

# Nanostructured Anode Material for Li-Ion Battery Obtained by Galvanic Process

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This work focused on the synthesis and characterization of nanostructured lead hydroxide chloride (PbOHCl) that is an innovative anode material for lithium-ion batteries (LIBs). In particular, we have obtained nanostructures of mixed PbOHCl and lead metal, directly into the pores of a commercially available alumina membrane, acting as template. The process was based on galvanic displacement reaction that was carried out in a two-compartment electrochemical cell without the use of an external power supply. This simple and cheap procedure gives regular array of Pb/PbOHCl composite nanowires.

To obtain nanostructured electrodes is a significant result because, it's well known that nanostructures have a variety of exceptional properties for Li-ion batteries applications such as high surface area, low diffusion path and good dimensional stability. This last property is fundamental because the active material of Li-ion battery are subject to very high strains due to volume change that occurs during charge/discharge cycles. In addition, the presence of lead creates a conductive network that reduces the resistivity of PbOHCl electrode.

## 1. Introduction

Electrochemical energy storage plays a fundamental role for efficient management of electrical energy. Among the different storage systems, lithium-ion batteries are considered the most challenging. Although their large commercial diffusion, they are still matter of hard research efforts, in order to improve costs, safety and energy density, that is low in comparison with fossil fuels (Scrosati, 2011). In this context, prevailing research efforts are directed toward finding alternatives to the current electrode materials, in order to extend the use of these batteries to applications of interest for the future.

Shu et al. (2013) early proposed the use of PbOHCl as anode for lithium-ion batteries, in order to improve the performance of lead-based anodes. In fact, although this material has shown clear advantages in terms of capacity and cost, it suffers severe limitations due to low cyclability. The high charge capacity is attributed to the formation of Li-Pb alloys with high content of lithium. The low lifetime is due to the fast degradation of the electrode due to its high expansion/contraction coupled to lithium alloying/de-alloying reactions (Martos et al., 2003; Ng et al., 2006; Pan et al., 2009).

The results by Shu et al. (2013) showed that performances of lead-based electrodes could be improved by a combined insertion of chloride and hydroxyl functional groups. By this way, it is possible to achieve a theoretical capacity of about 661 Ah/kg. The supposed reaction mechanism, involves initial conversion of PbOHCl into Pb, LiCl and LiOH. Then, the alloying reaction of Pb with Li can take place. According to this mechanism, the active material during repeated cycles undergoes pulverization and breakdown phenomena.

Starting from the results by Shu et al., (2013), we have investigated the synthesis and characterization of nanostructured PbOHCl. This is a key issue because nanostructures guarantee a high surface area enhancing the battery specific energy. In addition, they can limit active material pulverization because are able to better absorb mechanical stresses due to volume changes during charge/discharge cycles. The use of nanostructures also increases the penetration of Li alloying/de-alloying due to less diffusion path (Goriparti et al., 2014; Cheng et al., 2008). Consequently, nanostructured electrodes can sustain high charge/discharge rate favoring the possible use of these electrodes in batteries dedicated to applications requiring performances that only nanostructured materials can give.

In this work, we present the preliminary results of an innovative fabrication procedure that permit to obtain PbOHCl/Pb directly into the channels of a nanoporous template by a galvanic process (Inguanta et al., 2008, 2009a; Battaglia et al., 2013).

## 2. Experimental

For the fabrication of nanostructures, commercial anodic alumina membranes (Whatman, Anodisc 13), having a nominal pore diameter of about 200 nm, nominal thickness of 60  $\mu\text{m}$ , porosity of 25-30% and pore surface density of  $10^{12}$ - $10^{13}$  pores/ $\text{m}^2$ , were used as template. Prior to deposition, a thin gold layer was sputtered on one side of alumina membrane to make this surface electrically conductive (Inguanta et al., 2009b). A scheme of the experimental apparatus used for the fabrication of the nanostructures is showed in Figure 1. The fabrication process is based on galvanic contact between the gold layer at the base of membrane pores and a less noble metal, to create a potential difference. The galvanic couple was immersed in two different solutions contained into two separate cells ionically linked by a salt bridge. An adhesive copper tape at the bottom of membrane guaranteed the electrical continuity with the external circuit.

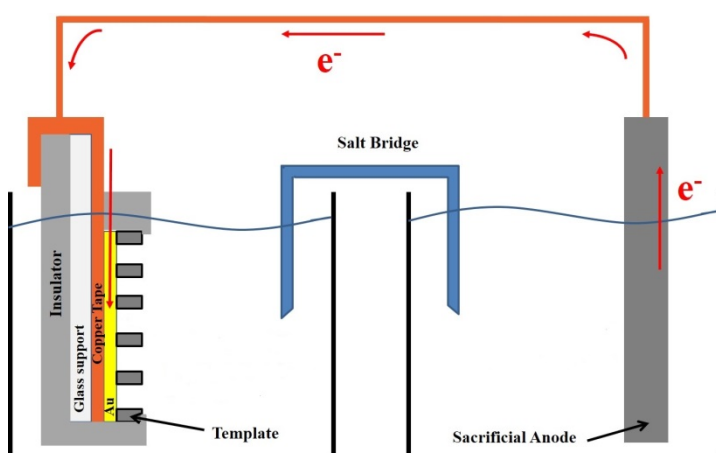


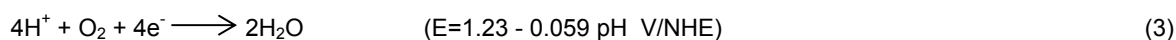
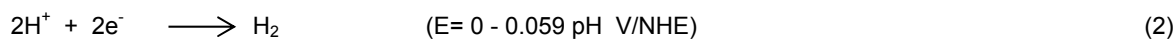
Figure 1: Scheme of the arrangement used for the fabrication of nanowires.

Working electrode consisted in gold covered anodic alumina membrane (AAM), with a surface area of the order of 0.785  $\text{cm}^2$ , that was immersed in the cathodic compartment containing 0.033 M  $\text{PbCl}_2$  aqueous solution. In the anodic compartment, a sacrificial aluminium, with a surface area of 3  $\text{cm}^2$ , was immersed in 1 M KCl solution. Deposition was conducted at room temperature for 24 hours.

The crystallographic structure of the nanowires was investigated by X-ray diffraction analysis (XRD), (Rigaku, D-MAX 25600 HK). All X-ray analyses were conducted in the  $2\theta$  range from  $5^\circ$  to  $80^\circ$  with a step of  $0.0263^\circ$  using the  $\text{Cu K}\alpha$  radiation ( $\lambda=1.54 \text{ \AA}$ ). Diffraction patterns were analyzed by comparison with ICDD database (ICDD, 2007). Nanowires morphology was investigated using a scanning electron microscopy (SEM, FEI mod.: QUANTA 200 FEG) equipped with an X-ray energy dispersive spectrometer (EDS). This analysis was carried out before the dissolution of AAM template to avoid deposit damage. Prior to SEM examination, samples were sputtered with a thin layer of gold in order to form a conductive film. Raman spectra were obtained at room temperature using a Renishaw (inVia model) micro-Raman spectrometer equipped with an Nd-Yang ( $\lambda=532 \text{ nm}$ ) laser giving a spot size of 2  $\mu\text{m}$ . Prior to Raman analysis, the system was calibrated by polycrystalline Si ( $520 \text{ cm}^{-1}$ ).

## 3. Results and Discussion

The scheme of the apparatus for the deposition is shown in Figure 1. The key feature is the galvanic contact between cathode (gold film covering the AAM bottom pores) and aluminum, acting as sacrificial anode. When the electrodes were immersed in the respective solutions, oxidation of aluminum occurred, with consequent electron flow through the external circuit from anodic area to the cathodic one, where the following reactions occurred:



The pH increase due to reactions Eq(2) and Eq(3) led to chemical precipitation of PbOHCl into the template channels, according to the reaction:



According to these reactions, the almost simultaneous occurrence of galvanic deposition Eq(1), and chemical precipitation Eq(4) likely should have to fill up pore template with Pb/PbOHCl composite compound.

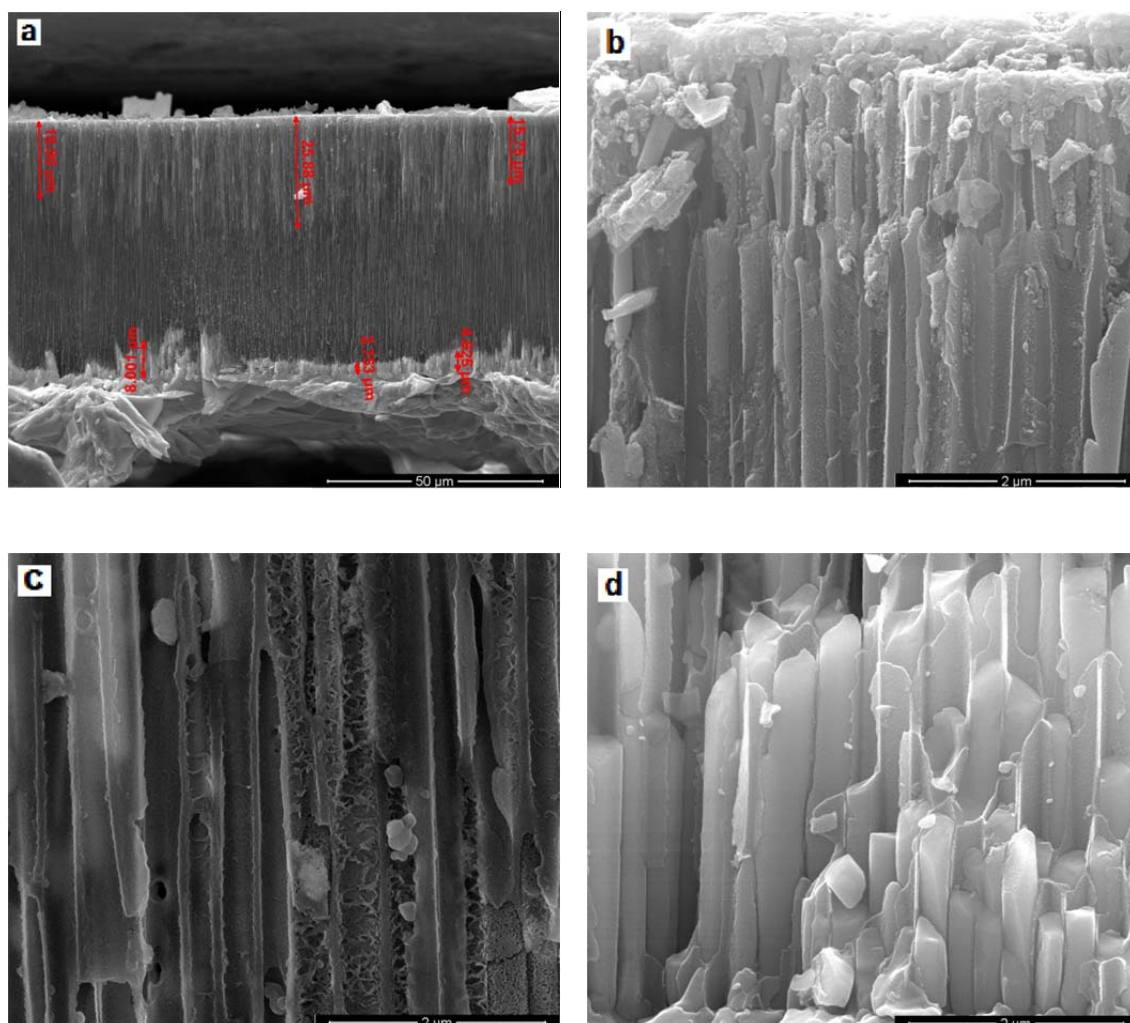


Figure 2: (a) SEM image of the template cross section view after galvanic deposition; (b), (c), and (d) high magnification images of bottom, central and top section, respectively.

This hypothesis was confirmed by the results of different analyses of the deposit. Initially, morphological analysis was carried out. Figure 2a shows the SEM image of alumina template cross section view after galvanic deposition. In this image, it is still possible to distinguish the vertical and parallel channels featuring the AAM template morphology. Porous nanostructures uniformly fill up for about 20  $\mu\text{m}$  the template bottom in contact with the gold film (top of the Figure 2a). At higher magnification, this morphology is shown in Figure 2b. Figure 2a shows also that a tubular shape deposit covers the channel walls, at the middle section. This

morphology is better visible at the higher magnification shown in Figure 2c. Besides, Figure 2a shows that very compact nanostructures fill up top of the template, for about 5  $\mu\text{m}$  in length. This morphology is better evidenced in Figure 2d. An abundant deposit covering the template surface is shown at the bottom of Figure 2a.

The chemical composition of the nanostructures was identified by EDS analysis carried out in different sections of the template. Elemental analysis revealed the only presence of the expected elements according to reactions Eq(1) and Eq(4): Pb, Cl, O. In addition, Al due to alumina membrane was also revealed. The Cl atomic fraction ( $\text{Cl}/(\text{Cl}+\text{Pb})$ ) was 30% at bottom and middle section of the template, while reached about 48% at top. Since Cl atomic fraction in PbOHCl is 50%, we can conclude that an excess of metallic lead was deposited at the bottom and middle height of the template pores. Instead, the deposit at the top of the channels and on the external surface was practically pure PbOHCl. These findings give a first confirm about formation of PbOHCl with the excess of Pb present in metallic form. Thus, a mixture of Pb/PbOHCl at about 43% of PbOHCl was approximately estimated at the bottom of the membrane.

A further confirm of the above assumption was found by XRD and Raman analysis. X-ray diffraction showed only PbOHCl which crystallizes in orthorhombic phase. As shown in Figure 3, the peaks of PbOHCl found in the ICDD database (ICDD card 31-680) exactly coincide with that ones of our sample. Instead, lead (ICDD card 4-686) is difficult to identify, because its main peak is located at  $31.3^\circ$ , among the two peaks of PbOHCl at  $31.138^\circ$  and  $31.475^\circ$ .

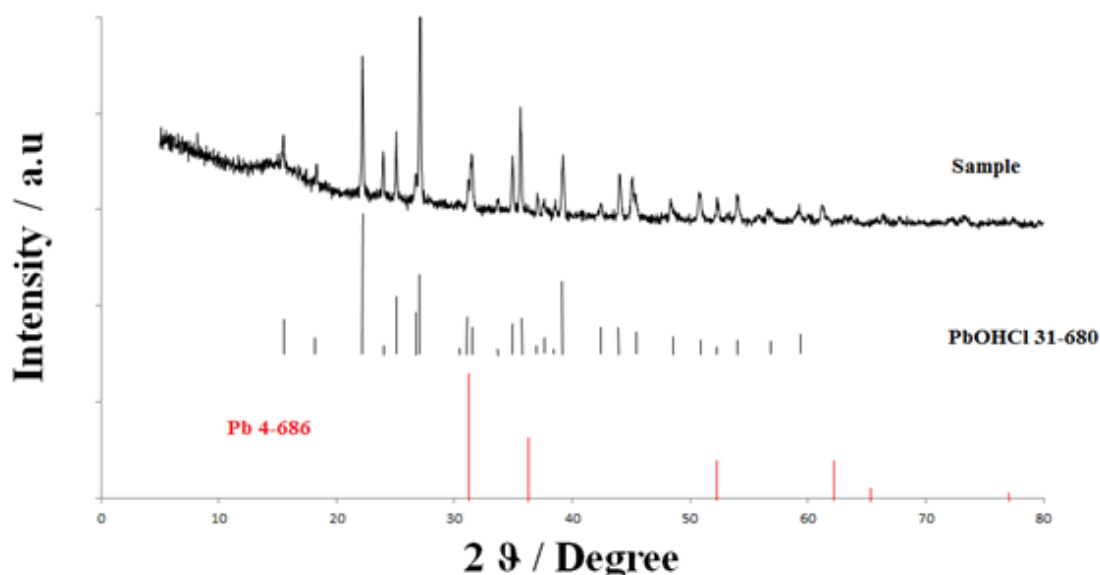


Figure 3: Diffraction patterns of the sample of Figure 2. For comparison, the peaks of Pb and PbOHCl of the ICDD cards are also reported.

In Figure 4, the Raman spectrum of the same sample is reported. For comparison, PbOHCl powder (hydrothermally prepared) and lead foil spectra were also acquired, in order to better identify the peaks in the spectrum of our samples. By comparing the spectrum of our sample with that one of PbOHCl powder, it can be observed that they are coincident except for the mode at about  $139\text{ cm}^{-1}$ , which is present only in the spectrum of sample. This mode can be probably associated at the presence of lead in mixture with PbOHCl, because it is almost coincident with the main Raman mode present in the spectrum of lead foil, that is located at about  $141\text{ cm}^{-1}$ . The Raman shift of about  $2\text{ cm}^{-1}$  is within the instrument detection limits. Thus, Raman spectroscopy confirms the results of EDS and XRD analyses supporting the formation of Pb/PbOHCl composite nanowires by galvanic deposition. This is a significant finding, because indicates the possibility of synthesizing a compound of high applicative interest by a cheap and facile procedure.

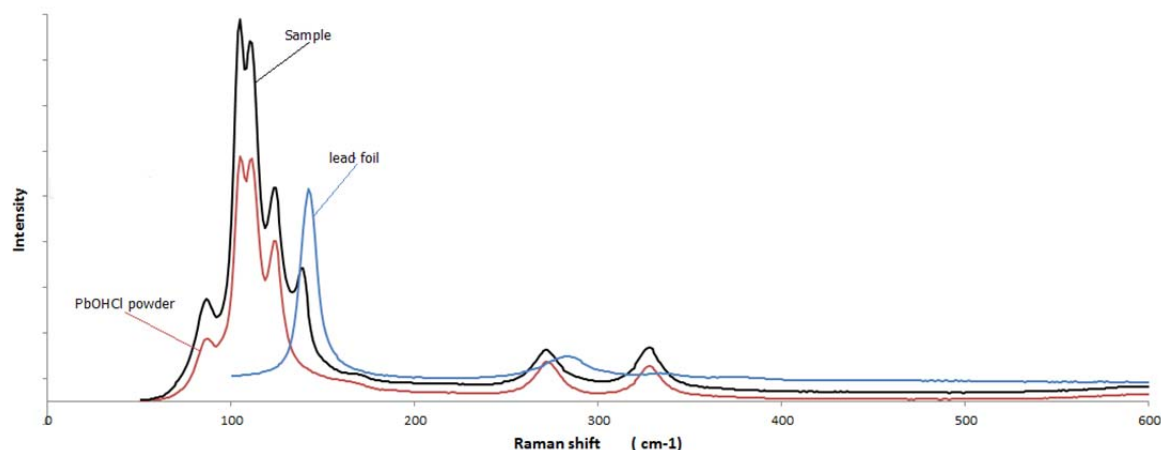


Figure 4: Raman spectra of the sample of Figure 2. For comparison, also the spectrum of the PbOHCl powder and of pure lead foil were reported.

In the light of these findings, we can shortly summarize the global process leading to the formation of Pb/PbOHCl. Initially, the hydrogen evolution reaction Eq(2), localized at the pore bottom, leads to a porous morphology. As pH increases inside the channels, precipitation of Pb/PbOHCl is occurring with progressive increase of the ohmic drops due to the high electric resistance of the precipitated phase, even if the presence of metallic lead guarantees the electrical continuity with gold film. Consequently, the base generation reaction continues inside the pores but at lower rate, because it takes place on Pb/PbOHCl. Being insulating, the reactions proceed at a lower rate than the initial one, determining a reduction of the quantity of Pb and PbOHCl deposited at the middle section. Besides, in this zone, the low rate of Pb/PbOHCl precipitation competes with the detachment rate of the hydrogen bubbles, which accumulate inside the pore forcing the deposit to assume a tubular shape, as demonstrated by other studies (Battaglia et al., 2013; Inguanta et al., 2011). Close to the pore inlet, solution is oxygen richer than interior because the mass transport is easier in this zone. Therefore, reaction Eq(3) contribution to base generation is enhanced with consequent fast and abundant precipitation of PbOHCl alone.

#### 4. Conclusions

A new method to obtain Pb/PbOHCl nanostructures without supplying external electrical energy was developed. The nanostructures were grown directly inside the channels of anodic alumina membrane used as template. For this purpose, a specific experimental arrangement based on galvanic contact between two differently noble metals was used. By this way, PbOHCl mixed with Pb metal was obtained. The presence of Pb metal is a key aspect for the application of these nanostructures as active anode material for Li-ion battery, because it creates a conductive network that reduces the PbOHCl resistivity. Morphology of the deposit was studied by SEM analysis that showed a uniform array of nanowire grown for a length of 20  $\mu\text{m}$  at the bottom of membrane in contact with gold. Close to the top and on the surface exposed to the solution, a pure PbOHCl deposit was obtained. EDS, X-Ray diffraction and Raman spectroscopy, confirmed these results. XRD analyses revealed also that the deposit was crystalline. Further work will be conducted for exploring the application of this deposit.

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