

Short communication

Nanostructured PbO materials obtained in situ by spray solution technique for Li-ion batteries

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Abstract

This paper describes a systematic study of the effect of various spray pyrolysis parameters, such as temperature, solution concentration and solution flow rate on the morphology, crystallization process, crystal size, specific surface area and electrochemical performance of in situ prepared α -PbO spherically agglomerated nano-structured powders. Different analytical methods such as XRD, SEM, TEM, BET gas sorption specific surface area measurements and electrochemical tests were performed. Crystallites in the range of 20–120 nm and easily dispersed powders were reproducibly prepared by optimization of the spray conditions. An increase of the temperature from 600 to 800 °C was found to lead to a three times increase in the average crystal size, from 31 to 102 nm. An increase of concentration from 0.15 to 0.5 M dramatically suppresses the crystal size from 127 to 25 nm. The BET surface area of sprayed PbO powders is increased up to 6.6 m² g⁻¹. For such PbO powders applied as anode materials in Li-ion batteries, we have managed to retain a reversible capacity above 60 mAh g⁻¹ beyond 50 cycles.

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1. Introduction

Modern technology, nowadays, appears impossible without the use of different portable rechargeable batteries in various electronic devices. The Li-ion batteries are among the most promising ones, and comprehensive research on novel cathode or anode materials is going on all over the world. During the last few years, the application of nano-structured oxide materials as anodes in Li-ion batteries has attracted considerable attention [1,2]. Among the different approaches the spray pyrolysis technique appears to be a fast, versatile and industry scalable method that is able to produce in situ, various nano-structured oxides [3,4]. This method is quite versatile and applicable for preparation of a large number of simple or complex oxides. Among them, PbO powders remain widely used because they are cheap and reliable materials for battery applications. The in situ preparation of such nano-structured materials with controlled structural and morphological characteristics has both scientific and practical importance [5–9]. At present there is only

scattered information regarding the influence of various spray pyrolysis process parameters on preparation of PbO powders with increased surface area [10] and their application as anode materials in Li-ion batteries. This paper describes a systematic investigation of the effect of temperature, solution concentration and solution flow rate on the morphological, physical and electrochemical characteristics of in situ prepared α -PbO spherically agglomerated nano-structured materials.

2. Experimental

All powders were obtained in situ by spraying various concentrations of Pb(NO₃)₂ aqueous solutions under different conditions, which are summarized in Table 1. A vertical-type spray pyrolysis reactor has been used for the experiment. Powder samples were analyzed by X-ray diffraction (XRD), using the diffractometer method with Cu K α radiation and graphite monochromator. Scanning electron microscopy (SEM) was performed using a JEOL JSM 6460A scanning electron microscope. Transmission electron microscopy (TEM) investigations were performed using a JEOL 2011 analytical electron microscope. TEM samples were prepared by deposition of ground particles onto lacey carbon support films. Gas sorption analysis using

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Table 1
Summary of experimental conditions and some physical characteristics for the sprayed PbO nano-structured oxides

Sample no.	1	2	3	4	5	6	7
Furnace temperature, T (°C)	600	700	800	700	700	700	700
Solution concentration, C (M)	0.50	0.50	0.50	0.15	0.30	0.50	0.50
Solution flow rate, Q (ml min ⁻¹)	3.14	3.14	3.14	1.57	1.57	1.57	4.71
Average crystal size, D_p (nm)	31	53	102	127	75	25	62
Specific surface area, S_{BET} (m ² g ⁻¹)	4.5	2.4	2.2	6.6	2.6	1.8	2.0

the Brunauer–Emmett–Teller (BET) method was employed to determine the specific surface area.

The anode was prepared by mixing PbO powders with 20 wt.% carbon black and 10 wt.% polyvinylidene fluoride (PVDF) binder in *N*-methyl-2-pyrrolidinone (NMP) solvent to form a homogeneous slurry, which was then spread onto a copper foil. The coated electrodes were dried in a vacuum oven at 100 °C for 24 h and then pressed. Electrochemical characterizations were carried out using coin cells (CR 2032) assembled in argon filled glove box. The electrolyte used was 1 M LiPF₆ in a 50:50 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) provided by MERCK KgaA. Subsequently, electrochemical tests were performed by galvanostatically charging/discharging the cells in the range of 0.01–1.50 V at a constant current density of 0.1 mA cm⁻² via a Neware Battery Tester.

3. Results and discussion

The XRD analysis shows that all powders exhibit either single tetragonal α -PbO phase with lattice parameters; $a = 0.3973$ nm and $c = 0.5022$ nm (ASTM 05-0561) or additional traces of orthorhombic β -PbO phase with lattice parameters; $a = 0.5489$, $b = 0.4755$ and $c = 0.5891$ nm (ASTM 05-0570), when the furnace temperature is increased from 600 to 800 °C. There were no traces of Pb₃O₄ in all materials. Some typical X-ray patterns are shown in Fig. 1. The well-known Debye–Scherrer formula was used to calculate the average crystal size using crystalline silicon as the reference material. Additional confirmation of crystallite size was obtained by TEM centered dark-field imaging (Fig. 2), where individual lead oxide crystallites were obtained by imaging particle clusters using lead oxide diffraction spots. Fig. 2 shows dark-field images of crushed particles showing approximate lead oxide crystallite size in samples sprayed at 600 °C (Fig. 2(a)) and at 800 °C (Fig. 2(b)).

First of all, the effect of furnace temperature on the average crystal size has been evaluated (Table 1). As seen from Table 1, a temperature increase from 600 to 800 °C leads logically to a crystal size increase from 31 to 102 nm (samples 1, 2 and 3). To determine the temperature effect, both the concentration and flow rate were kept constant (0.5 M and 3.14 ml min⁻¹). Contrary to the temperature effect, an increase in the solution concentration has a pronounced negative effect on the crystal growth (samples 4, 5 and 6). The average crystal size decreases almost linearly from 127 to 25 nm when the concentration increases from 0.15 to 0.5 M. All materials were sprayed at 700 °C using a flow rate of 1.57 ml min⁻¹. This result can be explained by

the increased number of crystallization centers in solutions with higher Pb concentration and the consequent blocking effect on crystal growth due to the simultaneous crystallization of more crystallites within the particles. Finally, we have studied the effect of the flow rate on the crystallization process and average crystal size. The result for samples 2, 5 and 7 show that there is no clear dependence between these parameters. These materials were sprayed at 700 °C using 0.5 M solutions.

It was expected that variation of the flow rate could affect the particle size of the in situ obtained PbO powders. However, SEM results did not confirm this assumption either. The agglomerates with spherical shape, which is typical for the spray process, are in the range of 0.5–5 μ m for all powders and the size is not dependent on the flow rate. The temperature has a small effect for this temperature range (Fig. 3), and the materials obtained at 800 °C reveal more crystalline and inter-growing particles, while powders obtained at 600 °C have particles with fine nano-porous structure. The particle size appears to increase at higher temperature due to the intergrowth process. This would be expected to result in a lower specific surface area of materials (S_{BET}).

The BET results clearly confirm the SEM observations. An increase of the temperature causes a pronounced decrease of the S_{BET} (see the results for samples 1, 2 and 3 in Table 1). The powders obtained at 600 °C exhibit a remarkably high S_{BET} value of 4.5 m² g⁻¹ (for comparison, the conventional Aldrich

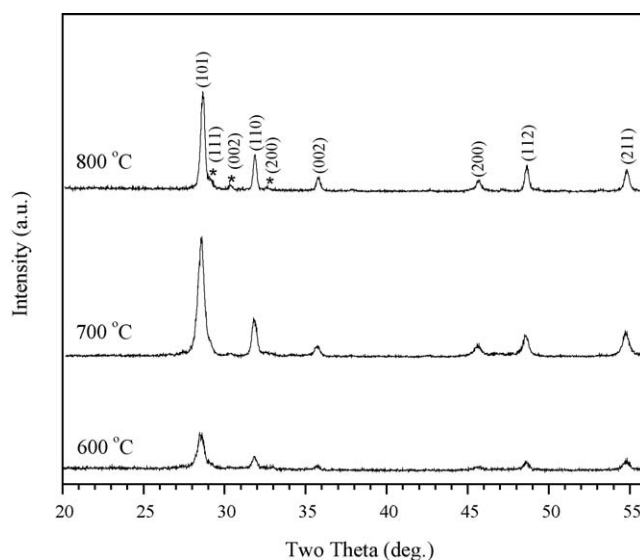


Fig. 1. Typical XRD patterns of α -PbO powders sprayed at different temperatures. The solution concentration was 0.5 M and the flow rate was 3.14 ml min⁻¹. The traces of β -PbO are marked by asterisk (*).

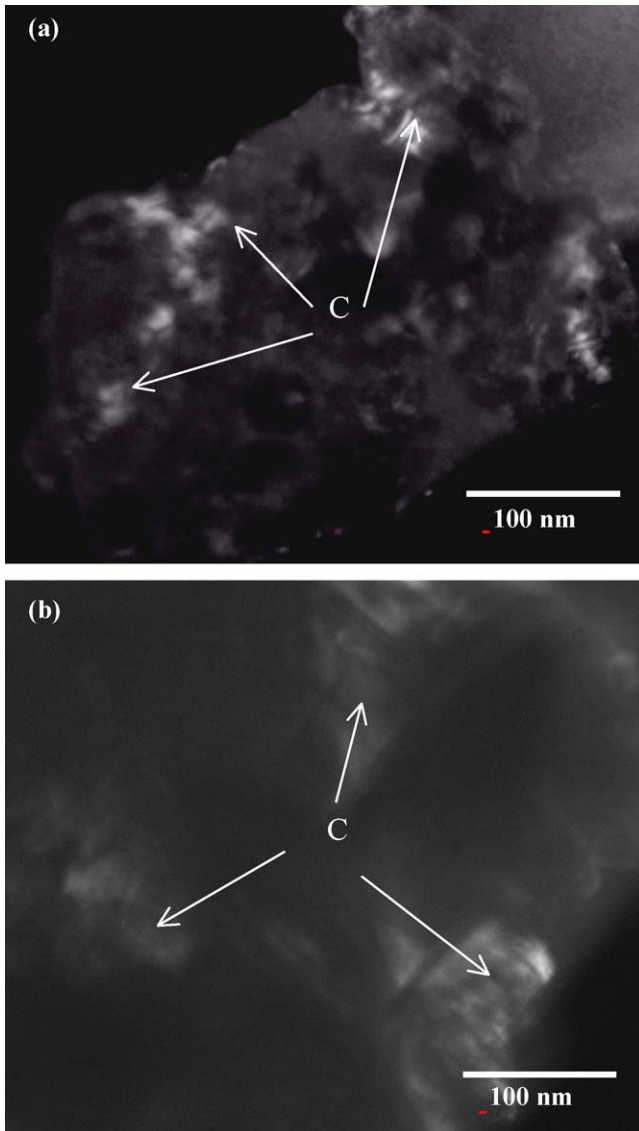


Fig. 2. TEM dark-field images obtained from samples sprayed at (a) 600 °C and (b) 800 °C. Individual crystallites are marked as C.

PbO has only $0.5 \text{ m}^2 \text{ g}^{-1}$). The materials obtained at 800 °C have only $2.2 \text{ m}^2 \text{ g}^{-1}$; all other factors were kept constant: solution concentration 0.5 M and flow rate 3.14 ml min^{-1} .

The effect of solution concentration on S_{BET} was found to be similar (Table 1, samples 4, 5 and 6). A higher concentration promotes a lower specific surface area. Increasing the concentration from 0.15 to 0.5 M causes a decrease of S_{BET} from 6.6 to $1.8 \text{ m}^2 \text{ g}^{-1}$. These results are obtained for 700 °C and a flow rate of 3.14 ml min^{-1} . The results regarding the S_{BET} are very important because they demonstrate that large specific surface area should not be always associated with the small crystal size. We have already reported [3] similar results for nano-structured oxides, e.g. Co_3O_4 , CoO , NiO , SnO_2 obtained in situ by spray technology. Quite often the very small nano-crystallites stack together due to their high surface energy and create very dense packing, which reduces the specific surface area. The strong agglomeration effect observed for nano-structured oxides is an

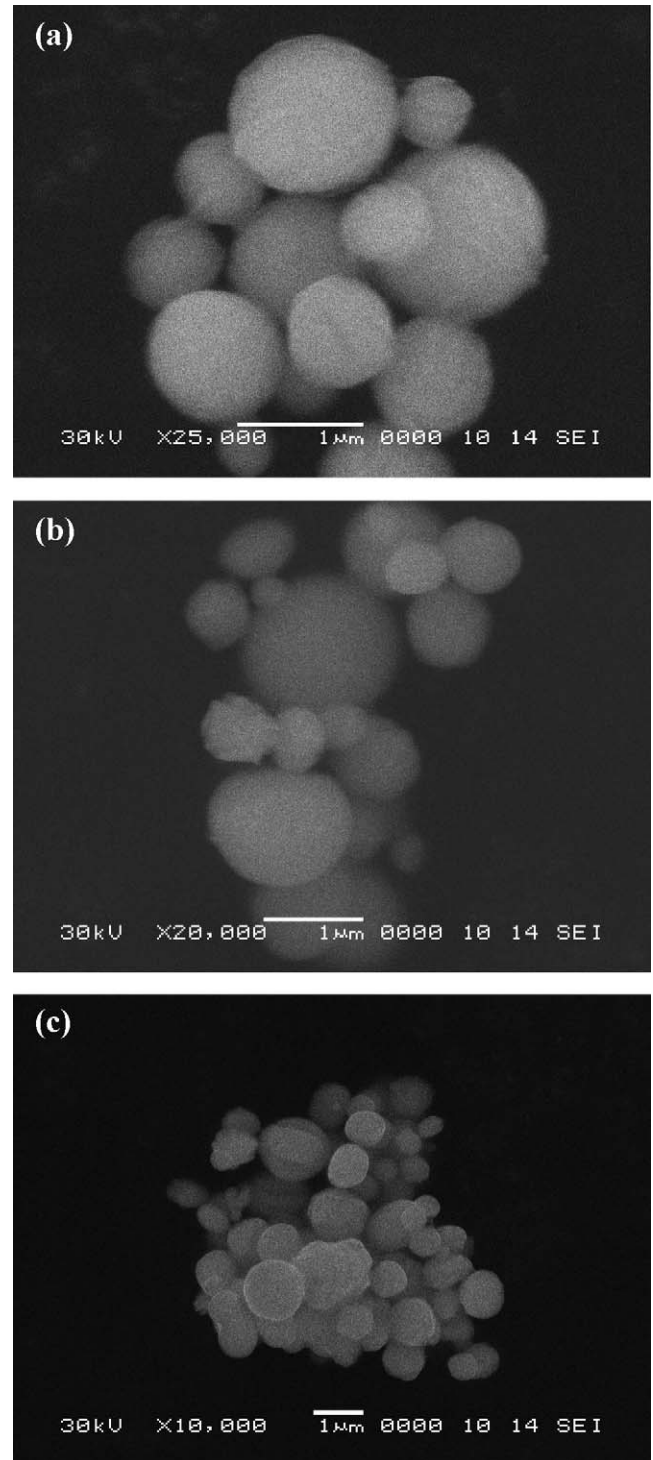


Fig. 3. Typical SEM images of powders sprayed at (a) 600 °C, (b) 700 °C and (c) 800 °C. The solution concentration is 0.5 M and the flow rate was 3.14 ml min^{-1} .

important problem, which should be taken into account for practical utilization of such materials in energy savings applications where a large specific surface area is an important factor.

In Fig. 4 some typical discharge capacity dependencies for materials obtained under different conditions are given. We could not find a simple dependence between the irreversible capacity or cycle life and specific surface area or average crys-

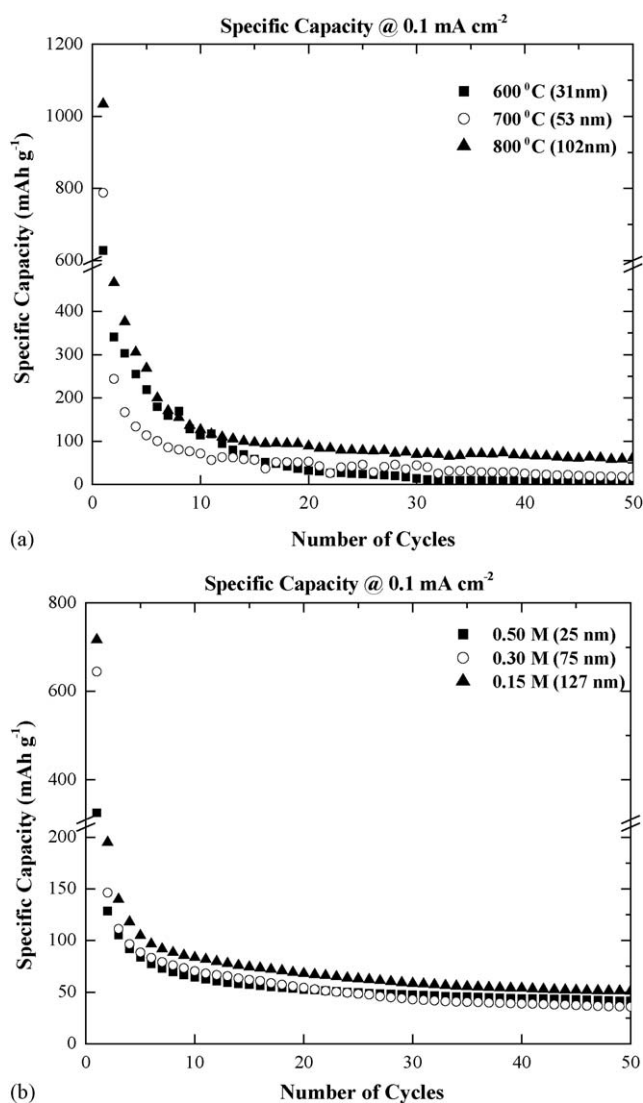


Fig. 4. Discharge capacity dependencies of PbO materials sprayed at (a) different temperatures at 0.5 M and 3.14 ml min⁻¹, and at (b) different solution concentrations at 700 °C and 1.57 ml min⁻¹.

tal size. As a general trend, materials with crystal sizes around 100–120 nm exhibit better cycle life compared to the powders with small crystal size. However, it is worth remembering that the cycle life and capacity depend on many other factors, including preparation conditions, and complementary detailed experiments are needed before making any definitive conclusions regarding the role and dependency of all these parameters. The best performing powder was the PbO sprayed at 800 °C from a 0.5 M solution at a flow rate of 3.14 ml min⁻¹. It had a discharge capacity of 61 mAh g⁻¹ after 50 cycles. This result is much better than those produced by Martos et al. [6], where the PbO powders give a discharge capacity less than 20 mAh g⁻¹ beyond 30 cycles only.

According to the literature data, during the first discharge, there will be a reduction peak between 1.45 and 0.9 V on the CV dependence. The peak between 1.45 and 0.9 V can be denoted to the replacement reaction of PbO to Pb and formation of Li₂O. According to Martos et al. [6,7], this transformation of Pb (II) → Pb (0) takes place through some intermediates, i.e. Pb (I). The low potential region (<0.9 V) will exhibit several peaks correspond to the formation of Li_xPb alloys. Huggins [8] identified four potential plateaus at 0.601, 0.449, 0.374 and 0.292 V over the composition range 0 < x < 4.5 (i.e. LiPb, Li_{3.0}Pb, Li_{3.2}Pb and Li_{4.5}Pb). The alloying and de-alloying of lithium with lead over the 1.0–0.01 V yield various Li_xPb (x < 4.5) alloys.

4. Conclusions

Single-phase α-PbO powders were obtained in situ by a spray pyrolysis technique. An increase of the furnace temperature from 600 to 800 °C leads to a three times increase of the average crystal size from 31 to 102 nm. An increase of concentration from 0.15 to 0.5 M dramatically suppresses the crystal size from 127 to 25 nm. The BET surface area of the sprayed PbO powders was increased up to 6.6 m² g⁻¹. Applied as anode materials in Li-ion batteries, the PbO sprayed materials retain a reversible capacity above 60 mAh g⁻¹ beyond 50 cycles.

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References

- [1] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.-M. Tarascon, *Nature* 407 (2000) 496.
- [2] Y. Li, C. Wan, Y. Wu, C. Jiang, Y. Zhu, *J. Power Sources* 85 (2000) 294.
- [3] K. Konstantinov, Z.W. Zhao, L. Yuan, H.K. Liu, S.X. S. Dou, *Proceedings Advanced Materials for Energy Conversion II TMS Annual Meeting, Charlotte, USA, 2004*, pp. 331–338.
- [4] L. Yuan, K. Konstantinov, G.X. Wang, H.K. Liu, *Proceedings European Micro and Nano Systems, Paris, France, 2004*, pp. 257–260.
- [5] Z.W. Zhao, K. Konstantinov, L. Yuan, H.K. Liu, S.X. Dou, *J. Nanosci. Nanotech.* 4 (2004) 861.
- [6] M. Martos, J. Morales, L. Sanchez, R. Ayouchi, D. Leinen, F. Martin, J.R. Ramos Barrado, *Electrochim. Acta* 46 (2001) 2939.
- [7] M. Martos, J. Morales, L. Sanchez, *Electrochim. Acta* 48 (2003) 615.
- [8] R.A. Huggins, *Solid State Ionics* 113–115 (1998) 57.
- [9] H. Li, X. Huang, L. Chen, *Solid State Ionics* 123 (1999) 189.
- [10] K. Konstantinov, J. Wang, S. Bewlay, G.X. Wang, H.K. Liu, S.X. Dou, J.-H. Ahn, *J. Metastable Nanocryst. Mater.* 15–16 (2003) 325.