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Performance of Nanostructured Electrode in Lead Acid Battery

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Lead acid batteries have a large number of potential advantages, but the high weight of lead limits their use in new technologies, like hybrid or electrical cars, which require light batteries with high specific energy. We tried to overtake this limit with nanostructured electrodes of PbO_2 and Pb, obtained by electrodeposition in polycarbonate template. In the case of lead, to obtain electrodes with very good mechanical stability, a systematic investigation of electrodeposition process was needed to overcome the formation of dendrites that is the principal limitation of electrochemical production of metal lead.

Nanostructured electrodes were tested in a zero gap configuration, using commercial plates as counter-electrode and an AGM type separator in a 5M H_2SO_4 aqueous solution. Electrochemical tests were performed in very stressing conditions, cell was discharged up to 90% of the gravimetric charge of nanostructured electrode up to a cut-off voltage of 1.2 V. Charge/discharge tests were carried out at high C-rate (2C, 5C and 10C) and excellent results have been obtained. After a short stabilization period (about 100 cycles), the nanostructured electrodes are able to work for more than 1,000 cycles with high discharge capacity. These findings indicate that lead-acid batteries made with nanostructured electrodes are able to work at high C-rate, never reached with commercially available lead-acid batteries.

1. Introduction

Lead acid batteries are widely diffuse thanks to their advantages like availability, low cost, safety and stable performances. Nevertheless, their use in hybrid or electric vehicles is not possible because of the low specific energy. In fact, as reported by Moseley (2009), in order to use a battery in electric vehicles (PHEVs) it is necessary that it is able to operate at partial-state-of-charge and to provide and accept charge, for short periods, at very high rates. Under this condition, conventional lead-acid batteries accumulate lead sulphate which limits the cycle life of battery, because the presence of this non-conductive phase interrupts the electrical continuity of the active mass. To overcome this problem the most common approach is that to add conductive additive, such as different type of carbon nanostructures, with very high surface area (1,000-2,000 m^2 g^{-1}), to active negative paste. Following this approach, Pavlov et al. (2009) have obtained the improvement of efficiency and life cycle, because the presence of active carbon changed the structure of negative active mass and reduced the charge potentials. Also Hong at al. (2014), using negative plate composed by nano lead and active carbon (nano-Pb/AC), obtained higher capacity and better performance than conventional battery. Another interesting method is that to increase the porosity of active paste, by adding non-conductive additive, in order to improve the diffusion of electrolyte. In a very recent study, Liu et al. (2014) have studied the effect of use of nanocrystalline $PbSO_4$ of different sizes. They showed that it is possible to obtain stable and high discharge capacity utilizing the smallest $PbSO_4$ crystal.

For the same purpose, Lang et al. (2014) used nanometer tetrabasic lead sulphate (4BS) as positive active material additive, showing that it doesn't affect positive active material specific capacity. Besides they have found that the addition of 4 % nanometer 4BS can effectively improve the cycle life of the battery. Recent improvements on performance of positive plate were also obtained by Chen et al. (2013) that prepare a thin films of nanostructured PbO_2 by galvanostatic oxidation. Besides Zhang et al. (2014), using galvanostatic electrodeposition, have realized lead oxide electrodes using three-dimensional porous titanium as substrate,

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which has good electrical conductivity, high surface area and good corrosion resistance. They obtained electrodes with small charge transfer resistance, large electrochemical active surface area and a specific capacity of 132 mAh g^{-1}.

It is well known that the effective surface area is a critical parameter to obtain a very efficient electrode, because the electrochemical reactions take place at electrode/solution interface. For this reason the aim of our work is the fabrication of Pb and PbO_2 nanostructured electrodes, with not only high specific electroactive-area, due to the presence of array of nanowires, but with a high porosity that ensures the diffusion of electrolyte from surface to inner core of nanostructured electrode. This goal was achieved by the use of polycarbonate template that allows to obtain nanostructured electrode with an excellent grade of porosity. These nanostructured electrodes ensure stable performance in terms of discharge capacity for a high number of cycles and are able to delivery, at 1C rate, a specific capacity of about 190 mAh g^{-1}, close to the theoretical value of 224 mAh g^{-1} (Moncada et al., 2014). Considering these results, electrodes were tested at different C-rate, from 2C to 10C, for analysing their performances in very stressing conditions.

2. Experimental

2.1 Fabrication of electrodes

The experimental details for obtaining nanostructured electrodes were reported in our previous work (Inguanta et al. 2013). In particular, nanostructured electrodes were obtained by electrodeposition in polycarbonate template, with mean pore diameter of 200 nm and 15 µm thick. A two steps procedure was adopted in order to obtain in the first step the current collector, acting as electrical contact and support for nanowires, and in the second step the growth of nanowires into the pores of template. In both cases, a solution of 1 M $Pb(NO_3)_2$ and 0.3 M HNO_3 was employed, using a PAR Potentiostat/Galvanostat (mod. PARSTAT 2273). Current collector was obtained by galvanostatic deposition at room temperature while nanowires growth was carried out at 60 °C by potentiostatic deposition. After electrodeposition, polycarbonate was dissolved in pure $CHCl_3$, for exposing the nanostructured electrode.

Nanostructured Pb electrodes were obtained by pulsed current deposition at room temperature. This procedure was optimized in order to avoid the formation of dendritic structures. Thickness of current collector and length of nanowires were controlled by the number of applied pulsed cycles.

Morphological analysis were carried out by using a Scanning Electron Microscope (model FEI Quanta 200) before and after the electrochemical tests.

2.2 Electrochemical tests

Nanostructured electrodes were assembled in battery and tested in H_2SO_4 5M, using a commercial plate and a AGM type separator. Electrode capacity was calculated by gravimetric measurements, considering only the array of nanostructures as active material, using a Sartorius microbalance with high precision (mod. Premium Microbalance ME36S).

Mass of commercial plate is largely in excess in order to assure that the performances are completely ascribable to nanostructured electrode.

In the case of PbO_2 electrode, tests were conducted at different C-rate (2C, 5C and 10C); instead, Pb electrodes were tested only at 1C. In both cases, cut-off potential was fixed at 1.2 V and the battery was discharged up to 90 % of the gravimetric capacity. Even if cut-off potential should be set in depending on C-rate, we decided to maintain the value of 1.2 V for better comparing results.

3. Results and discussion

After membrane dissolution, SEM analysis were conducted on lead and lead dioxide in order to check the morphology and verify the absence of fractures or un-dissolved polycarbonate. SEM images of as prepared PbO_2 electrodes were reported in our previous paper (Moncada et al., 2014). The method of fabrication led to obtain straight nanowires perfectly connected to current collector.

Also in the case of Pb electrode we obtained regular nanowires with a height of about 15 µm, with a good adhesion to a current collector. Preliminary tests are in progress at 1C, using Pb electrodes obtained with different thickness of current collector in order to find the best working condition.

Very interesting are the results obtained in the case of PbO_2 electrodes that were tested from 1C to 10C (Moncada et al., 2015). In all conditions, for the first charge, the multi current step procedure was adopted that consists in increasing charge current from C/5 up to C or C-rate of working.

The first charge is a key step because, if electrode potential reaches high values, the parasitic reaction of gas evolution becomes favourite leading the breakage of nanostructured electrode. Gas evolution, in addition, causes water loss that must be replenished in order to prevent concentration of sulphuric acid (Pavlov, 2011).

Starting from the results discussed in (Moncada et al., 2014) we have adopted two different procedure of charge/discharge. In this our previous work, it was showed that in the first part of life cycle (for about 50-80 cycles) of electrode, a progressive increase of capacity occurs up to a quasi constant value of about 190 mAh g^{-1}. As reported in (Pavlov, 2011) this behaviour is typical of lead battery and was associated to a progressive change of morphology of electrode. Also in the case of nanostructured electrode, during this initial stabilization phase, a quasi radical modification of nanowires morphology was found. In particular as reported in (Moncada et al., 2014) during this phase an increase of electrode porosity was detected accompanied by the increase of wettability as measured by the contact angle measurements. To verify if this stabilization period is influenced by the C-rate we have tested some electrode directly at high C-rate, while others was initially stabilized for 100 cycles at 1C, and then the C-rate was increased up to the value of the test.

In the case of electrodes directly tested at high C rate we observed, mainly at 10C, a premature damage of electrode caused by high cell voltage that was reached during the first charges. Instead, the electrodes firstly stabilized at 1C for 100 cycles were able to work also at high C rate with a very high efficiency and for more than 1,000 cycles. Consequently, the modification of morphology that occurs during the stabilization phase is essential, especially at high charge/discharge rate, because the new form of active mass is able to drive a better diffusion of sulphuric acid onto the entire electrodic surface where electrochemical reactions happen. As mentioned above, after this short period of conditioning (one week), electrodes were tested at high C rate, reaching a capacity of about 200 mAh g^{-1} in few cycles and remaining constant for all lifetime of battery. These results were reported in Figure 1, where the discharge capacity of nanostructured electrodes (after the stabilization phase) was reported for different C rate.

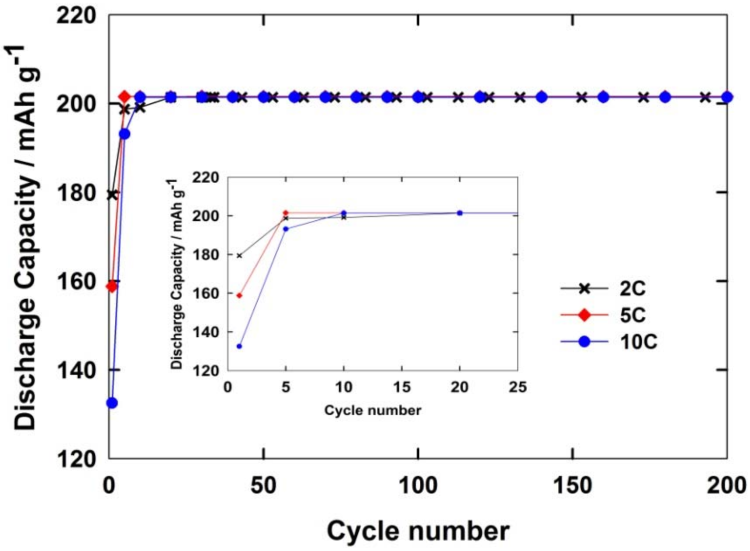

Figure 1: Discharge capacity of nanostructured electrodes obtained for charge/discharge performed at 2C, 5C and 10C, after 100 cycles at 1C.

In Figure 1 it can be observed that after the 20th cycle, in all cases, electrodes reached an efficiency of 90 %. It is important to highlight that at the end of 100 cycles at 1C, the efficiency of electrodes reaches a value of about 80 %. When C rate was increased from 1C to the test value, we have measured a drop on efficiency electrode that was more marked at 10C rate, where efficiency decreased instantaneously up to about 59 %. Despite this drop of efficiency, Figure 1 shows that the nanostructured electrodes are able to achieve a rapid adjustment at the new work conditions, obtaining high efficiency after few cycles at high C-rate.

From charge and discharge curves reported in figure 2, it is possible to observe the change of performances with cycle number. In particular in Figure 2 a) the first cycle, after conditioning, for the electrodes tested at different C rate was reported. From discharge curves we observed that the cut off potential was reached and the cell voltage of discharge decreases passing from 2C to 10C. This behaviour is coherent to that reported in the literature by Linden and Reddy (2007) for VRLA batteries. In fact, at higher current, the decrease of cell voltage is due to the increase of concentration polarization. In order to minimize this polarization, it is suggested to use electrode with appropriate porosity and pore size (Linden and Reddy, 2007). In addition porous electrode provides a high electrode surface area that reduces also charge-transfer polarization. For the same reasons, on the contrary, the cell voltage is the highest at 10C and lowest at 2C.

In the Figure 2 b) the charge/discharge curves of 100th cycle were reported. This figure shows that the cut-off voltage is not reached; the final cell voltage is equal to 2.02 V for the tests at 5C and 10C and it is higher at 2C, about 2.11 V. In all cases, the discharge curves showed a quasi-constant voltage for entire duration of discharge process. This result is very important because it means a quasi-constant energy supply during fast discharge. The charge curves presented at the beginning a rapid increase of the voltage, and then showed a constant trend and, at the end of charge, in the worst conditions, there is an increase up to 2.5 V.

In Figure 2 c), where the charge/discharge curves relative to 1,000th cycle were reported, no important differences in comparison to that described above can be observed. This confirms the stability of performance under cycling.

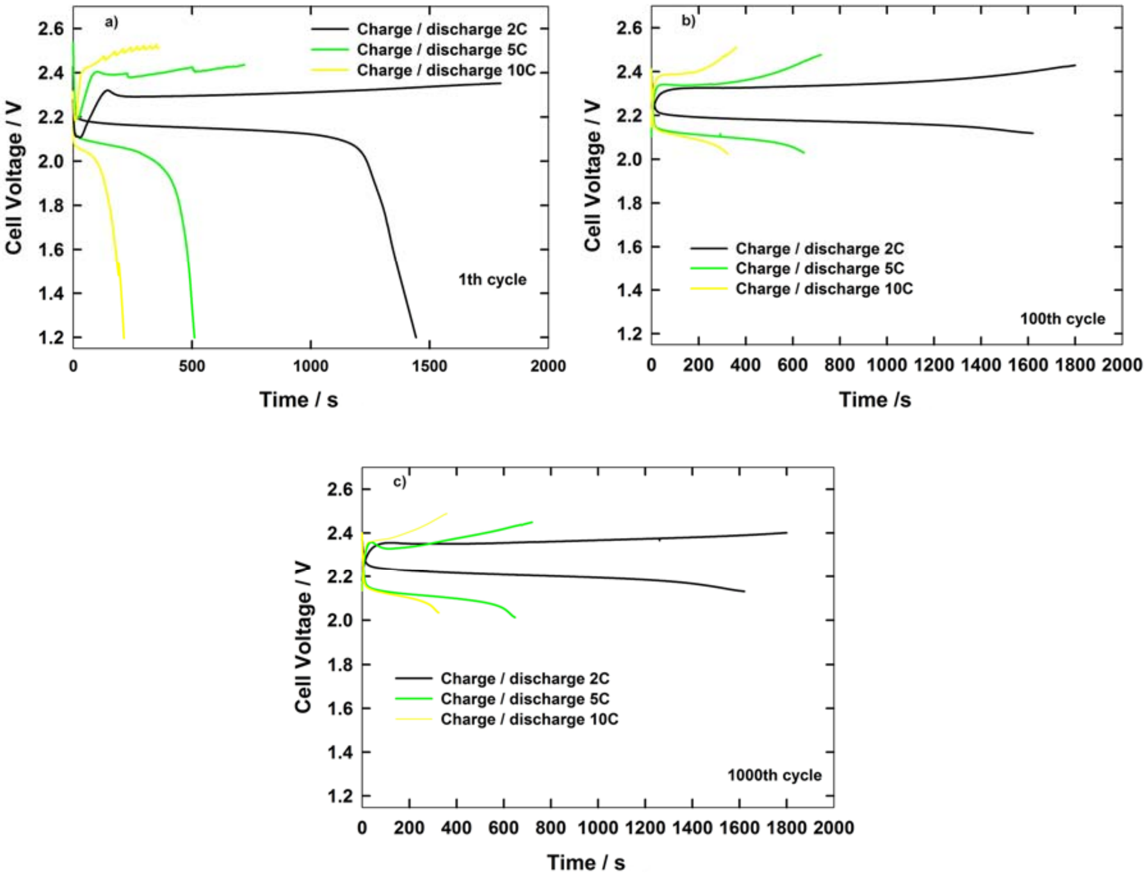

Figure 2: Charge and discharge curves at 2C, 5C and 10C, after conditioning period conducted at 1C for 100 cycles: a) 1th cycle, b) 100th cycle and in c) 1,000th cycle.

SEM analysis were carried out after cycling at high C-rate and, also in this case, we observed a substantial change in the nanowires shape. In Figure 3 a) was reported the SEM image of the as prepared PbO_2 nanowires, while Figures 3 b), c) and d) showed the morphology of the electrodes after more than 1,000 cycles carried out at 2C, 5C and 10C. If one compares these different SEM images, it is possible to see that at all C-rate a strong modification of electrode morphology occurred. Figures 3 b), c) and d) show a well-detailed morphology of the nanostructure evidencing that the initial cylindrical shape of nanowires was transformed in a very irregular profile extremely rough, forming a highly porous mass that favours the diffusion of electrolyte and thus is perfectly able to bear charge/discharge cycle at high C-rate. It is important to highlight that this feature is achievable thanks to the very high specific area of initial nanostructured electrode.

Here presented and discussed results indicate that template electrodeposited PbO_2 nanowires are an attractive alternative to the currently used pasted electrodes, because the nanostructured surface typically formed under cycling guarantees performances not achievable by usual pasted electrodes.
Further work is in progress concerning nanostructured Pb electrodes in order to assembly a battery with both nanostructured electrodes, in view of innovative technological application in the immediate future.

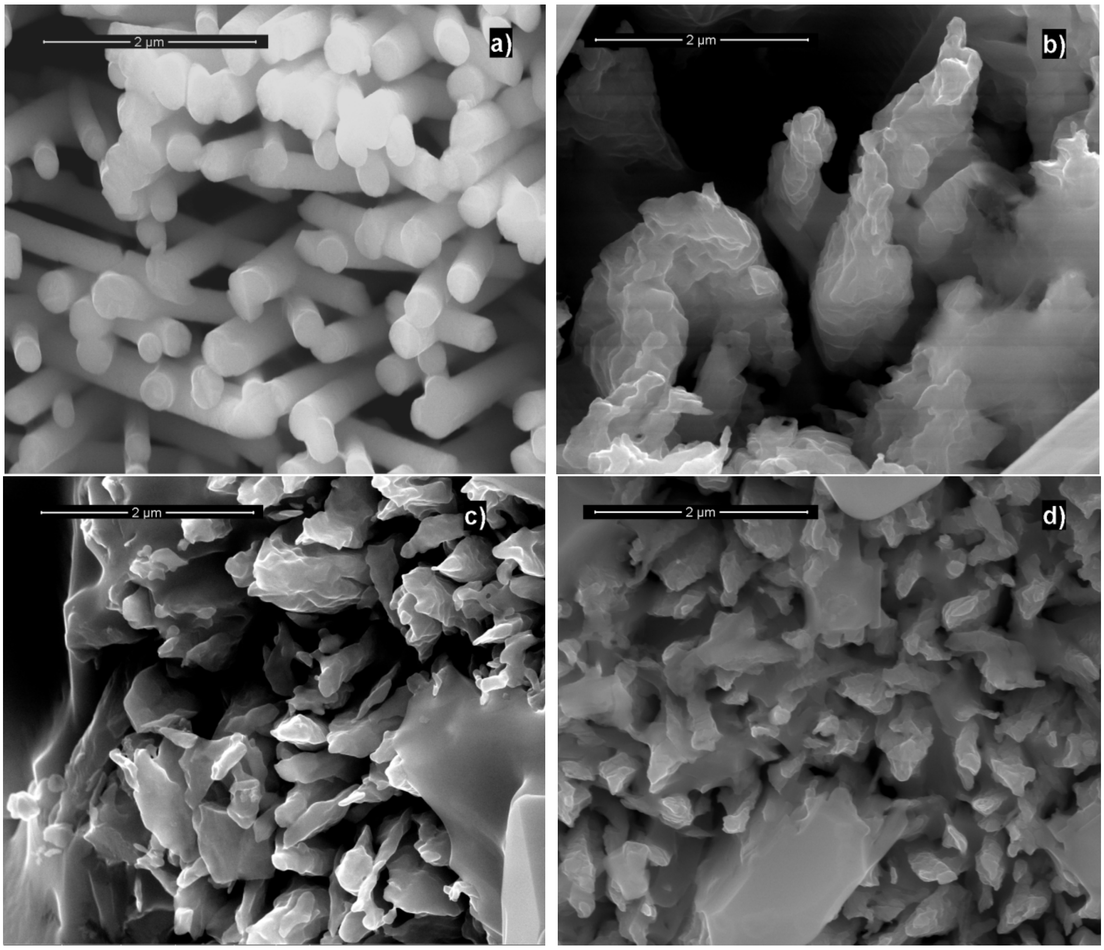

Figure 3 SEM images of nanostructured electrode; a) as prepared PbO_2 nanowires; b) c) and d) electrodes after more than 1,000 cycles at 2C, 5C and 10C.

Conclusions

In this work we have obtained nanostructured lead and lead dioxide electrodes by a simple template electrodeposition. After a systematic investigation we have obtained Pb nanowires well connected to a very compact lead current collector. Electrochemical tests in battery are in progress. Instead tests on PbO_2 electrodes permit us to confirm that high and stable discharge capacity was obtained.
These results show that thank to template electrodeposition, we are able to produce nanostructured electrode with very high surface area that favours the complete utilisation of active material. Electrochemical tests, in particular, show that in the initial phase of charge/discharge process a radical transformation of the initial electrode morphology occurs with the formation of a very spongy structure characterized by presence of high grade of porosity that assures penetration of the electrolyte in inner electrode area. In these conditions these new type of lead-acid batteries are able to work in condition never obtained by conventional batteries. Electrodes were tested at different C rate from 1C to up 10C and the results obtained at high C-rate are very encouraging because makes possible the use of nanostructured electrodes in advanced applications for lead acid battery such as electric mobility. It is important to highlight that conditions imposed at our tests are very stressing not only in terms of C-rate, but also for cut-off potential. In fact, commercial lead acid batteries work at C/5 in the best conditions whit a cut-off potential of about 1.75 V.

After the stabilization phase we obtain a discharge capacity of about 200 mAh g^{-1} for more than 1,000 cycles at all C-rate. Another important finding is that at each C-rate, after few initial cycles, discharge occurs without reaching the cut-off potential of 1.2 V. Besides, a quasi-constant voltage of about 2.1 V was recorded for almost all discharge curves that implies a quasi-constant energy supply during discharge at very fast C-rate.
We think that nanostructured electrodes can substitute the conventional plates and for these reasons our aim is to test a battery with both nanostructured electrodes.

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