

Spray pyrolysis as a method for preparing PbO coatings amenable to use in lead-acid batteries

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Abstract

Lead(II) oxide thin films were prepared by spray pyrolysis of aqueous solutions of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and deposited onto a lead substrate. A homogeneous coating was obtained at 260 °C that consisted of well-crystallized α -PbO. Following soaking and curing, the oxide became a phase mixture the main component of which was PbO-PbSO₄. The electroformation of the cured plate produces dense agglomerates of small β -PbO₂ particles accompanied by unreacted α -PbO. Preliminary electrochemical tests of the cell revealed a progressive decrease in polarization during charging in the first few cycles probably associated to improved adherence of active particles to the substrate. The cell was found to maintain a discharge capacity of ca. 100 A h/kg (40% of the theoretical value) upon extensive cycling. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lead-acid technology currently remains the most reliable, safe and affordable power source. None of the new developed battery types (e.g. Li-ion and Ni-MH batteries) has so far reached the commercial success of the lead-acid battery. This is partly a result of the continuous development and evolution of the lead-acid battery, which has led to major improvements in performance [1]. The substantial growth in new demands (e.g. telecommunication networks, electronics, computers) has raised new challenges for lead-acid batteries. Such is the case with uninterrupted power supplies (UPS), where lead-acid batteries dominate the world market. The main requirements for these batteries are high power and discharge rates, a long life and, increasingly, a substantial weight reduction [2]. One approach to increasing high-rate positive plate performance involves increasing the total surface area [3] by replacing conventional plates with thinner ones. In addition to delivering the electrical energy required to satisfy local demands (frequency and duration of the current interruption), the use of thin plates will also result in reductions in size and weight of the battery.

The layer thickness of active paste applied to the lead substrate is one of the cell variables to be reduced in size. A number of methods are available for preparing thin film materials such as oxidation of an evaporated metal film, reactive and non-reactive sputtering techniques and chemical vapor deposition. In this context, the spray pyrolysis method is a simple, inexpensive alternative with the added advantage that it allows the preparation of large films [4]. Moreover, the simplicity of the equipment required and the high productivity of this method on a large scale provide an attractive way of obtaining thin film materials for industrial applications. In spite of its simplicity, the spray pyrolysis method possesses a number of advantages [5]. Thus, dope films are easily prepared; also, unlike alternative techniques, spray pyrolysis requires no high quality targets and/or substrates, nor the use of vacuum at any stage; film thickness can be controlled by changing the spray parameters; it can be used over a wide temperature range (100–600 °C); it provides well-compacted films.

The purpose of this work was to assess the usefulness of spray pyrolysis for obtaining lead-oxide thin films and their potential as positive active masses for lead-acid batteries. In this paper, we report on the characterization of the films by using two different techniques, viz. X-ray diffraction (XRD) and scanning electron microscopy (SEM), and the results of preliminary electrochemical tests conducted to evaluate cell performance.

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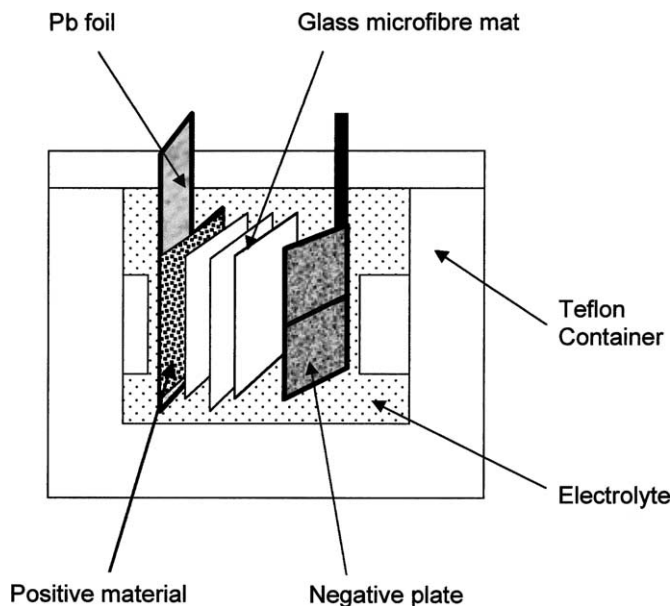


Fig. 1. Scheme of the cell used in the electrochemical experiments.

2. Experimental

Positive plates were prepared by using a precursor method by which a lead(II) solution was deposited onto lead foils 0.35 mm in thickness using a spray pyrolysis technique described elsewhere [6]. Compressed air from the atmosphere was used to atomize a solution containing the precursor compounds through a spray nozzle over the heated substrate. The precursor was pyrolyzed on the heated substrate, equipped with thermocouples and heating elements, the latter being governed by a temperature controller. The substrate was moved forward and backward at a fixed frequency by an electronically controlled step motor. An aqueous solution of 0.5 M $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ was used as precursor. An air stream at 140 l h^{-1} , measured under atmospheric conditions, was used to pump and atomize the solution. In order to obtain films of a large, uniform area (20 cm long \times 2 cm wide), the aqueous solution was kept at 80°C throughout the experiment in order to avoid a drastic bubbling of water. Lead sheets were kept at 150°C . The conversion into lead oxide, PbO , was accomplished by heating the films at 260°C for 24 h. A coating of 3 mg/cm^2 was obtained under these conditions.

Plates were prepared following a two-step procedure. The first involved immersing the films in sulfuric acid solutions to obtain basic lead sulfates. The second step was a curing process in which the films were kept at a temperature of 45°C and a relative humidity above 90%. Each step took 2 days to complete. Finally, the plates were dried at 60°C in the air for 1 day.

Films were cut into 1 cm^2 pieces for structural characterization. XRD patterns were recorded on a Siemens D5000 X-ray diffractometer, using $\text{Cu K}\alpha$ radiation and a graphite

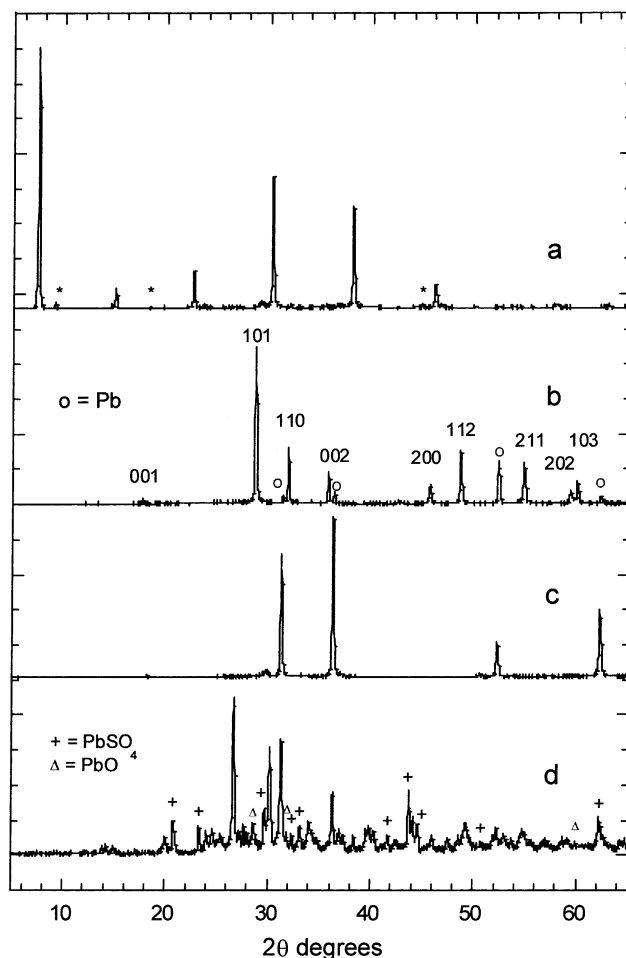


Fig. 2. XRD patterns for deposited lead acetate (a); α - PbO obtained after a post-deposition heat treatment at 260°C for 24 h (b); lead substrate following heat treatment at 260°C for 24 h (c); plate after soaking and curing (d).

monochromator. SEM images were obtained on a Jeol JMS 6400 microscope.

Electrochemical experiments were carried out using two electrodes Teflon cells (Fig. 1). The electrolyte used was a 5 M H_2SO_4 solution. The electrodes were cut into L-shaped pieces where a square surface of $10\text{ mm} \times 10\text{ mm}$ was coated with the active material, the uncovered surface being used to make the electric connections. Negative plate and glass fiber furnished by Exide Ltd. (Spain) were used as anode and separator, respectively. Unless otherwise noted, a 0.5 mA/cm^2 current density, controlled via a MacPile potentiostat-galvanostat, was applied to the cells for electrochemical measurements.

3. Results and discussion

Thick films of lead acetate compounds were obtained by deposition of an aqueous solution of $0.5\text{ M Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ onto a lead sheet at $150\text{ }^\circ\text{C}$. The XRD pattern for the film thus formed is shown in Fig. 2a. The main phase identified was a lead acetate oxide hydrate, $((\text{CH}_3\text{COO})_2\text{Pb})_3 \cdot \text{PbO} \cdot \text{H}_2\text{O}$ (JCPDS number 18-1739). Anhydrous lead acetate, $(\text{CH}_3\text{COO})_2\text{Pb}$ (JCPDS number 18-1738) was also found, as minor component, the peaks for which are marked with asterisk. On heating at $260\text{ }^\circ\text{C}$, the salts decomposed to

$\alpha\text{-PbO}$ (litharge) strongly oriented along the $[1\ 0\ 1]$ direction (see Fig. 2b). In addition to this phase, the XRD pattern also exhibits peaks associated to metal lead the origin of which could be loosening of the coating in some areas of the film during preparation for X-ray characterization. In fact, scanning electron micrographs revealed a uniform coating about $50\text{ }\mu\text{m}$ thick (Fig. 3a). Oxidation of the lead substrate during the heating process can be discarded as the origin of the PbO coating. Under the same heating conditions, a lead sheet failed to react with oxygen to yield PbO , at least on the detection scale of conventional X-ray powder diffraction (see Fig. 2c).

The positive plate was prepared by soaking and curing. The soaking process was restricted by the dimensions of the sheets ($100\text{ mm} \times 20\text{ mm}$) and the mass ratio between the active material and the Pb substrate. This entailed the use of highly diluted sulfuric acid solutions, which made it difficult to accurately reach the optimum sulfuric acid/lead oxide ratio to obtain tribasic (3BS) or tetrabasic (4BS) lead sulfates [7]. In fact, the 3BS phase was obtained as a minor component and only after very long soaking periods. Normally, the main components formed under the aforementioned conditions were $\text{PbO} \cdot \text{PbSO}_4$ (1BS) and PbSO_4 phases. Fig. 2d shows the X-ray pattern obtained after the curing process, which reflects the predominance of the 1BS phase. Also, the main peak for $\alpha\text{-PbO}$ is still present.

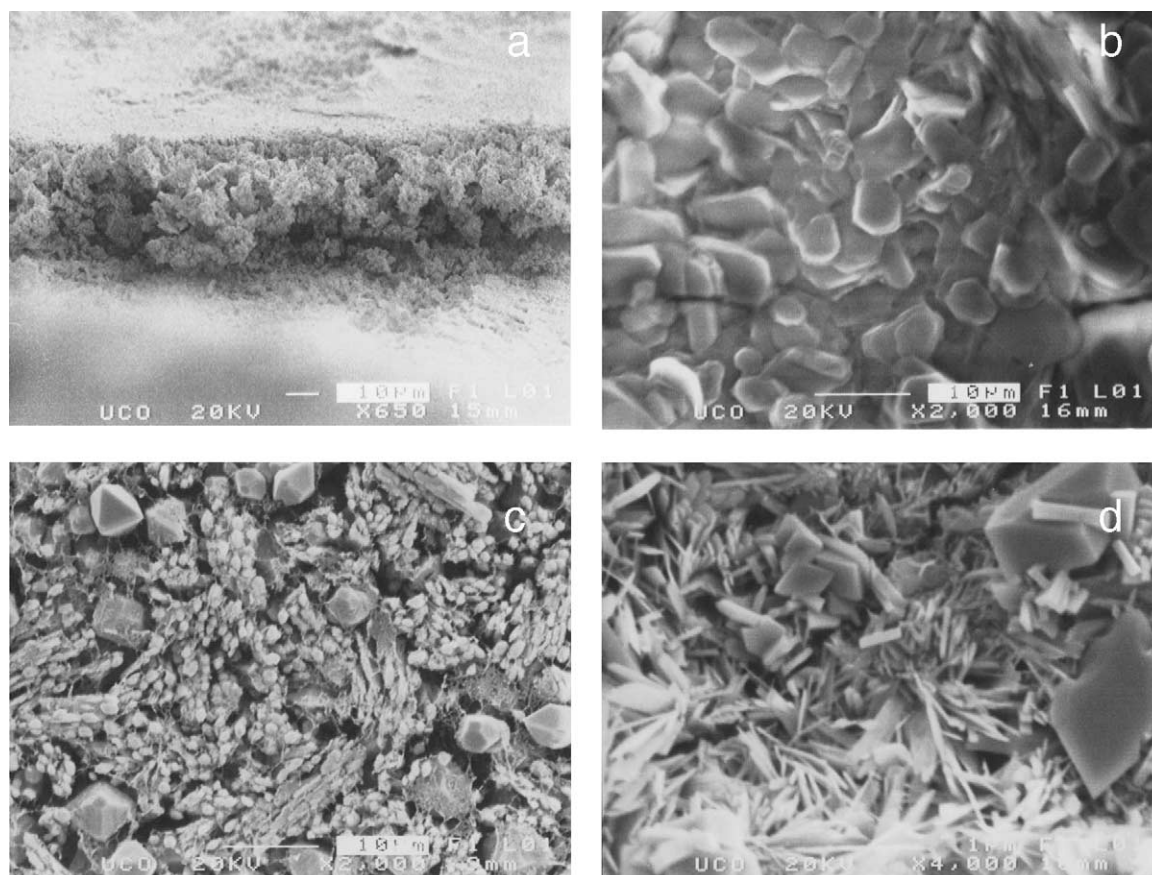


Fig. 3. SEM images of the precursor deposited at $150\text{ }^\circ\text{C}$, before (b) and after heating at $260\text{ }^\circ\text{C}$ (a) and (c); plate after soaking and curing (d).

The morphological evolution of the coating at the different stages is shown in Fig. 3. A completely uniform coating over the substrate was observed in the micrographs of the lead acetate films. In spite of the high temperature of the substrate during spray deposition, 150 °C, there was no indication that drastic bubbling occurred. Under these conditions, a compact film was obtained where the lead acetate compounds crystallized as aggregates of *pseudo* hexagonal particles 3–10 μm in size (Fig. 3b).

The transformation into lead(II) oxide does not affect the homogeneity of the coating. A significant change in particle morphology is observed, however. Most particles adopt a round prismatic form and a size smaller than 1 μm (Fig. 3c). Only a few particles, 5–10 μm in size, adopt a well-defined octahedral shape. The film appears to be less compact and to contain abundant small pores. The latter feature helps increase the surface area and hence the reactivity of the oxide towards H_2SO_4 . In fact, the soaking and curing processes result in a high conversion into lead sulfates. The new surface film (Fig. 3d) consists of an intergrowth of particle aggregates of $\text{PbO}\cdot\text{PbSO}_4$ (needle shape) and PbSO_4 (polyhedral shape) phases with open paths between them.

Various tests were performed in order to find the best conditions for the electrochemical formation of the positive active material (PAM). Low current densities and an invariant current regime were avoided. These conditions lead to the formation of a passive film of PbSO_4 over the substrate. Formation of the cured plate was accomplished by using a long step pulsed-current technique at 25 °C for 4 h at a current density of 0.22 mA/mg (1 C A) that was applied over 30 min intervals. A relaxation time of 10 s was inserted between current steps. The final current used during the electrochemical formation process was over of 400% higher than the calculated theoretical value.

The XRD pattern for the PAM revealed the formation of $\beta\text{-PbO}_2$ as the dominant phase (Fig. 4a). In addition to reflections for the lead substrate, a peak at 28.65° 2θ was observed that could be assigned to either $\alpha\text{-PbO}$ or $\alpha\text{-PbO}_2$. However, the shoulder at 48.66° 2θ on the right of the peak suggests the presence of $\alpha\text{-PbO}$, the origin of which could be the large *pseudo* octahedral particles that remain unoxidized after the PAM is formed. The plate formed consists of a dense agglomerate of small $\beta\text{-PbO}_2$ particles and some well-crystallized particles that protrude over them (Fig. 5a). The presence of $\alpha\text{-PbO}$ particles, also confirmed by SEM images of Fig. 5b, can be explained in the light of various models. Thus, during the electroformation, the dissolution and further oxidation of the lead sulfates can leave some PbO and PbSO_4 particles (probably those of greater size) in isolated places, as can be seen in the SEM micrographs (Fig. 5c). The PbO_2 phase occurs as conglomerates of small rounded particles in minimal contact with the larger octahedral ($\alpha\text{-PbO}$) and square (PbSO_4) particles [8] (in fact, the XRD pattern, Fig. 4a exhibits weak reflections that can be assigned to the latter phase). This results in a loss of

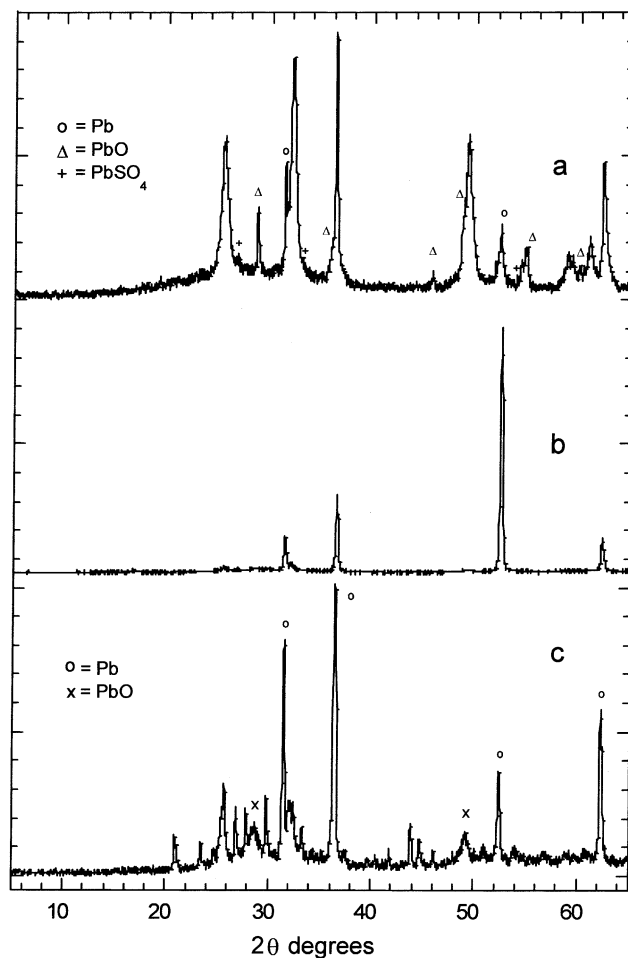


Fig. 4. XRD patterns of the plate formed (a); uncoated lead sheet after successive cycling (fifth cycle) (b).

connectivity between the particles themselves and also with the substrate, thus increasing the resistivity and hindering their oxidation and conversion into PbO_2 . On the other hand, the thermodynamic instability of some PbO_2 particles may be increased by the potential decrease in the cell after the electroformation process has finished, and by the high Pb substrate/PAM ratio [9]. One other possibility is anodic oxidation at the metal interface and subsequent formation of a $\alpha\text{-PbO}$ layer. However, no passivating PbO layer was detected on uncoated faces of the Pb substrate.

Fig. 6a shows the cell voltage after a variable number of cycles, recorded under the following conditions: a cell cut-off voltage of 1.85 V and an overcharge 110% of the previous discharge capacity. The charge and discharge curves are similarly shaped to those for other cells made using conventional pasting procedures. Thus, in the first few cycles, and on charging, a peak was observed that was followed by a minimum and a potential rise. On increasing the number of cycles, the peak and the minimum tended to disappear, the slope of the charge process decreased and the discharge depth increased. An abrupt increase in the

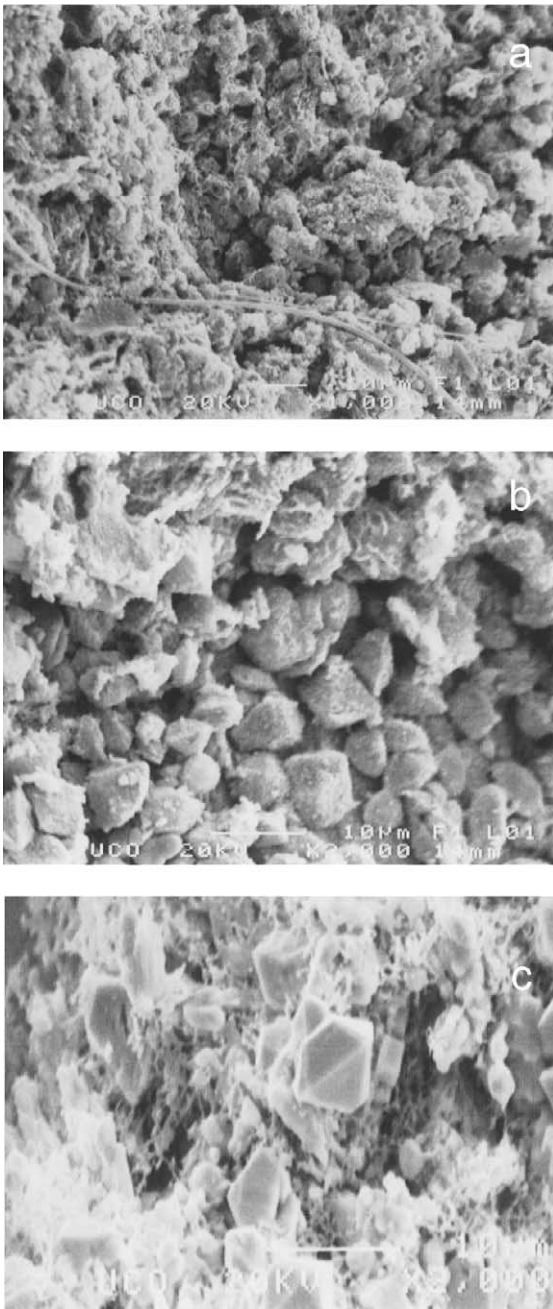


Fig. 5. SEM images of the plate formed (a) and (b); isolated *pseudo* octahedral particles (c).

potential alongside the presence of the peak observed on successive cycling [10] have been ascribed to the formation of a crystal structure of a high resistance, that diminishes the cell capacity. Although this model cannot be applied as such to our results, certainly the strong polarization observed over the first few cycles must be due to a cell resistance the origin of which is unclear at present. However, we can discard the disappearance of large particles of α -PbO and their conversion into electrochemically active β -PbO₂ as the former phase is still present on

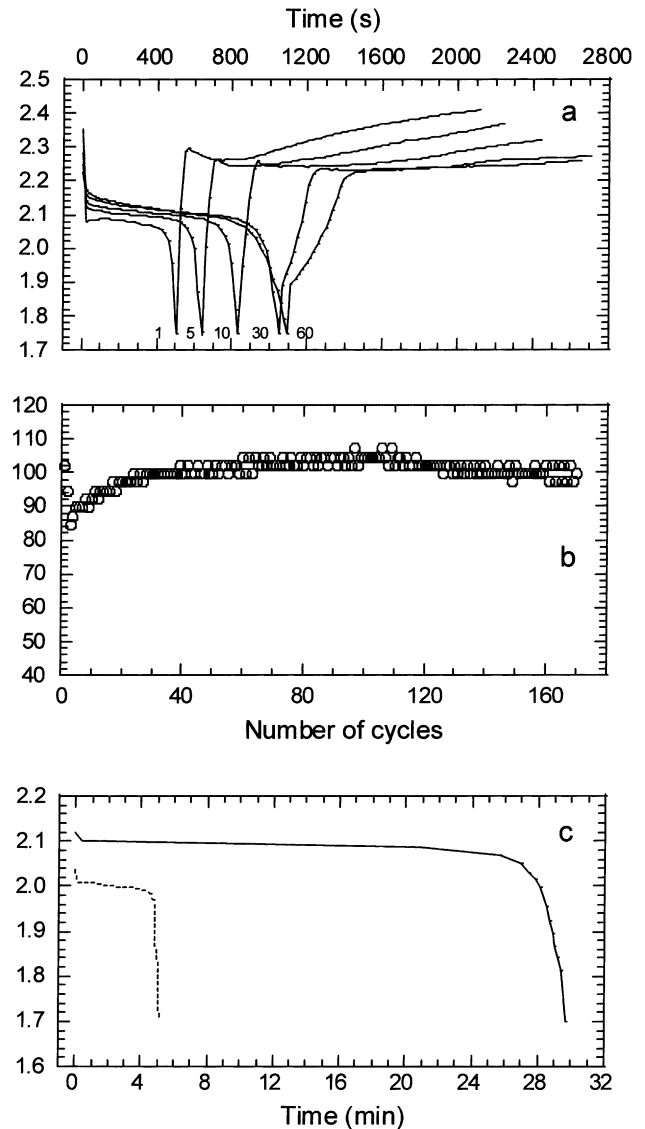


Fig. 6. Discharge and charge curves recorded at different cycles (a); variation of the discharge capacity as a function of the number of cycles (b); cell voltage during constant current discharge (c): (—) 0.56 mA, (---) 2.24 mA.

cycling. In fact, there were no significant changes in the composition as derived from X-ray data on cycling. It is interesting to note that the electrochemical performance of unsoaked PbO thin films acting as electrodes in lithium cells also improves with cycling [11]. One plausible explanation for this finding is improved adherence of active particles to the lead substrate, which lowers the energy barriers of the charge transfer processes. This model can be extended to the lead-acid cell data as follows: the binding properties of the corrosion layer formed during curing, otherwise responsible for the adherence of active particles to the grid in conventional batteries, must be enhanced by the electrochemical processes undergone by lead. In fact, uncoated lead foil subjected to analogous cycling tests, exhibited not only the formation of a passivating layer of

PbSO₄ but also the presence of nanocrystals of PbO₂ (as suggested by the very weak, broadened XRD peaks, Fig. 4c). These particles, firmly bound to the surface and occurring at the interface PAM/substrate, must facilitate electron exchange between the plate and agglomerates, thus favoring development of the electrochemical reaction. This must be the origin of the decreased polarization in the electrochemical reaction and the subsequent increase in discharge capacity. Also, a small contribution to this increase arises from the PbO₂ formed at the expense of the lead substrate. The capacity delivered by the cell on successive cycling is shown in Fig. 6b. After the 15th cycle, the cell maintained a nearly constant capacity of about 100 A h/kg (40% of the theoretical value). Fig. 6c shows the cell voltage recorded at two different discharge rates. In both cases, the voltage–time discharge curves exhibit a voltage plateau of similar value that reflects a low cell impedance. Moreover, the cell has the ability to deliver acceptable amounts of specific energy at moderate discharge rates.

4. Conclusions

Thin films (ca. 50 μm) of α-PbO highly oriented along the [1 0 1] direction deposited on Ca- and Sn-alloyed lead sheets were prepared by spray pyrolysis of 0.5 M Pb(CH₃COO)₂·3H₂O solutions followed by heating at 260 °C for 24 h. SEM micrographs revealed most particles to be round in shape and less than 1 μm in size. These films were tested as active materials for lead-acid cells and found to preserve a uniform coating after soaking, curing and PAM electrochemical formation. Cells exhibited the expected charge and discharge curve shapes and maintained a discharge capacity of ca. 100 A h/kg upon extended cycling.

In summary, chemical spray pyrolysis is a suitable method for depositing active materials with a view to positive plate of a lead-acid battery once the essential requisites for obtaining quality films (substrate temperature, spray rate, concentration of solution/emulsion, etc.) have been optimized.

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