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Nanostructured Pb Electrode for Innovative Lead-acid Battery

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Lead-acid batteries are widely used for energy storage, due to a well-established and reliable technology. Over the years, various studies for improving the performance of this battery have been performed. The main goal is to replace conventional plates with innovative electrodes having good stability, high capacity and high surface area. In particular, it is necessary to improve the kinetics of electrochemical conversion reactions at the electrode-solution interface, and to guarantee good electrical continuity during repeated charge/discharge cycles. To achieve these goals, the attention was focused on nanostructured electrodes. Up-to-date, two principal approaches have been followed. In the first approach, 3D nanostructured current collector, such as carbon foam or 3D porous titanium, was used in place of conventional lead grid. The second method is based on the fabrication of nanostructured active material, such as nanoparticles. Our idea follows the last approach, making nanostructured active material through the synthesis of nanowires. In particular, we have obtained Pb nanostructured electrodes by template electrosynthesis in nanoporous polycarbonate membrane. These electrodes have high surface area, and allow high utilization of the active material leading to high specific energy.

Here, we show that battery with nanostructured Pb electrode works at 1C charge and discharge with very good stability for over 1200 cycles, and discharge efficiency around 90%. It is important to highlight that the C-rate here tested is far higher than that of commercial batteries, whose highest operative rate is C/5 while at 1C typically provide a capacity of 30 mAh g^{-1} for only 20-30 cycles.

1. Introduction

Despite lead-acid battery has been worldwide used for over a century, its production continues to grow owing to new applications such as emergency devices and electric and hybrid vehicles. Lead-acid batteries also have a cost of production/management among the lowest in comparison with modern energy storage devices. The raw materials for their manufacture are practically unlimited, and about 95% of battery mass can be recovered and recycled. Unfortunately, the low specific energy (about 30-40 Wh/kg) limits the use in emerging and highly challenging applications, like electrical mobility. Over the years, various studies aimed to improving the performance of lead-acid battery have been conducted. Bača et al. (2015) used different types of carbon powder, carbon nanotubes, titanium dioxide, glass fibres, silicon dioxide and aluminium oxide as additives to the negative active mass to obtain electrodes with greater surface area and an increased utilization of the active material. Sugumaran et al. (2015) studied addition effects of carbonaceous materials to the negative active paste founding that battery added with carbon nanotubes (CNT) shows a small variation of the reserve capacity, a better cold cracking, a greater charge acceptance and a greater overall efficiency of the system. In order to improve VRLA battery life cycle, for hybrid electric vehicle, Zhu et al. (2016) added graphene to the negative active material. The results obtained suggest that the addition of graphene to the negative mass may decrease the charge cut-off voltage, increase the cut-off voltage of discharge and improve cycle life of VRLA batteries during partial state of charge (PSoC) cycles. The main goal of our research activity on lead-acid battery is to replace conventional plates with innovative nanostructured Pb and PbO_2 electrodes having good stability, high capacity and high surface area. These electrodes not only have high specific area, due to the presence of array of nanowires, but also a high porosity that ensures the electrolyte permeation from surface to inner core. In this work, specifically, we present some results dealing with the use of nanostructured lead

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electrode acting as an anode in lab cell assembled with positive commercial paste plate. The Pb anode shows stable performance in terms of discharge capacity for high number of cycles (>1200 cycles) with efficiency around 90%. The tests were conducted at 1C, which cannot be proposed for commercial battery, because a fast decay occurs at such a C-rate.

2. Experimental

2.1 Electrode Fabrication and Characterization

The experimental details for obtaining nanostructured electrodes were described in a previous work (Inguanta et al., 2013). The polycarbonate membrane, used as a template for growing the nanostructures, is a track etched polymeric sheet with pores each other interconnected. Initially, a gold thin film was sputtered on one side for making conductive the membrane. Then a Pb layer, acting as a current collector, was electrochemically deposited on the gold film. Specific attention was applied for obtaining a highly compact and uniform layer, since it has to act as an electrical collector and also a mechanical support for the nanostructures, which have the nanowires (NWs) shape.

Synthesis of Pb nanostructured electrodes was conducted in two steps: deposition of the current collector followed by NWs deposition. In both steps, a 4.5 g/l $C_{20}H_{26}O_{10}S_2$, 15 g/l H_3BO_3, 35.2 g/l HBF_4, and 40.9 g/l $Pb(BF_4)_2$ solution was employed for the electrodeposition, supplying a pulse current at room temperature. Electrodepositions were performed with a PAR Potentiostat/Galvanostat (mod. PARSTAT 2273). Current collector was deposited through three identical steps of 960 s each. At the end of each step, the solution was replaced with a fresh one, so to avoid degradation effects and conduct a more efficient deposition. On the contrary, NWs growth was carried out in a single step of 330 s. After electrodeposition, polycarbonate was dissolved in pure CH_2Cl_2. This is a very challenging operation, because a partial collapse of deposited Pb NWs can occur, leading to morphological structure not usable for the desired application. In particular, the membrane dissolution was carried out in multiple, successive steps for its complete removal (Inguanta et al. 2009, 2011). Morphological analysis was carried out before and after the electrochemical tests by Scanning Electron Microscope (model FEI Quanta 200), while solid-state characterization was conducted through X-ray diffraction (XRD), using a RIGAKU X-ray diffractometer (model: D-MAX 25600 HK). X-ray diffraction patterns were obtained in the 2θ range from 10° to 100° with a sampling width of 0.004° and a scan speed of 3 deg./min, using Ni-filtered Cu Kα radiation (λ= 1.54 Å), while diffraction peaks were identified by comparison with ICDD database (International Centre for Diffraction Data 2007).

2.2 Electrochemical tests

The experimental details for electrochemical tests were reported in a previous work (Moncada et al. 2015a,b).

Pb nanostructured electrode was assembled in a zero gap cell and tested in 5M H_2SO_4 solution, using a commercial plate of PbO_2 as a counter electrode and an AGM separator. Nanostructured electrode capacity was calculated through gravimetric measurements, considering only the array of nanostructures as an active material. The commercial plate active paste was largely in excess so to be able to attribute the cell performance to the nanostructured electrode. Tests were conducted at 1C-rate, with a cut-off potential of 1.2 V.

3. Results and discussion

After membrane dissolution, SEM analysis was conducted on lead nanostructured electrode in order to check the morphology and verify the absence of undissolved polycarbonate. Figure1 shows that the surface of Pb current collector is totally covered by nanowires well adherent to it.

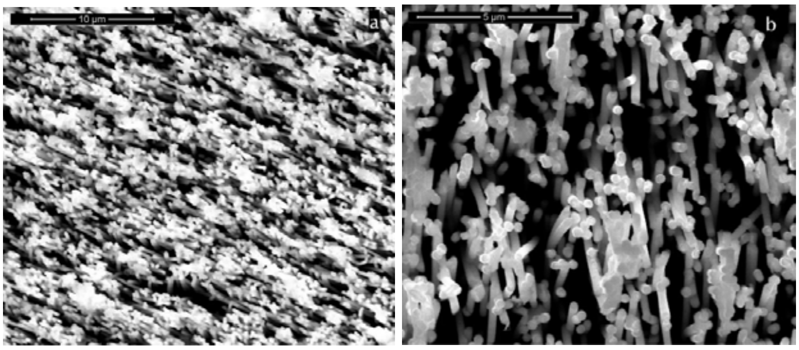

Figure 1: SEM images of Pb nanowires after total dissolution of the polycarbonate membrane in CH_2Cl_2

After SEM analysis, nanostructured electrode was analysed by X-ray diffraction to verify the Pb crystalline structure. A typical XRD pattern is shown in Figure 2. The peak identification was conducted through ICCD cards, and in addition, a perfect overlapping of the peaks with those characteristic of the Pb reported in the literature by Pavlov (2011), was found at 2θ of 31.27°, 36.26°, and 55.22°.

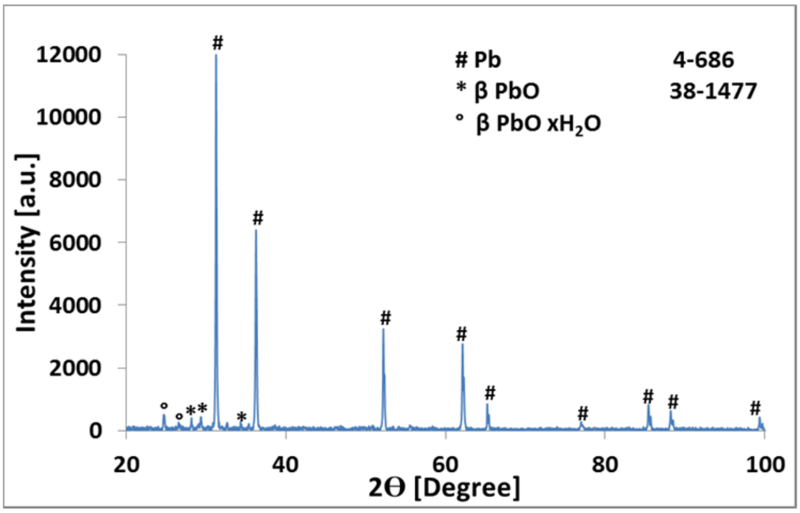

Figure 2: XRD pattern of a Pb nanostructured electrode after total dissolution of the template

The electrochemical behaviour of the Pb NWs electrode was investigated at room temperature in a zero gap configuration cell using a commercial separator. Battery was discharged up to 90% of the gravimetric capacity with a cut-off of 1.2V. Last parameter is of high technological relevance, because in the commercial lead-acid batteries, repeated deep discharge shortens greatly the life time.
Progressively, the charge drained on discharge is diminishing up to definitive battery decay, which can occur quickly when repeatedly cycled to 1.2 V.

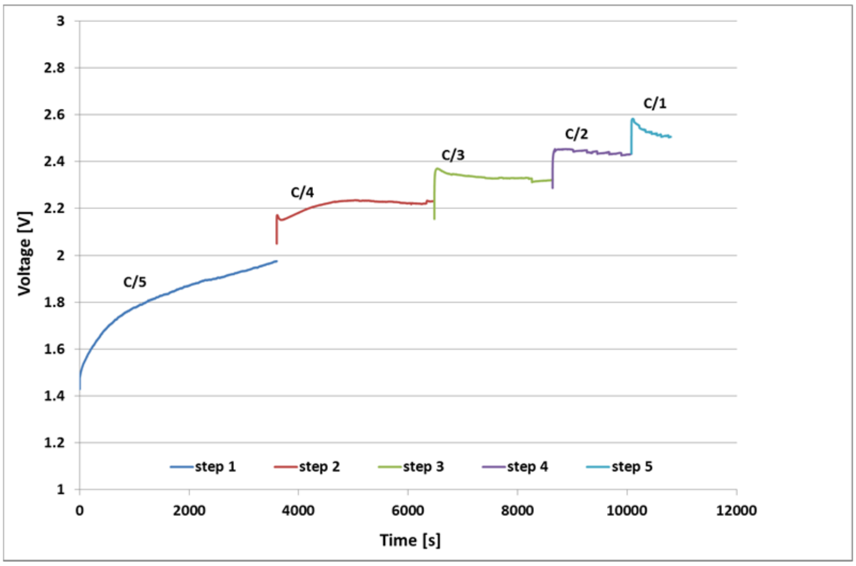

Figure 3: First charge of a nanostructured Pb electrode with a step-wise increase of the charge current

In all cycling tests, the first charge was conducted according to the multi current step procedure previously envisaged (Moncada et al. 2014), consisting in a step-wise current increase from C/5 up to C, letting an electric charge equal to the gravimetric capacity of electrode pass in each step. A typical profile voltage vs time for the first charge is shown in Figure 3. The first step must be conducted at low C-rate, usually 1C, for guaranteeing the nanostructured electrode mechanical stability, which could be jeopardized if the cell voltage abruptly increases up to a value where abundant and turbulent gas evolution occurs. After first cycle, nanostructured Pb electrode was tested at C-rate equal to 1C. Figure 4 shows a typical discharge capacity vs. cycles number plot.

It shows that the battery assembled with Pb NWs drains electrical charge increasing with cycles number, up to a value of 216.2 mAh g^{-1}. This value is highly satisfying as compared with 233.04 mAh g^{-1} that is the maximum drainable specific charge, since the discharge was set for an upper limit of 90% of the electrode capacity that is 258.93 $mAhg^{-1}$ for lead.

In practice, the value of 216.2 mAg^{-1} is the 92.77% of the expected drainable charge. For comparison, commercial lead-acid battery shows efficiency not more than 50% at C/5.n Figure 4 also shows that the under cycling drained charge growth rate decreases after about 100 cycles, which can be considered as a curing period for achieving the best performance.

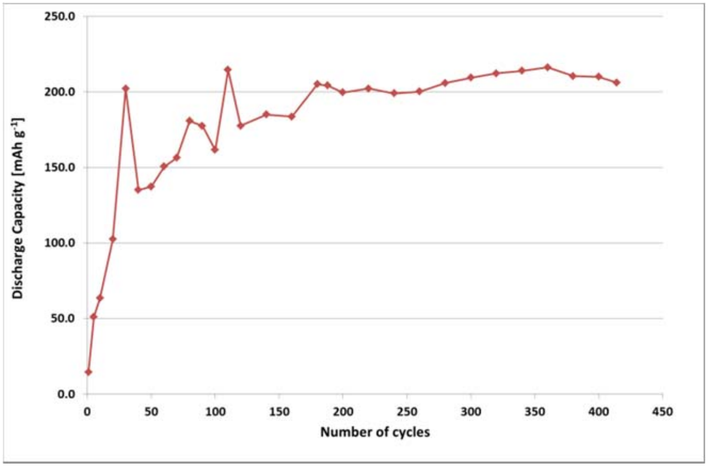

Figure 4: Discharge capacity of nanostructured electrodes obtained for charge/discharge performed at 1C.

This conclusion is further confirmed by Figure 5 curves, evidencing that the discharge curves remain constant for a longer potential interval as cycles number increases. Also this result is of technological relevance because evidences the true utilization interval of the battery, which have to be as long as possible for a better utilization degree over cycling. The ideal potential vs. time discharge curve is rectangular in the shape, with final fall when the stored charge has been completely drained. Unfortunately, the real battery is affected by kinetic polarization determining more or less sloping discharge curve, so that the potential utilization interval is more or less narrow, with consequent waste of the electrical charge drained outside the constant interval. From this point of view, therefore, a battery is so much more than value how much more elevated it is the discharge rate that preserves a long constant potential interval.

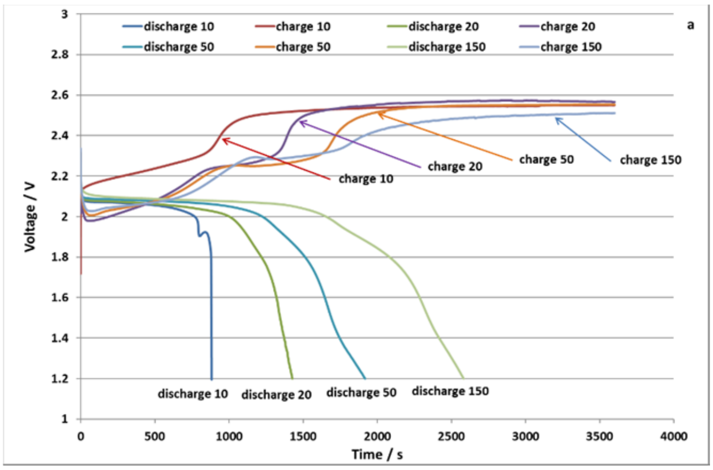

Figure 5: Charge/discharge curves at 1C: a)Charge/discharge curves from the 10th cycle to the 150th cycle; b) Charge/discharge curves from the 150th cycle to the 450th (continue)

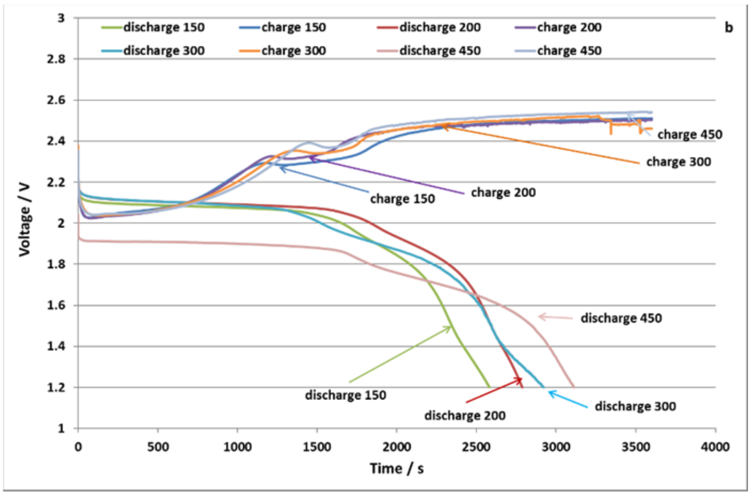

Figure 5: Charge/discharge curves at 1C: a)Charge/discharge curves from the 10th cycle to the 150th cycle; b) Charge/discharge curves from the 150th cycle to the 450th

Figure 6 shows the morphology of Pb electrode at end-of-life after 1200 cycles. In practice, electrode, initially, consists of Pb NWs, more or less interconnected in dependence on the morphology of the template. On cycling, the NW morphology is lost, but the nanostructured one is saved owing to the formation of a porous mass that guarantees good permeation of the sulphuric acid for high number of cycles, without fast agglomeration that, on the contrary, negatively affects the commercial lead-acid battery.

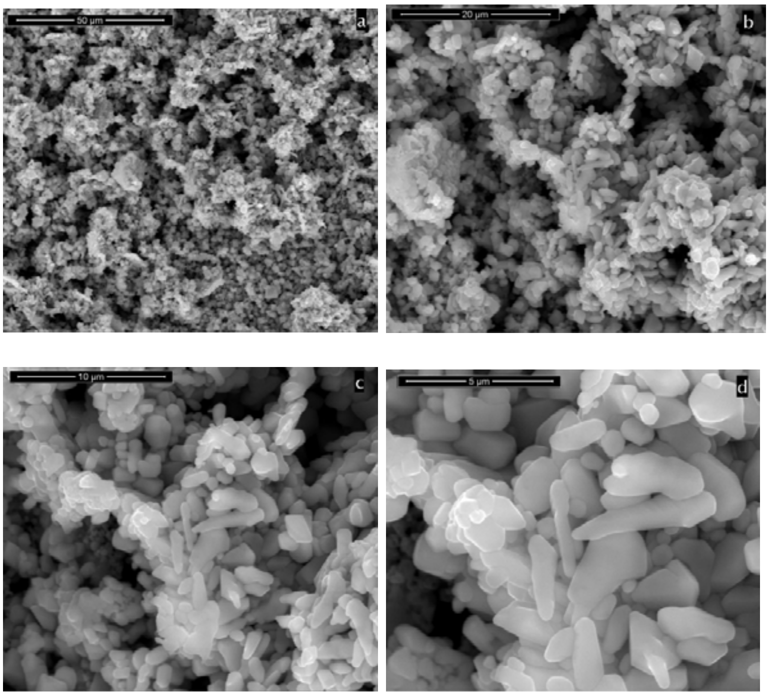

Figure 6: SEM images of nanostructured Pb

The typical X-ray diffraction pattern of a nanonostructured lead electrode at end-of-life of Figure 7 evidences the presence of $PbSO_4$, as expected for an electrode at end-of life. In turn, it must be emphasized that despite the presence of $PbSO_4$, which, likely, does not convert in metallic lead, the micrographs of Figure 6 shows the presence of a high number of empty places, so that the decay of the nanostructured electrode can be attributed to its sulphatation, which occurs after about 1200 cycles, for the conditions of the present study, which was very severe.

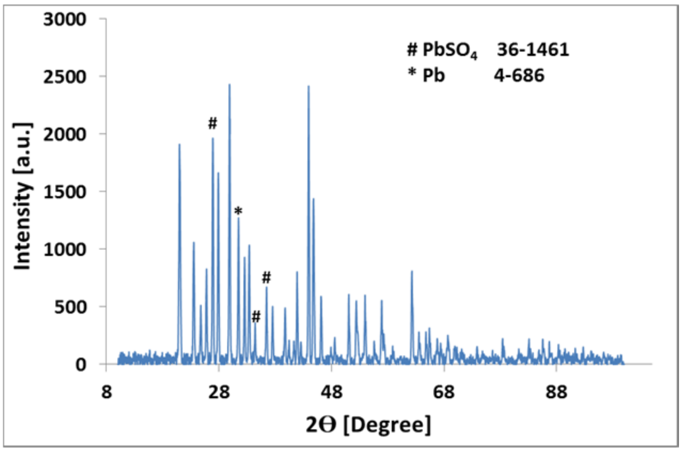

Figure 7: XRD pattern of a Pb nanostructured electrode at end-of-life after 1200 cycles

4. Conclusions

Lead NWs were synthesized through electrodeposition in polycarbonate membrane acting as a template, and were investigated as an anode in electrochemical cells simulating, at lab scale, a lead-acid battery. The results are highly encouraging, because, after a suitable initial charging and a curing period about 100 cycles long, the battery works at C-rate as high as 1C with coulombic efficiency of about 90% and long interval of constant potential. The results are much more valuable taking into account the strong stressing conditions that were selected for cycling the battery. For instance, the cut-off potential was set at 1.2 V, which is strongly discouraged for commercial lead-acid battery. The high performance of this kind of electrode was attributed to a distinctive morphology that can be obtained only starting from NWs.

Moving from the present results, and ones relative to PbO_2 NWs, investigated in the past, further work is in progress for studying the performance of battery assembled with both nanostructured electrodes.

Reference

Bača P, Křivík P., Tošer P., Vaculík S., 2015, Negative Lead-Acid Battery Electrodes Droped with Glass Fibres, Int. J. Electrochem. Sci, 10, 2206 – 2219.

Inguanta R., Randazzo S., Moncada A., Mistretta M.C., Piazza S., Sunseri C., 2013, Growth and Electrochemical Performance of Lead and Lead Oxide Nanowire Arrays as Electrodes for Lead-Acid Batteries, Chemical Engineering Transactions, 32, 2227-2232

Inguanta R., G. Ferrara, Piazza S., Sunseri C., 2011, Fabrication and characterization of metal and metal oxide nanostructures grown by metal displacement deposition into anodic alumina membranes, Chemical Engineering Transactions, 24, 199-204

Inguanta R., G. Ferrara, Piazza S., Sunseri C., 2009, Nanostructures fabrication by template deposition into anodic alumina membranes, Chemical Engineering Transactions, 17, 957-962

International Centre for Diffraction Data 2007 , Power Diffraction File (2007), Pennsylvania USA

Junsheng Zhu, Guangzhou Hu, Xiaoming Yue1, Dianlong Wang, 2016, Study of Graphene as a Negative Additive for Valve-Regulated Lead-Acid Batteries Working under High-Rate Partial-State-Of-Charge Conditions, Int. J. Electrochem. Sci., 11, 700 – 709

Moncada A., Inguanta R., Piazza S., Sunseri C., 2015a, Performance of Nanostructured Electrode in Lead Acid Battery, Chemical Engineering Transactions,43, 751-756

Moncada A., Piazza S., Sunseri C., Inguanta R., 2015b, Recent improvements in PbO2 nanowire electrodes for lead-acid battery, J. Power Sources, 275, 181-188

Moncada A., MIstretta M.C., Randazzo S., Piazza S., Sunseri C., Inguanta R., 2014, High-performance of PbO2 nanowire electrodes for lead-acid battery, J. Power Sources, 256, 72-79

Nanjan S., Paul E., Steven W. S., Dubey D.P., 2015, Lead acid battery performance and cycle life increased through addition of discrete carbon nanotubes to both electrodes, Journal of Power Sources 279, 281-293

Pavlov D., 2011, Lead-Acid Batteries: Science and Technology, Elsevier, Amsterdam, The Nederlans.