

Effect of Carbon Source as Additive in Spray-Pyrolyzed PbO as Anode for Li-Ion Batteries

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Nanostructured lead oxide-carbon (PbO-C) composites were synthesized via a spray pyrolysis technique using lead nitrate as the lead precursor and sucrose as the carbon source. The combination of spray technology and carbon addition increased the specific surface area (above $6 \text{ m}^2 \text{ g}^{-1}$) and the conductivity of PbO, improved the specific capacity, and maintained cycle life with a reversible capacity above 110 mAh g^{-1} beyond 20 cycles.

1. Introduction

During the past few years, the application of nano-structured oxide materials as anodes in Li-ion batteries has attracted considerable attention [1-2]. However, a substantial change in specific volume of the electrode upon continuous charging/discharging leads to loss of electrical contact, and thus capacity loss as well as macroscopic dimensional problems within the cell structure [3-4]. Studies by Martos *et al.* [3] using sprayed lead oxide powders as anode material in Li-ion batteries show that the specific capacity fades on cycling when bulk powders are used. Therefore, we suggest the addition of a carbon source (sucrose solution) to enhance the electric conductivity of PbO and also increase its specific capacity and cycle life. This concept has proven to be successful in other studies [5]. In this work, we produced both nanostructured PbO and nanocomposite PbO-carbon using an in-situ spray pyrolysis approach and investigated their electrochemical performance as anode materials for Li-ion batteries.

2. Sample preparation

Lead oxide powders were prepared using a 0.5 M aqueous solution of lead nitrate, $\text{Pb}(\text{NO}_3)_2$ (Aldrich Chemicals), as the precursor, while the composite materials were prepared by mixing the initial solutions with aqueous sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) solutions in weight ratios ($\text{Pb}(\text{NO}_3)_2$:sugar) of 70:30 and 15:85, respectively. The materials were obtained in-situ via spraying at $800 \text{ }^\circ\text{C}$ using a flow rate of 3.14 ml min^{-1} in a vertical type spray pyrolysis reactor.

The anode was prepared by mixing PbO or PbO-carbon composites as active materials with 10 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 $100 \text{ }^\circ\text{C}$ for 24 hrs and then pressed. The electrochemical characterizations were carried out using coin cells. CR 2032 coin-type cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany) by stacking a porous polypropylene separator containing liquid electrolyte between the PbO electrode and a lithium foil counter electrode. The electrolyte used was 1 M LiPF_6 in a 50:50 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) provided by MERCK KGaA, Germany.

3. Results

3.1 Estimation of the amount of carbon in the sprayed PbO-C nanocomposites

For quantifying the amount of carbon in the PbO-C composite materials, TGA analysis was carried out in air. The samples were heated from 60 °C to 600 °C at a rate of 5 °C min⁻¹. It was found that the amounts of carbon in the composites are 3.3 wt.% and 9.5 wt.% for the precursor solutions with weight ratios (Pb(NO₃)₂/sugar) of 70/30 and 15/85, respectively.

3.2 Structure and morphology analysis of PbO-C nanocomposites

X-ray diffraction patterns (Fig. 1) revealed products comprising nanocrystalline PbO and PbO-carbon nanocomposites with confirmation of both the α -PbO phase (ASTM 05-0561) and the β -PbO (ASTM 05-0570) phase. Fig. 1 also reveals that as the carbon content increases (from Fig. 1(a) to (c)), the intensity of the orthorhombic β -PbO phase increases significantly while the intensity of the tetragonal α -PbO phase is reduced.

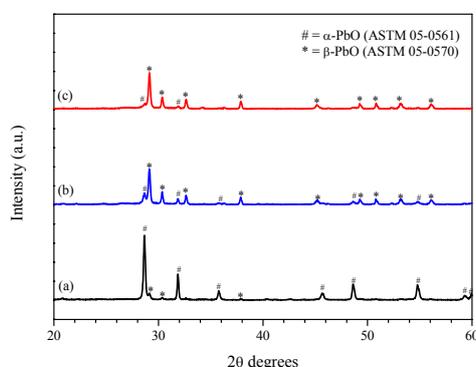


Fig. 1. XRD patterns of (a) PbO, (b) 97PbO/3C and (c) 90PbO/10C.

The well-known Debye-Scherrer formula was used to estimate the approximate average crystal size using crystalline silicon as the reference material. The estimated average crystal size was reduced from 102 nm to 26 nm when the carbon content was increased. The reduction of the average crystal size led to an increase in specific surface area (S_{BET}) from 2.2 m² g⁻¹ to 6.5 m² g⁻¹. Table 1 summarizes the physical properties of PbO-C nanocomposites.

Table 1. Physical properties of PbO-C nanocomposites.

Sample	Average Crystal Size, D_p (nm)	Specific Surface Area, S_{BET} (m ² g ⁻¹)
Commercial PbO	> 500	0.4
Spray-Pyrolyzed PbO	102	2.2
97PbO/3C	74	2.5
90PbO/10C	26	6.5

From SEM observations (Fig. 2), it was revealed that the particles are mainly spherical agglomerates, which is typical for the spray process, with sizes in the range of 0.2-2 microns for all powders. All the samples sprayed with sugar addition were morphologically alike, presenting a structure resembling broken hollow spheres with porosity on both the inside and the outside particle surfaces.

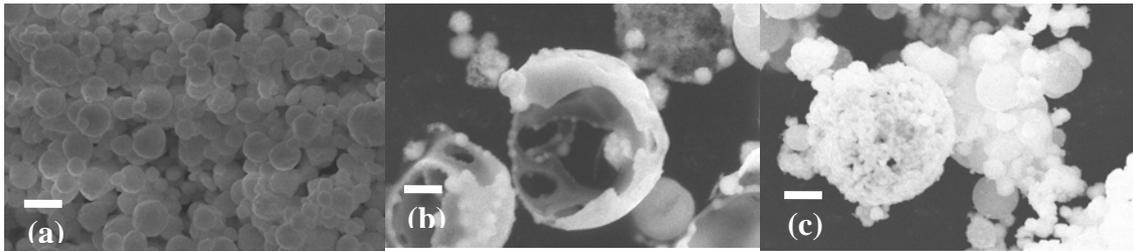


Fig. 2. SEM images of (a) PbO, (b) 97PbO/3C and (c) 90PbO/10C. Scale bar fixed at 2 μm .

3.3 Electrochemical performance of PbO-C nanocomposites

The specific discharge capacities as a function of cycle number are compared in Fig. 3. Initial discharge capacity is as high as 680 mAh g^{-1} for the 90PbO/10C nanocomposite electrodes. Subsequently, the reversible capacity was maintained above 110 mAh g^{-1} beyond 20 cycles for the 90PbO/10C nanocomposite electrodes, which is higher than the values reported by Martos *et al.* [3] for lead oxide powder anodes in lithium-ion rechargeable batteries. The increase in capacity retention for PbO-carbon compared to that of pure PbO was due to the presence of a conductive and highly developed carbon matrix that can absorb large volume changes during the alloying/de-alloying of lead with lithium over the 1.50 V to 0.01 V potential range, which yields Li_xPb alloys ($0 < x < 4.5$) [6]. This shows that PbO-carbon nanocomposites are promising as anode materials for Li-ion batteries.

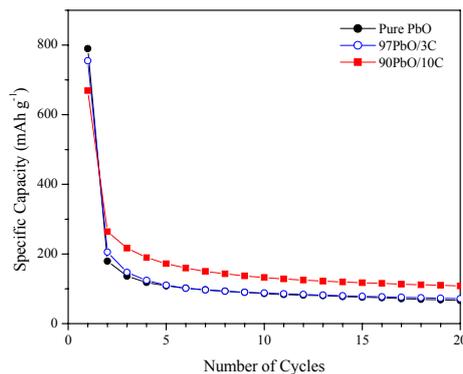


Fig. 3. Cycle life of PbO-C nanocomposites. The current density was 0.1 mA cm^{-2} .

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