sufficiently high to allow the oxidation of $PbSO_4$. The $PbSO_4$ crystals are dissolved as Pb^{2+} and SO_4^{2-} into the solution in the pores of the lead anodic film. The Pb^{2+} ions diffuse to the nearest reaction site where they are oxidized to Pb^{4+} ions. As the Pb^{4+} ions are thermodynamically unstable in solution, they combine with water to form $Pb(OH)_4$ which then is dehydrated to form $PbO(OH)_2$, and finally converted to form PbO_2 [24].

The objective of this work is to seek for a new and more efficient method for recycling the active anodic and cathodic electrodes directly from spent lead-acid bateries. Such a new recycling method needs to fulfill the requirements of an eco-innovative technology concerning both economic aspects (reduction of production costs, improving of energy efficiency) as well as environmental ones (the environmental friendly character). On the other hand, focus will be addressed electrochemical and electrical characterization by cyclic voltammetry and electrochemical impedance spectroscopy of the recycled samples in view obtaining of new and more performing electrodes for rechargeable batteries.

2. Experimental procedure

Glasses and vitroceramics were prepared using as starting materials active electrodes of disassembled car batteries mixed in suitable proportions. The mixtures presented in the Table 1 were melted in sintered corundum crucibles at 900 °C, in an electric furnace. After 10 min the molten material was quenched at room temperature by pouring it onto a stainless-steel plate.

X-ray diffraction (XRD) data were collected from the obtained samples using a XRD-6000 Shimadzu diffractometer with a graphite monochromator for the Cu-Kα radiation (λ = 1.54 Å) at room temperature.

The electrochemical properties were characterized by cyclic voltammetry measurements using a VERSASTAT3 potentiostat and the V3Studio software. Discs of obtained samples were used as working electrode, platinum as counter electrode, calomel as reference electrode (SCE) and sulfate acid solution as liquid electrolyte. All experiments were conducted in a solution of H_2SO_4 with the concentration of 38%, in agreement with the electrolyte solution used in the car batteries.

The impedance spectra were obtained over the frequency range between 0.1 and 10^6 Hz by using a small sinusoidal excitation signal (10 mV amplitude). Data fitting was carried out using ZSimpWin software (Princeton Applied Research).

Table 1
Mass ratios of the active anodic and cathodic electrodes originated by spent lead-acid bateries using as starting materials for recycled electrodes.

PbO_2:Pb mass ratio (mass %)	PbO_2 mass (g)	Pb mass (g)
9:1	1.8121	0.1879
8:2	1.6216	0.3784
7:3	1.4286	0.57134
6:4	1.2329	0.7671
5:5	1.0346	0.9654
4:6	0.8334	1.16656
3:7	0.6294	1.3706
2:8	0.4226	1.5774
1:9	0.2128	1.7872

3. Results and discussion

3.1. XRD investigations

A typical composition of a spent paste of the lead acid battery is lead sulfate (nearly 60%), lead (IV) dioxide (nearly 28%), lead (II) oxide (nearly 9%), metallic lead (nearly 3%) and a small but significant concentration of impurities such as iron, antimony, tin and barium [25,26]. Environmentally sensitive recovery of spent lead-acid battery pastes has attracted considerable interest from researchers [26–28].

The prepared samples were photographed using a FUJIFILM camera (Fig. 1). Figs. 2 and 3 show the XRD diffractograms of the synthesized samples in the anode:cathode system with the recycled Pb, PbO_2, $Pb:PbO_2$ = 1:9; 2:8; 3:7; 4:6; 5:5; 6:4; 7:3; 8:2; 9:1 compositions. It can be seen that for all samples there are two solid phases, one of a metallic nature and the second of a vitroceramic nature. Thus, the diffractograms consist of an overlap of some sharp diffraction peaks characteristic of the metallic phase and the two broad diffraction halos characteristic of the glassy structure. In order to determine the crystalline phases present in the samples, the Bragg peaks from the XRD diffractograms shown in Fig. 2 were indexed. A comparison of the diffractograms obtained for the prepared samples, the cathode (PbO_2) and anode (Pb) is presented in Fig. 3. This analysis suggests that the crystalline phases present in the studied samples are PbO, PbO_2, $PbSO_3$ and $PbO_{1.44}$, respectively.

For samples with $Pb:PbO_2$ = 1:9 and 2:8, the intensity of the diffraction peaks corresponding to the PbO and $PbSO_3$ crystalline phases is more intense than that of those of other crystalline phases.

In the case of the samples with $Pb:PbO_2$ = 3:7, 4:6 and 5:5 one can observe the intense diffraction peaks located at about 28.2^0 (attributed to the $PbO_{1.44}$ crystalline phase), 28.7^0 (corresponding to orthorhombic PbO_2 crystalline phase) and 29.6^0 (derived from an unknown crystalline phase).

The analysis of the XRD patterns is presented in Fig. 3 and shows the presence of the metallic lead crystalline phase. The metallic Pb phase can be identified from its intense lines situated at about ~31.5° (111 Miller index), 36.7° (200 Miller index), 52.7° (220 Miller index), 62.8° (311 Miller index) and 65.7° (222 Miller index), corresponding to the face centered cubic system. Then, for the samples with $Pb:PbO_2$ = 1:1 (5:5), 2:8 and 4:6, the intensities of the diffraction peaks situated at about 30.5° are intensified. In Fig. 3b, the diffraction peak located at about 36.7° corresponding to the crystal surface of metallic Pb phase (200 Miller index) is more sharp and strong for the sample with $Pb:PbO_2$ = 1:9 compared to their analogues.

In conclusion, the presence of two separate phases, a metallic lead crystalline phase and a vitroceramic phase, can be observed for all samples. XRD patterns permit the identification of the metallic lead phase and of the vitroceramic one with different oxide crystalline phases of the lead ions. The fact that a separation of the two mentioned phases (the metallic lead phase and the vitroceramic one) occurs, offers two major advantages of this synthesis method, namely: i) the recovery of the metallic lead via an environmental friendly procedure and ii) the gathering of the impurities from the active electrodes of the batteries in the vitroceramic phase. Note that the recycling of lead acid batteries by melt-quenching is a method implying a separation of the components from battery electrodes by a lead recovery process of lower energy consumption and the absence of toxic residuals by integration of these ones in a vitroceramic phase.

This method, applicable in recycling the secondary batteries, is equivalently in terms of low cost of production, energy and time saving with those used currently. We propose this new method of recycling the active electrodes from spent lead-acid bateries having as result some new materials containing a metallic lead phase and