

Growth and Electrochemical Performance of Lead and Lead Oxide Nanowire Arrays as Electrodes for Lead-Acid Batteries

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In this work, we present the growth and electrochemical performance of nanostructured lead and lead oxide electrodes for lead-acid batteries. The electrodes were obtained by template electrodeposition in polycarbonate membranes, acting as template. Electrochemical tests were conducted at constant current in 5M aqueous solution of sulphuric acid, after assembling nanostructured lead and lead oxide electrodes in a zero-gap configuration using a commercially available separator.

The main advantages of these electrodes are the high specific energy and power density, and the wide surface area, about 70 times higher than the geometrical one. These features allowed high discharge rates, up to 20C. Moreover, in comparison with commercial lead-acid batteries that usually deliver about 30 mAh/g for only 15-20 cycles at 1C rate, our batteries are able to charge and discharge at very high rate (1C and more) without decay up to 1200 cycles.

1. Introduction

Lead-acid batteries are still extensively used in the field of energy storage, owing to a well-known and reliable technology. Lead-acid batteries are capable to deliver high power and can store its energy for a very long time. In addition, they are reliable and easy to produce. The raw materials for their manufacture are practically unlimited, and about 95% of the materials can be recovered and reused. However, the lower specific energy storage (about 30-40 Wh kg⁻¹), in comparison with other galvanic generators, limits the possibility of their application in advanced systems. This limit is due to the high atomic weight of lead, which limits up to date emerging and challenging applications, like in electrical mobility. Accordingly, lead-acid batteries are generally used only in micro-hybrid electric vehicles adopting a start-stop system which turns off the engine when the car stops; also the battery takes over the electric supply needed for all accessories (Pavlov, 2011).

One of the principal limitation in the use of lead-acid batteries either in electric vehicles (EV) or hybrid electric vehicles (HEV) is related to the inadequacy of the negative plates in accepting the high charge/discharge currents. Besides, in HEVs batteries operate at partial state-of-charge (SOC), which leads to rapid sulphation of the negative plates (Pavlov and Nikolov, 2012). Many approaches were proposed in order to overcome these problems and make lead-acid batteries suitable for hybrid electric vehicle applications. Recently, Moseley (Moseley, 2009) has shown that the addition of 2–4 wt% of a suitable form of carbon can result in a dramatic improvement in high-rate, partial-state-of-charge cycling performance in comparison with batteries with a conventional formulation. Another approach is based on the use of carbon foam in place of the usual lead grid supporting the negative active material in order to maintain a stable 3D structure with widely open pores (Ma et al., 2009). Ultra Battery™ have been developed and tested cells with negative plates comprising half regular lead plate and half carbon supercapacitor plate (Nakano et al., 2007).

These problems could be overcome through the fabrication of electrodes with nanostructured active materials. In fact, nanostructured electrodes are progressively emerging as an alternative to the conventional ones because their high aspect ratio and the consequent high superficial area allow to fabricate batteries with small size (high specific energy, Wh kg⁻¹) and light weight (high energy density, Wh L⁻¹).

Aim of this work was to investigate template electrodeposition as an easy and direct technique for fabrication of nanostructured electrodes, with very large active area, consisting of PbO₂ (Inguanta et al. 2008, 2010a) and Pb (Inguanta et al., 2010b, 2012) on a current collector of the same material. Both active materials were electrodeposited using commercial polycarbonate membrane in order to obtain regular arrays of nanowires. Nanostructured PbO₂ and Pb electrodes were assembled and tested in lead-acid batteries.

2. Experimental

Nanostructured electrodes were fabricated by a two-step procedure based on electrodeposition from lead solution using polycarbonate membrane as a template. The first step was to deposit onto one side of the template a uniform layer of either Pb or PbO₂ acting as current collectors. Finally, nanostructures were grown inside the channels of a polycarbonate membrane by potentiostatic deposition for PbO₂ or by pulsed current deposition for Pb. Electrodeposition were performed with a PAR Potentiostat/Galvanostat (mod. PARSTAT 2273) connected to a PC for data acquisition and control by a POWERSUITE™ software. Bath and electrodeposition conditions are listed in Table 1.

For PbO₂ deposition, a standard three-electrode cell was used with a graphite sheet as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. SCE electrode was connected to electrochemical cell through a salt bridge. Otherwise, Pb electrodeposition was conducted in a simple two-electrode cell. After complete template dissolution in CHCl₃, arrays of either Pb or PbO₂ nanowires electrically connected to the current collector were obtained. The active mass of nanostructured electrode was evaluated by gravimetric measurements performed by a Sartorius microbalance (mod. Premium Microbalance ME36S).

Table 1: Bath and electrodeposition conditions of nanostructured lead and lead oxide electrodes.

	Bath	Electrodeposition conditions
Pb Current Collector	40 g/L Pb(BF ₄) ₂	
Pb Nanowires	34 g/L HBF ₄ 5 g/L C ₂₀ H ₂₆ O ₁₀ S ₂ 15 g/L di HBO ₃	Pulsed current between 10 mA/cm ² and 100 mA/cm ² Room temperature
PbO ₂ Current Collector		Amperostatic deposition at 10 mA/cm ² Room temperature
PbO ₂ Nanowires	1M Pb(NO ₃) ₂ 0.3M HNO ₃	Potentiostatic deposition at 1.5 V(SCE) At 60°C

Samples were characterized by X-Ray diffraction (XRD), energy dispersive spectroscopy (EDS) and Raman spectroscopy, whose details are described elsewhere (Inguanta et al., 2008, 2010a, 2010b, 2012). Morphology was evaluated by Scanning Electron Microscopy (SEM), using a FEI field-emission gun (FEG) environmental scanning electron microscope (model QUANTA 200) equipped with EDS. Details on characterization method were reported in (Inguanta et. al, 2007, 2009).

The wettability of nanostructured electrodes was also evaluated by contact angle measurements using a 5M aqueous solution of sulphuric acid as wetting liquid in a FTA 1000 (First Ten Ångstroms) instrument. The wettability measurements were conducted on different area of nanostructured electrodes in order to evaluate their uniformity.

All characterization method were performed on nanostructured electrodes before and after their operation in lead-acid battery, in order to study the changes that occurs on electrode structure.

Electrochemical performances were tested in a 5M sulphuric acid aqueous solution, after assembling nanostructured lead and lead oxide in a zero-gap configuration using a commercially available separator (Inguanta et. al. 2012). In order to evaluate also the electrochemical performance of a single nanostructured electrode, it was assembled with commercial lead or lead oxide plates. Charge/discharge cycles were carried out by a multi-channels cell test system (Solartron, 1470E) at room temperature. Data were acquired and processed using MULTISTAT™ and CorrView2™ software, respectively.

Charge/discharge were performed at a 1C rate and a cut-off potential of 1.2 V. In all conditions, cell was discharged up to 90% of gravimetric charge. Rates higher than 1C were also used in order to evaluate the performance of nanostructured battery at high charge/discharge rate.

3. Results and Discussion

Different procedures were investigated in order to find the best conditions leading to straight lead nanowires, well attached to the current collector. As well known, one of the major problems of lead electrodeposition is the formation of dendritic deposit, especially close to the edges of the cathode (Schlesinger and Pauvonic, 2010). As reported in (Inguanta et al., 2010b, 2012) this problem occurs also in the case of electrodeposition of nanostructures. The first solution, that we have proposed, was based on an "indirect" two-step procedure, consisting in the anodic electrodeposition of α -PbO₂, followed by its reduction to metallic lead.

Despite the encouraging results, this procedure appears too long for a large-scale production of nanostructured electrodes. For this reason, in this work we have developed a new procedure, based on different deposition bath and electrodeposition conditions. In particular, we used a lead fluoroborate solution as electrolyte containing two additives (C₂₀H₂₆O₁₀S₂ and HBO₃) and the electrodeposition was conducted under a pulsed current. In this way, it was possible to obtain metallic lead film (used as current collector) and nanowires without the formation of undesired dendrites. Both XRD and EDS analysis evidenced that nanostructured Pb electrode is extremely pure, due to the optimized electrodeposition procedure. In particular, a polycrystalline metal lead was obtained, identified by the card 4-686 of XRay database (ICDD, 2007).

Morphology of the lead nanostructured electrodes is shown in the SEM images of Figure 1, where it is possible to observe that the surface of Pb current collector is totally covered by straight nanowires, well attached to it.

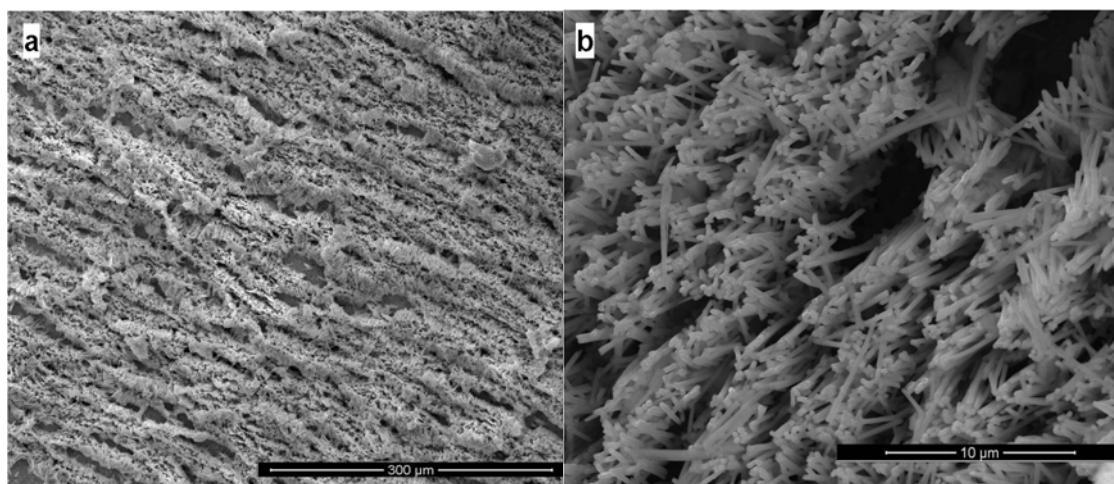


Figure 1: SEM images of metal lead nanowires on current collector after total dissolution of the polycarbonate membrane in CHCl₃.

The electrodeposition of PbO₂ was simpler: with respect to our previous paper (Inguanta et al., 2008), in this work we have optimized only the electrodeposition conditions of PbO₂ current collector, which was deposited at an anodic constant current of 10 mA cm⁻², while nanowires were grown at the constant potential of 1.5 V(SCE).

Different crystallographic structures were obtained in the two cases, since current collector was deposited at room temperature and nanowires were grown at 60°C. In particular, current collector consisted of a mixture of α and β -PbO₂ phases, whilst nanowires were pure either α - or β -PbO₂. This conclusion was supported by both RAMAN spectroscopy and XRD analysis, and crystallographic structures were identified by comparison with the ICDD database (ICDD, 2007). Also in this case, EDS analysis confirmed the formation of pure lead oxide deposit.

Morphology of the nanostructured PbO₂ electrode, after total dissolution of template, is shown in Figure 2. The entire surface of lead oxide current collector is covered by nanowires having a uniform length of about 10 μ m. An interconnected morphology, due to the characteristic original morphology of the track-etched polycarbonate membranes, is clearly visible in Figure 2.

Both Pb and PbO₂ nanowires have a mean diameter of about 220 nm equal to that of the template while the length was controlled by electrodeposition time.

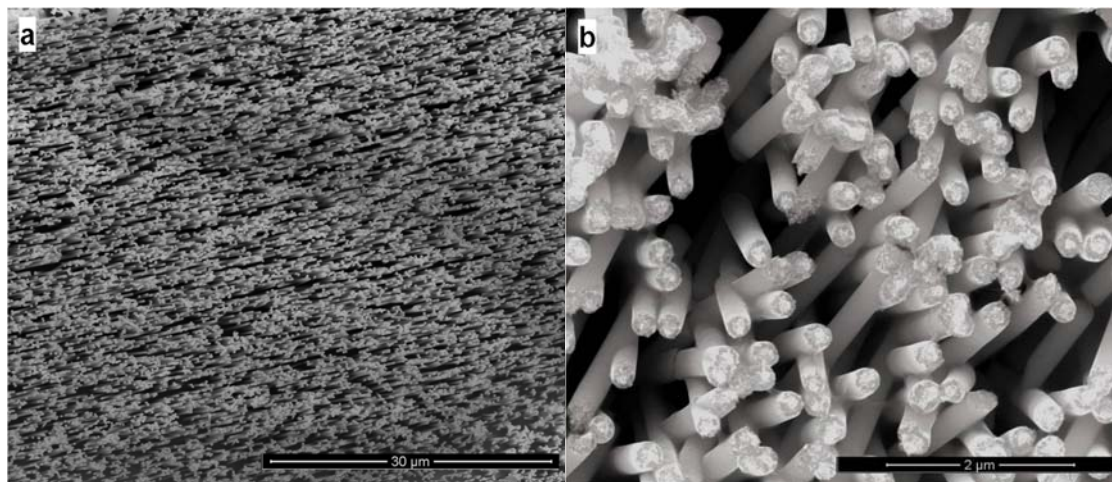


Figure 2: SEM images of lead oxide nanowires attached on current collector after total dissolution of polycarbonate membrane in CHCl₃.

Performance tests were conducted assembling the nanostructured electrodes with a commercial Pb or PbO₂ plate, in a sulphuric acid solution (specific weight: 1.28) at room temperature in a zero gap configuration using a commercial separator. Battery was discharged up to 90% of the gravimetric capacity with a cutoff of 1.2 V. In these conditions, in the case of PbO₂ electrodes, a capacity of about 190 mAh/g (theoretical charge 224 mAh/g) was delivered at 1C rate, with very good cycling stability maintained for more than 1000 cycles. This is a significant improvement in comparison to commercial PbO₂ electrodes that usually deliver about 30 mAh/g for only 15-20 cycles, whilst a capacity of 125mAh/g can be delivered at a C/10 rate (Linden and Reddy, 2007; Morales et al., 2004). Also in the case of Pb nanostructured electrode very good results were obtained. In the same cycling conditions of PbO₂, Pb electrodes delivered a capacity of about 233 mAh/g (theoretical charge 258 mAh/g) at 1C rate up to 700 cycles with an efficiency of about 90%.

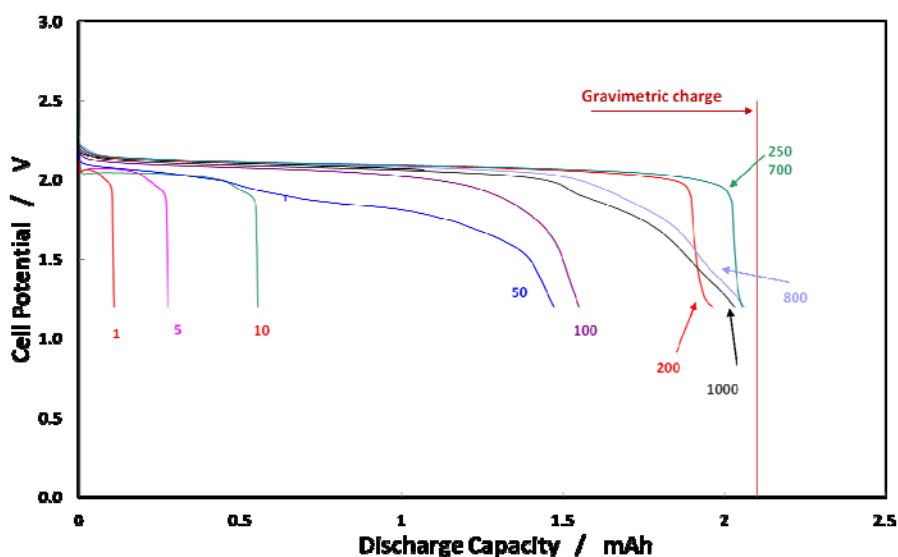


Figure 3: Electrochemical performance of an assembled nanostructured lead acid battery: discharge curves vs. discharge capacity. The red line indicates the gravimetric capacity of PbO₂ nanostructured electrode.

The electrochemical performance of our assembled nanostructured lead acid battery[®] (Sunseri et al., 2012) is shown in Figure 3 and 4. Figure 3 shows the discharge curves as function of discharge capacity, whilst Figure 3b shows the discharge capacity vs. cycles number.

The good cycling stability during 1000 charge/discharge cycles of the battery can be attributed to the nanostructured morphology. In comparison to commercial battery, the larger specific surface area of the active materials should be responsible for the increased capacity of our battery. Also, the gap between nanowires, clearly shown in Figures 1 and 2, favours a considerable contact area between the electrolyte and the active material. Both these two features allow our battery to sustain high rate charge/discharge cycles. In fact, when a commercial battery is cycled at high discharge rates, sulphate ions exceeding the fast conversion of the plate outer part can be transported toward the inner regions only by transport through a porous medium, at a velocity that is largely lower than that required for sustaining a high rate cycling. Accordingly, the utilization level of the active mass decreases, together with battery performance (Linden and Reddy, 2007). Besides, Figure 4 shows a wide discharge plateau from the hundredth cycle, whose extent depends on number of cycles.

Figure 4 shows an initial increase of capacity during cycling up to an almost constant value of about 105 mAh/g, that we have attributed to two principal causes. The first is a morphology change of nanostructured electrodes with number of cycles. In fact, after cycling we found very significant changes with respect to the original morphology of the nanostructured electrodes. This behaviour is also present in commercial batteries, where morphology of the active material changes during battery operation both for positive and negative plates (Pavlov, 2011). The second cause determining the initial increase in capacity shown in Figure 4 is likely due to the wettability of nanostructured electrodes: this increases with cycling, as supported by contact angle values passing from 105° (i.e. a very low wettability) for as-prepared electrodes to 18°, after cycling.

Further studies are in progress in order to investigate the electrochemical performance of these nanostructured electrodes under different charge/discharge conditions. In particular, tests at different temperatures and at high-rate partial state of charge cycling are currently performed.

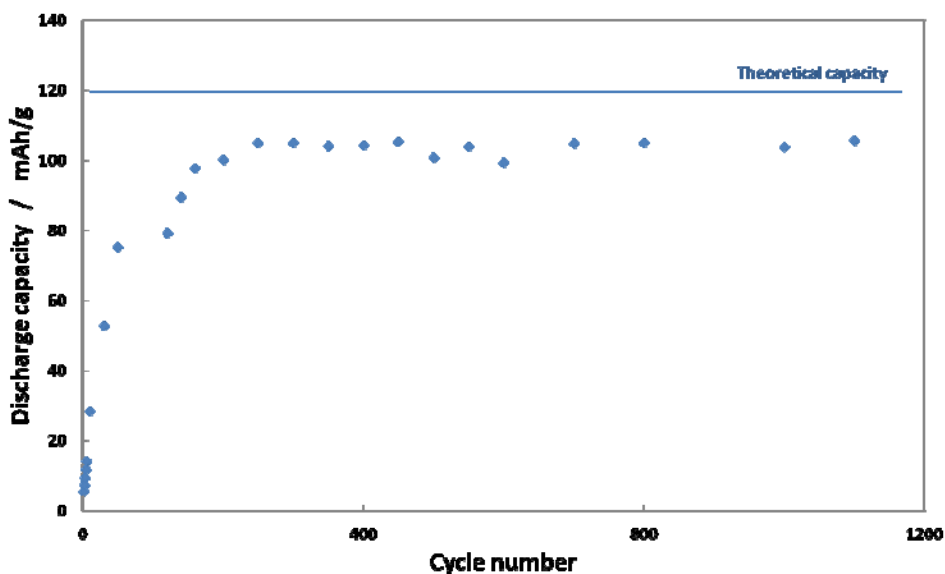


Figure 4: Electrochemical performance of an assembled nanostructured lead acid battery: discharge capacity vs. number of cycles.

Assembled nanostructured battery delivers a capacity of about 105 mAh/g (theoretical charge 120 mAh/g) at 1C rate up to 1000 cycles with an efficiency of about 85-90% after stabilization of electrode morphology. A detailed discussion of these results will be presented in a forthcoming paper.

4. Conclusions

We have found that it is possible to obtain nanostructured electrodes of Pb and PbO₂ by means of a simple electrodeposition inside pores of a polycarbonate membrane template. Both electrodes were obtained by a two-step procedure that permits to obtain nanowires well attached to a compact film of the same material, acting as both current collector and mechanical support of the nanostructures. In the case

of Pb electrodes, it was necessary to use a specific electrodeposition bath and operate with a pulsed current in order to avoid the formation of dendritic structures.

These electrodes were tested in lead-acid battery using an aqueous 5 M sulphuric acid solution. In comparison to commercial lead-acid batteries, which usually deliver about 30 mAh g^{-1} for only 15-20 cycles at 1C rate, our batteries are able to charge and discharge at very high rate without fading up to 1200 cycles with an efficiency of about 90%. These special properties of our electrodes are attributable to their large surface area (about 70 times higher than the geometrical one), leading to a new lead acid battery with high specific energy and power density. Another interesting results obtained is the ability of nanostructured electrodes to charge and discharge up to 20C.

Acknowledgements

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