
TECHNICAL NOTE

ELECTROCHEMICAL EVALUATION OF PbO NANOPARTICLES AS ANODE FOR LITHIUM ION BATTERIES

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(Received: October 28, 2010 – Accepted in Revised Form: October 20, 2011)

doi: 10.5829/idosi.ije.2011.24.04b.05

Abstract PbO nanoparticles were synthesized using hydrothermal process. Scanning electron microscopy (SEM) was used in order to investigate of PbO powders. X-ray diffraction (XRD) pattern confirmed β -PbO formation during this process. The crystallite size of the powders was calculated to be about 74.6 nm using Scherrer formula. Electrochemical evaluation of PbO nanoparticles as anode for Li-ion batteries shows that two reactions have occurred during the first discharge. Some intermediates also were seen during Pb alloying with Li. The cyclic loading of PbO nanoparticles show reversible capacity higher than 125 mAh g⁻¹.

Keywords Anode material, Lead-oxide, Hydrothermal, Li-ion Batteries

چکیده نانوذرات PbO به روش هیدروترمال ساخته شدند. از میکروسکوپ الکترونی روبشی برای بررسی پودر PbO حاصل استفاده گردید. الگوی پراش اشعه ایکس تشکیل فاز β -PbO را تأیید می کند. اندازه کریستالیت ها به روش شرر محاسبه شده و حدود ۷۴/۶nm به دست آمدند. ارزیابی الکتروشیمیایی نانوذرات PbO به عنوان آند باتری های یون لیتیم دو واکنش را حین دشارژ اولیه نشان داد. همچنین فازهای میانی دیگری طی آلیاژ شدن سرب با لیتیم رخ می دهد. ظرفیت برگشت پذیر نانوذرات طی کار سیکلی مقدار ۱۲۵ mAh/g را نشان می دهد.

1. INTRODUCTION

Lithium batteries emerged as a promising storage system for portable devices such as cell phones and electrical vehicles (EVs) [1]. Lithium metal was used as anode in these batteries. Lithium has low melting point and is reactive to the air and water. Therefore, replacing the lithium anode with other stable materials would be welcome. Carbon is used now as anode in Li-ion batteries. Many alloys and compounds such as Ni-Sn, Cu-Sn, Si-Sn, N-Sn, Zr-Sn, Sn-Zr-Ag and Li-based alloys are introduced as negative electrode materials in

Li-ion batteries [2-7]. These materials have twice the theoretical gravimetric capacity than carbon [8]. However, it is revealed that substantial change in volume in these alloys during intercalation/deintercalation leads to loss of electrical contact and specific capacity during cyclic loading [8].

On the other hand, application of the oxide materials such as, SnO₂ and PbO has attracted much attention as anodes for Li-ion batteries due to their fully development production and recycling [8, 9]. Moreover, one dimensional (1D) nanostructures have attracted attention due to their

unique physical and chemical properties [10-12].

PbO nanoparticles were synthesized using hydrothermal process. Then, its potential as an anode for Li-ion batteries was evaluated using electrochemical methods.

2. EXPERIMENTAL

All materials that were used in this research were obtained from Merck, Germany. Firstly, $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ was dissolved in triply distilled water with a typical concentration of about 20 mM. CTAB was added to the above solution. Finally, 1M NaOH was added drop by drop to the solution. The mixture was transferred into a Teflon-lined stainless steel autoclave when a white precipitate appeared. The autoclave was heated at 180°C for 10h. Precipitates were collected using filtration, and dried at 80°C for 6h.

Morphology of the PbO nanoparticles was studied using scanning electron microscopy (SEM, VEGA, TESCAN). The structural characterization of powders was carried out by analyzing the X-ray diffraction patterns obtained using a Unisuntis (XMD 300) diffractometer ($\lambda = 1.5405 \text{ \AA}$ for $\text{CuK}\alpha$ radiation).

The anodes were prepared by mixing active material (85 wt%) with polyvinylidene fluoride (PVDF) (5 wt%), and acetylene black (10 wt%) in N-methyl-2-pyrrolidone (NMP) solvent. The mixture was spread onto an Al foil and cut into circles 1cm in diameter after drying in the vacuum oven at 100°C. The working electrolyte was 1M LiBF_4 in a 50:50 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Graphite was used as counter and reference electrode. The cells were galvanostatically charged and discharged in the range of 0-1.5 V at a constant current density of 0.1 mA cm^{-2} . Cyclic voltammetry measurements were performed at a scanning rate of 0.1 mV s^{-1} . All electrochemical measurements were carried out using an Autolab PGSTAT30.

3. RESULTS AND DISCUSSION

Fig. 1 shows SEM image of the powders. As it can be seen, spherical nanoparticles have been

synthesized during hydrothermal process of PbO. The particle size of the PbO powders is about 50-200nm. Some flake-like structures also could be seen which may be related to impurities.

The XRD pattern of the PbO (Fig. 2) reveals β -PbO crystallographic structure of the hydrothermally synthesized PbO powders. The three strongest peaks of (111), (020) and (200) are according to the literature (JCPDS Card, No. 38-1477).

The average crystallite size of the PbO crystallites were calculated to be about 74.6 nm according to XRD-Scherrer formula (Eq. (1)):

$$d = \frac{k\lambda}{B \cos \theta} \quad (1)$$

where d is the mean crystallite size, k a constant usually equal to ~ 0.9 , λ the wavelength of $\text{Cu K}\alpha$, i.e. $\lambda = 1.5405 \text{ \AA}$, B the full width at half

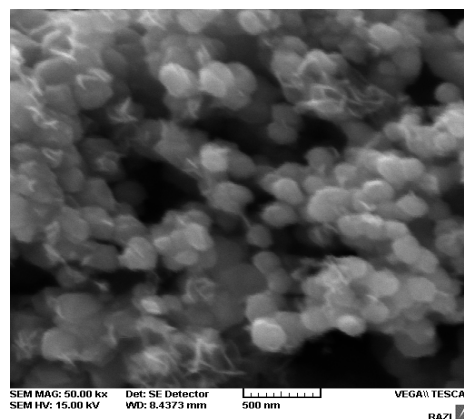


Figure 1. SEM images of PbO nanoparticles.

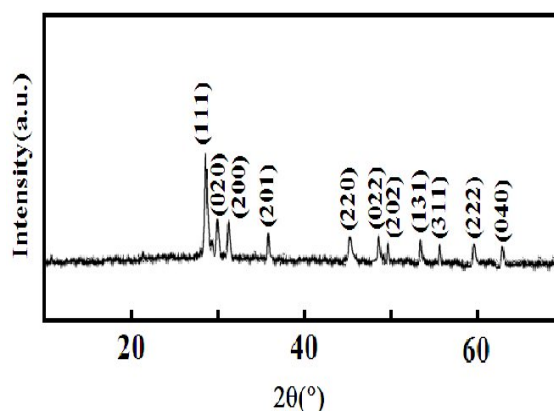
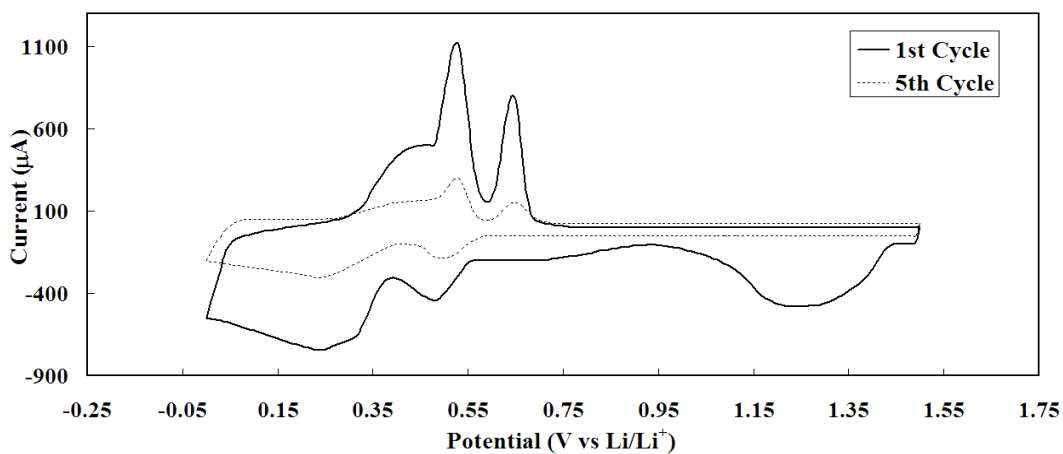
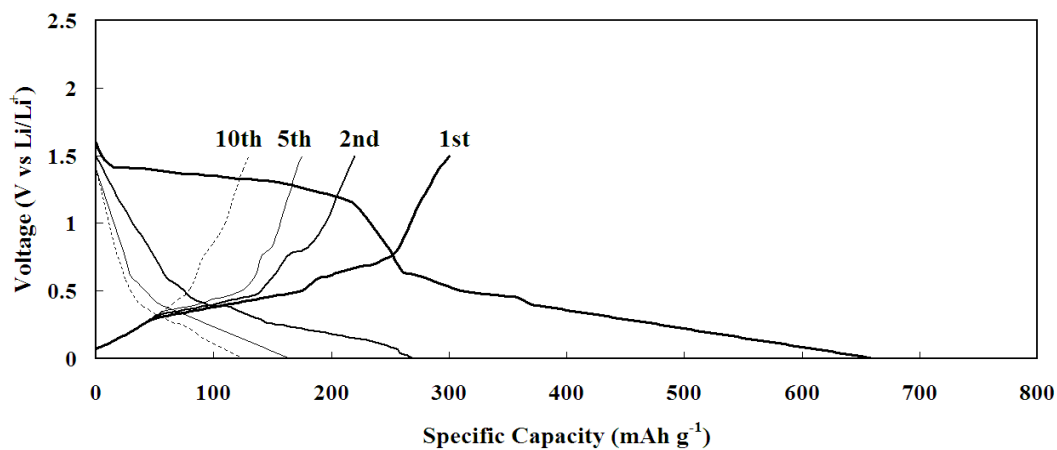


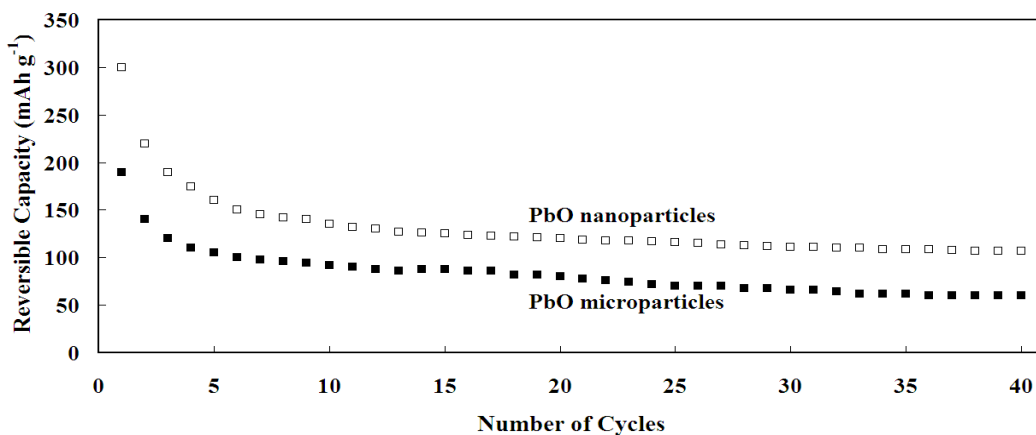
Figure 2. X-ray diffraction pattern of PbO nanoparticles.



(a)



(b)



(c)

Figure 3. (a) Cyclic voltammograms (scan rate=0.1 mV s^{-1}); (b) the first, second, fifth, and tenth charge/discharge curves ($i=0.1 \text{ mA cm}^{-2}$); and (c) Cyclic life of the PbO nanoparticles ($i=0.1 \text{ mA cm}^{-2}$).

maximum intensity of the peak (FWHM) in radians, and θ is Bragg's diffraction angle [13]. Such fine crystallite leads to broad and weak peaks in the XRD pattern.

Cyclic voltammograms (CVs) of PbO nanoparticles are presented in Fig. 3a. Some irreversible reactions could be observed during the first discharge with two reaction peaks, one between 1.45 and 0.9 V and the other at 0.7 V. The former can be assigned to the reduction reaction of the PbO to Pb with the formation of Li₂O [14]. Due to this reaction, some intermediate compounds are formed [14, 15]. According to the Ng et al [8], the latter peak at 0.7 V is a result of the solid electrolyte interface (SEI) layers which is detected only during first discharge cycle. Formation of Li_xPb alloys are accompanied by several peaks at lower potentials less than 0.7 V [8]. Four potential plateaus at 0.6, 0.45, 0.37, and 0.29 V over the composition range of 0 < x < 4.5 can be commenced out in the CVs [16, 17] which are related to LiPb, Li_{3,0}Pb, Li_{3,2}Pb, and Li_{4,5}Pb, respectively. In the case of PbO nanoparticles, three cathodic peaks were found at 0.53, 0.4, and 0.27 V. Continuing charging and discharging results to decrease of the current density, and subsequently, the specific capacity. During lithium insertion and extraction into/from the Pb, large volume changes occur. Therefore, mechanical stresses and aggregation of the particles leads to cracking of the electrodes. Consequently, electrical contacts between particles are lost and a sharp decrease in specific capacity and cyclic life of the electrode has occurred [8]. Fig. 3b represents the first, second, fifth, and tenth charge/discharge curves for the PbO nanoparticles electrodes. Irreversible capacity loses more than 400 mAh g⁻¹ during the first discharge. The special morphology of the PbO nanoparticles [18], as indicated in Fig. 1, leads to higher contact between the particles. Reversibility of the electrode is better than that of the PbO nanoparticles, as well. This morphology of the PbO nanoparticles behaves similar to high carbon content of the PbO nanocomposites [8]. The reversible capacity decreased severely during the initial cycles, in which, more than 140 mAh g⁻¹ decayed during the first five cycles as indicated in Fig. 3 c. After about 40 cycles the reversible capacity of the PbO nanoparticles is higher than

125 mAh g⁻¹ that is superior to the high carbon content of the PbO nanocomposites [8].

4. CONCLUSION

PbO nanoparticles were successfully synthesized using hydrothermal process with spherical morphology. The crystallographic structure of the powders was β -PbO which is a suitable material for Li-ion anodes. Cyclic voltammetry of the PbO nanoparticles embodied two major peaks related to the formation of Li₂O during reduction of PbO to Pb and SEI layers. Half of the specific capacity faded during formation of Pb alloys and cracking the particles. PbO nanoparticles have more reversible specific capacity in respect of the PbO nanocomposite with the carbon.

5. REFERENCES

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