# Preparation and characterization of thin electrodes for lead–acid batteries

A. Caballero, M. Cruz, L. Hernán, J. Morales[*], L. Sánchez

*Departamento de Química Inorgánica e Ingeniería Química, Facultad de Ciencias, Campus de Rabanales, Edificio C3, Universidad de Córdoba, Córdoba 14071, Spain*

## Abstract

Thin-film electrodes were prepared by spraying aqueous suspensions of soaked leady oxide over both sides of lead sheets previously heated at 150 °C. Uniform coatings of controlled thickness were obtained under optimum deposition conditions. The coatings, which retained their homogeneity after the electrochemical formation, were found to consist of small grains of $\beta$-$PbO_2$ that tended to coalesce into micron-size units. The best electrochemical response was obtained from coatings of reduced thickness (20–40 μm). Cells were found to retain a discharge capacity in excess of 100 Ah/kg after extensive cycling. Also, electrodes exhibited excellent electrochemical performance at different discharge rates. However, if the coating was too thick, the paste was easily sulfated and the cell capacity faded after the first few cycles.
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## 1. Introduction

The current growing trend to reducing the size of tools, electronic devices and the emergence of new technologies (e.g. telecommunications, computers) have opened up new prospects for rechargeable batteries to face up to this challenge. At present, most of the ensuing research is mainly focused on lithium batteries, about which a vast amount of information is currently available in most electrochemical journals. However, these energetic sources continue to have major weakness such as high costs and a limited specific power. In this context, the lead–acid battery remains an attractive choice for meeting the new requirements on account of its excellent performance and safety, and its low cost, which are the main reasons for its commercial success. Fulfilling some of such requirements entails overcoming one of its main drawbacks, namely: the excessive weight of the conventional battery. Substantial weight reductions can be achieved in two complementary ways, viz. (i) by using very thin lead-based alloy substrates (e.g. in the form of foil) [1] or (ii) by reducing the layer thickness of the active paste applied to the lead substrate. We recently demonstrated the usefulness of spray pyrolysis as a method for preparing lead-oxide thin films and their potential as positive active mass for lead–acid batteries [2]. In this work, we explored a spray-coating method using emulsions as the active material as a means for preparing thin electrodes. The coatings thus obtained were characterized in textural and structural terms, and the electrochemical properties of the resulting cells were determined.

## 2. Experimental

Positive plates were prepared by using an aqueous suspension of active paste supplied by S.E.A. Tudor. A Pb–Sn (1.14%)–Ca (0.03%) alloy was used as substrate that was previously rolled with a mechanical metal roller up to 0.35 mm in thickness and washed with toluene to eliminate grease impurities. The spraying equipment was described elsewhere [3]. The aqueous suspension was sprayed at a flow-rate of $140 \, l \, h^{-1}$ on lead sheets 20 cm long × 2 cm wide and kept at 150 °C. In order to ensure uniform coating, the substrate was moved forward and backward at a fixed frequency by means of an electronically controlled step motor. The sheets used to prepare the electrodes were cut into L-shaped pieces a square area of 10 mm × 10 mm of which was brought into contact with the electrolyte. Curing was done at 55 °C at a relative humidity about 98% for 2

* Corresponding author. Present address: Lab. de Quimica Inorganica, Facultad de Ciencias, Universidade de Cordoba, Avda. San Alberto Magno s/n, Córdoba E. 14004, Spain. Tel.: +34-957-21-86-21; fax: +34-21-86-06-14004.
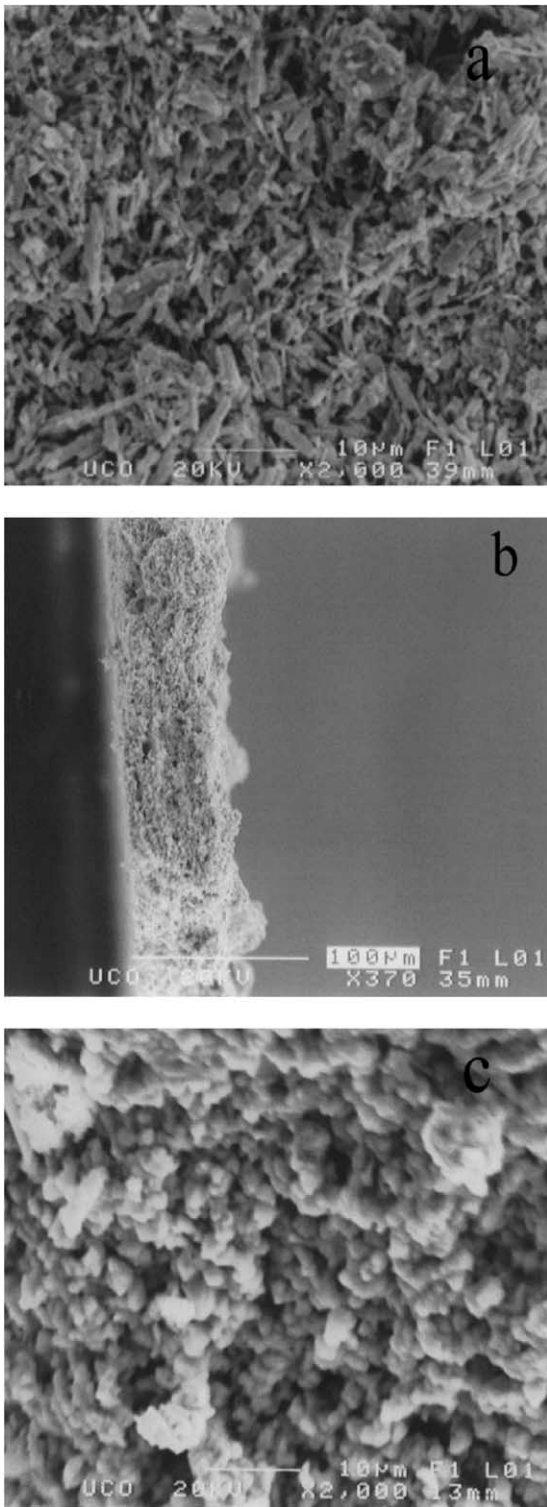*E-mail address:* iq1mopaj@uco.es (J. Morales).

Fig. 1. SEM images of a leady oxide coating: (a) after curing; (b) foil cross-section; (c) after formation (amount deposited 40 mg).

days. Then, the plates were dried at 55 °C in the air for 1 day. All negative plates were supplied by S.E.A. Tudor, and separators and the pasting paper by Bernard Dumas. The electrolyte used in all measurements was a sulfuric acid

solution of specific gravity 1.28. The electrochemical formation of the positive active material (PAM) was accomplished by charging the cell 600% over the nominal capacity as calculated from the amount of deposited material and a typical benchmark of 8.5 Ah/g [4]. The process was carried out in two steps. The first lasted 8 h and allowed 60% of the total capacity. The remaining 40% took 12 h. After formation, cells were subjected to cycling tests under different discharge regimes. All discharge measurements were performed up to a discharge depth of 100% as the limiting factor (cut-off voltage 1.6 V). An overcharge of 110% of the previous discharge capacity was set as the boundary condition for the recharge.

Phases were identified, and their composition and morphology determined by combining X-ray powder diffraction (XRD), chemical analysis and scanning electron microscopy (SEM). Formation and cycling tests were carried out using a Solartron battery testing 1470 A model.

## 3. Results and discussion

Three thin films were prepared by spraying emulsions of soaked leady oxide to obtain three different amounts of active deposited mass (viz. 10, 20 and 40 mg). As can be seen from the SEM images of Fig. 1, the three samples exhibited a completely uniform coating of the substrate with particles of highly uniform shape. A significant fraction of particles was needle-shaped, with a length of ca. 4–5 μm and an aspect ratio about 5. The X-ray analysis of the phase composition [5] revealed the major phase constituents to be
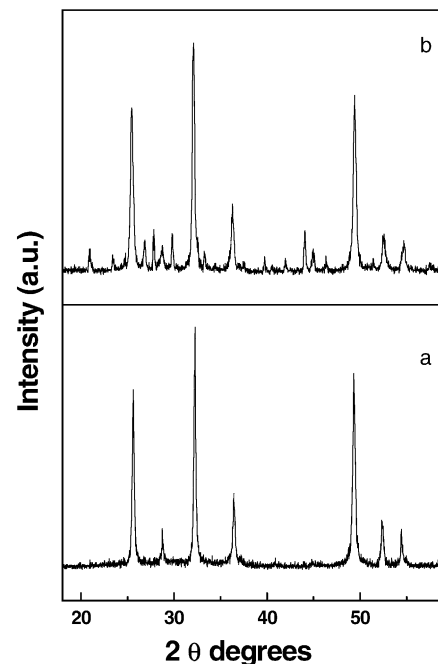


Fig. 2. XRD patterns for deposited soaked leady oxide after electrochemical formation. Thickness: (a) 20 μm; (b) 70 μm.
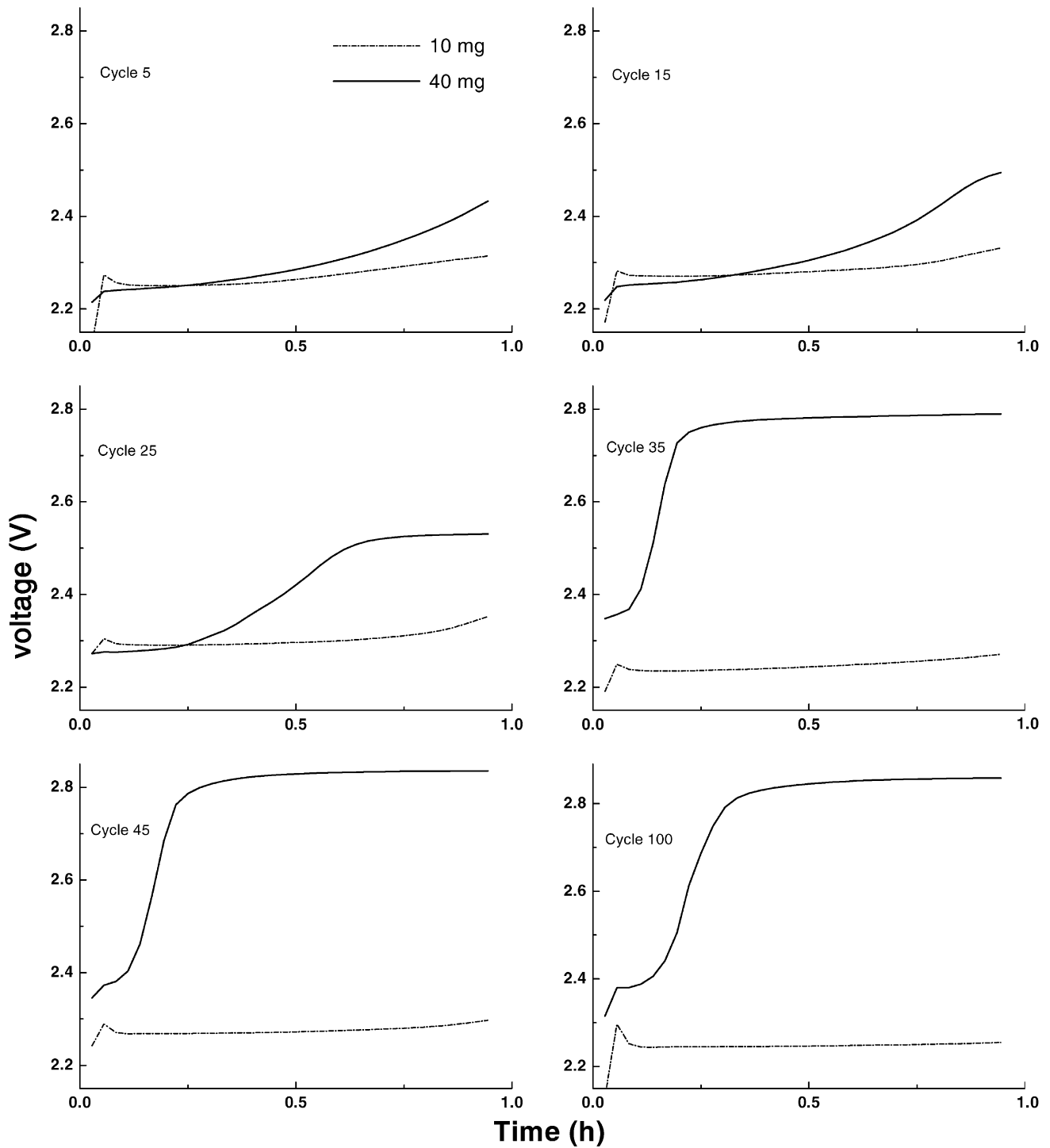
Fig. 3. Recharge curves obtained after different numbers of cycles.

basic lead sulfates (47.5% 3BS; 6.5% 1BS) which tend to crystallize as needle-shaped grains. α-PbO (the other phase involved in the active material), was also detected, in the form of flake-like particles. However, this morphology was scant in spite of the significant content of α-PbO as evaluated by XRD analysis (about 45%). The coating thickness was highly uniform: it varied from 20 (10 mg) to 70 μm (40 mg)

(Fig. 1b). Following electrochemical formation, the coatings retained their uniformity but particle shape underwent major changes (Fig. 1c). Thus, elongated crystals were essentially absent and samples consisted of many equidimensional grains that tended to coalesce into micron-size units.

The XRD pattern for the PAM of the thinner coatings, Fig. 2a, revealed the presence of $\beta$-PbO$_2$ as the dominant
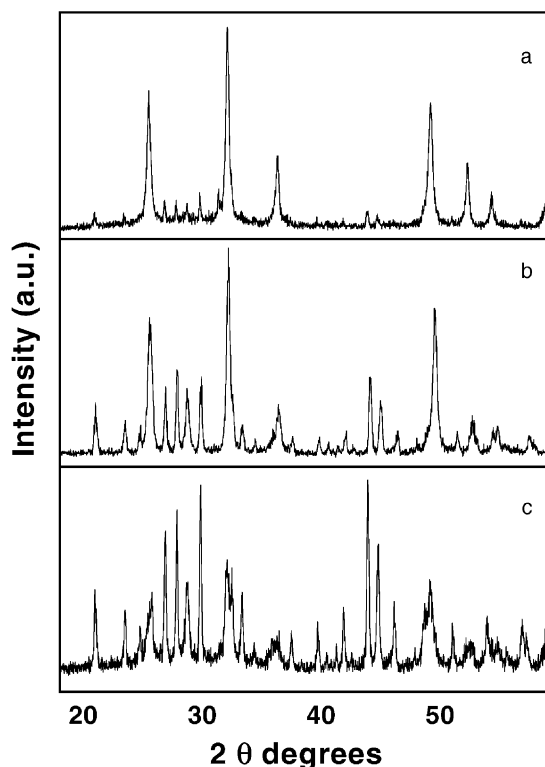
Fig. 4. XRD patterns for the plate formed after successive cycling. Coating thickness (a) 20 mm (15th cycle); (b) and (c) 70 mm (15th and 35th cycle, respectively).



Fig. 5. Discharge capacity vs. cycle number for the cells made with a positive plate obtained by emulsion spraying.

phase. A peak at $28.56°$ $2\theta$ was also observed that could be assigned to either $\alpha$-PbO or $\alpha$-PbO$_2$. Based on particle shape, the absence of particles with $\alpha$-PbO morphology suggests that this reflection peak is due to $\alpha$-PbO$_2$ crystals. However, the shoulder on the left of the peak at $48.66°$ $2\theta$ is consistent with the presence of unoxidized PbO. The X-ray analysis revealed a paste composition of 78% PbO$_2$ and 22% PbO. The presence of PbO particles can be explained in the light of various models. Thus, the dissolution and further oxidation of lead sulfate particles during electroformation can leave some PbO particles in isolated places, thereby hindering their further oxidation to PbO$_2$. One other possibility is anodic oxidation at the surface substrate and subsequent formation of a PbO layer. However, no PbO formation was detected on a clean surface of the lead substrate.

The XRD pattern was found to increase in complexity as the coating thickness increased. Thus, at a deposited mass of 40 mg, a series of peaks was observed consistent with the presence of significant amounts of PbSO$_4$ in addition to $\beta$-PbO$_2$ and $\alpha$-PbO (X-ray analysis: 46% PbO$_2$; 27% PbO; 27% PbSO$_4$) (Fig. 2b). At present, the origin of this differential behavior is unclear, but it seems plausible to associate it to problems of connectivity between particles (particularly those lying furthest from the substrate) [6]. This may increase the resistivity and hinder their oxidation and conversion into PbO$_2$ particles.
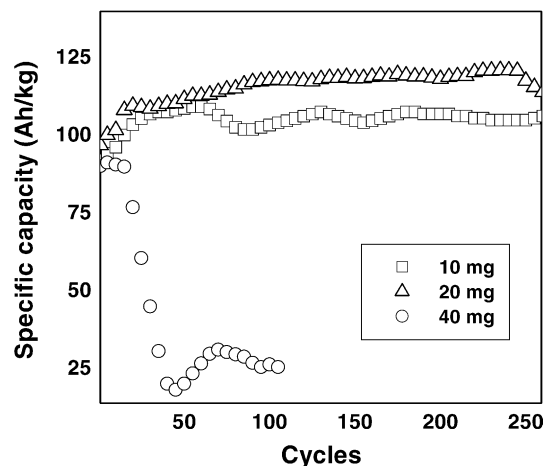
The charge and discharge curves were similarly shaped to those for other cells made by using conventional pasting procedures. However, the curves obtained at different coating thickness warrant some comments. Fig. 3 shows different recharge curves for electrodes coated with 20 and 70 $\mu$m thick layers, selected in terms of the number of cycles. The most salient differences are the increased polarization of the 70 $\mu$m thick electrode, particularly after the fifteenth cycle. Beyond that point, oxygen is seems to evolve and, by the 35th cycle, this becomes the main electrochemical reaction. On the other hand, the 20-$\mu$m thick electrode exhibits reduced polarization that decreases after the first few cycles. The XRD patterns (Fig. 4) also reflect the differential behavior. Thus, the recharge 70-$\mu$m thick electrode exhibits a substantially increased PbSO$_4$ content—much greater than that in the 20-$\mu$m thick electrode. The origin of the sulfate may be polarization of the electrode. In fact, the PbSO$_4$ content increased with increasing electrode polarization. On the other hand, the PbSO$_4$ content of the thinner electrode formed during the first few cycles changed very little after a number of cycling measurements.

Fig. 5 shows the variation of the measured discharge capacity versus the cycle number. A good cycling behavior was observed from coatings with low or moderate PAM contents; the delivered discharge capacity increased over the first few cycles, probably through improved adherence of active particles to the lead substrate. This must facilitate electron exchange between the plate and the active particles, thus, favoring development of the electrochemical reaction. The binding properties of the corrosion layer formed during curing, and responsible for the adherence of actives particles to the foils, must be enhanced by the electrochemical processes undergone by the lead. In fact, electrode polarization decreased after 35 cycles and resulted in increased electron conductivity at the PAM/substrate interface. Upon further cycling, the cells retained a nearly constant capacity of 100–115 Ah/kg (about 45% of the theoretical value) and
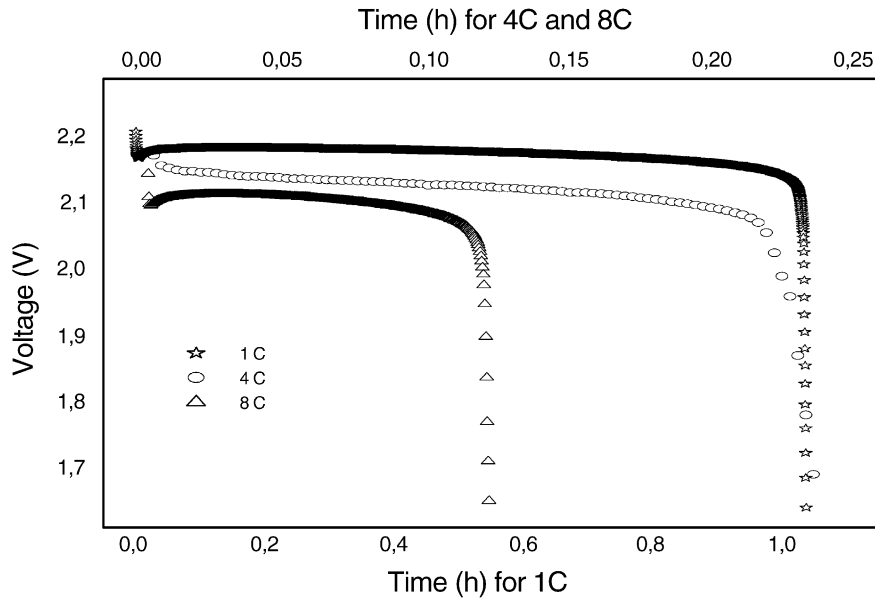
Time (h) for 4C and 8C



Fig. 6. Variation of the cell voltage during a constant current discharge. Electrode thickness 20 μm.

somewhat greater value for the 20 mg coating. In contrast, if the coating was too thick, the capacity continuously faded after the first few cycles. As stated above, the XRD analysis revealed that thick films were more easily sulfated in the formation step and subsequent cycling. Corrosion at the foil–paste interface was seemingly insufficient for a strong layer to be established, so a passivation layer composed primarily of lead sulfate was formed. Such a layer can act as an electrical insulator and decrease the conductivity between the foil and the active paste, thus, dramatically degrading the electrochemical properties of the cell. All electrochemical measurements were carried out using cells mounted without compression. The design of a compression system for these cells, now in preparation, could result in improved electrochemical performance of thicker electrodes.

Fig. 6 shows the cell voltages of the optimized electrodes recorded at different discharge rates. In the three cases the voltage–time discharge cur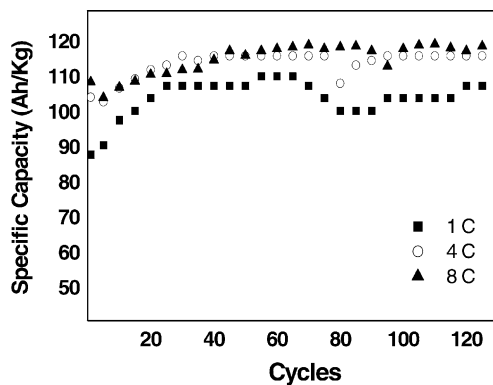ves exhibit voltage plateaux of similar values that reflect a low cell impedance. The electrodes exhibited an excellent response and retained their good cycling properties under the different conditions tested (see Fig. 7).

## 4. Conclusions

A method for the deposition of active paste on the positive plate of lead–acid batteries was developed. The method involves spraying a soaked leady oxide emulsion over both sides of lead foils. By carefully controlling the deposition variables (viz. substrate temperature, spray rate and emulsion concentration), a straightforward device allows electrodes of low, controlled thickness with uniform, porous coating of the lead substrate to be prepared. The films thus obtained were tested in lead–acid cells and found to retained their coating uniformity after curing and PAM electrochemical formation. With moderate coating thickness (20–50 μm), cells exhibit the expected charge and discharge curve shapes, and retain a discharge capacity in excess of 100 Ah/kg after extensive cycling. With greater thickness, the electrode is subject to major polarization problems in the cell recharge process that lead to significant sulfation. This results in the loss of some electrode capacity and in shortening of the cell lifetime. The low yield obtained may result from the lack of a device for compressing the cell electrodes during curing and PAM electrochemical formation.

## Acknowledgements

Fig. 7. Plot of discharge capacity vs. cycle number. Cell test conducted at different discharge rates (electrode thickness 20 μm).

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