



Strategy for yolk-shell structured metal oxide-carbon composite powders and their electrochemical properties for lithium-ion batteries



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ABSTRACT

A strategy for the preparation of metal oxide-carbon composite powders with yolk-shell structure by simple spray pyrolysis is introduced. Mn–Sn–O–C composite powders with yolk-shell structure representing the first target material are prepared by one-pot spray pyrolysis and their formation mechanism is evaluated. Phase separation of polyvinylpyrrolidone (PVP), Sn, and Mn components during the drying stage of droplets plays a key role in the formation of yolk-shell structured composite powders. The repeated combustion and contraction processes of the dried powders under N₂ atmosphere produce the desired Mn–Sn–O–C composite powders with yolk-shell structure. The shell and core parts of the yolk-shell powders prepared directly by spray pyrolysis at 900 °C are MnO–Mn₂SnO₄–C and Sn–Mn₂SnO₄–C composites, respectively. The initial discharge capacities of the composite powders prepared at 700 and 900 °C at the current density of 1 A g⁻¹ are 1058 and 1204 mA h g⁻¹, respectively. The discharge capacities of the composite powders prepared at 900 °C for the 2nd and 100th cycle are 803 and 784 mA h g⁻¹, respectively. The structural stability of the Mn–Sn–O–C composite powders with yolk-shell structure during cycling results in good electrochemical performance.

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1. Introduction

Yolk-shell or rattle-type structures, which are hybrids of core-shell and hollow structures with a distinctive core@void@shell configuration, have attracted tremendous interest in recent years owing to their unique characteristics that cannot be obtained in conventional materials [1–30]. Yolk-shell materials with homogeneous (MO_x@MO_x) and heterogeneous (MO_x@NO_x) structures have been developed over a wide range of compositions for a large variety of applications including energy storage [5–25]. Especially, various yolk-shell materials for lithium-ion batteries (LIBs) have been developed by various methods including hydrothermal, spray-pyrolysis, and spray-drying processes [6–27]. Carbon materials, such as amorphous carbon, carbon nanotubes, and graphene, have been applied to form nanostructured metal oxide-C composite materials with good electrochemical properties [31–40]. Inclusion of carbon material improved the electrochemical properties of metal oxide materials by improving the structural stability during cycling and by increasing the electronic conductivity [31–40].

However, to the best of our knowledge, the preparation of metal oxide-carbon composite materials with yolk-shell structures, and their electrochemical properties when used as anode materials for LIBs have not been reported.

In the literature, yolk-shell materials have been mainly prepared by a step-by-step etching process or by thermal treatments applying Ostwald ripening or the Kirkendall effect [1–5]. Recently, combustion of metal oxide-carbon composite materials formed as intermediate product in spray-pyrolysis and spray-drying processes produced various types of yolk-shell materials [20–25]. However, these processes applied for the preparation of yolk-shell materials, as described in the literature, cannot be applied for the preparation of metal oxide-carbon composite materials with yolk-shell structure. Therefore, it still remains a challenge to develop a process for the fabrication of yolk-shell metal oxide-carbon composite powders, in which core and shell parts are metal oxide-carbon composites. In addition, synergistic effects of structural features and chemical composition of anode materials have to be achieved to develop anode materials with superior electrochemical properties for LIBs.

In this study, a strategy for the preparation of metal oxide-carbon composite powders with yolk-shell structure by simple spray pyrolysis is introduced. Manganese oxide (MnO) and tin

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oxide (SnO_2) have attracted great attention as anode materials for LIBs owing to their high theoretical capacities, low discharge–charge potentials, low costs, and environmental friendliness [17–19,41–43]. Therefore, Mn–Sn–O–C composite powders with yolk-shell structure representing the first target material were prepared by one-pot spray pyrolysis. The formation mechanism of the yolk-shell metal oxide–carbon composite powder was evaluated in detail by investigating the morphological changes of the powders during the spray pyrolysis depending on the preparation temperature. In addition, the electrochemical properties of the Mn–Sn–O–C composite powders with yolk-shell structure were investigated.

2. Experimental

2.1. Synthesis of the yolk-shell Mn–Sn–O–C composite

Mn–Sn–O–C composite powders with Sn/Mn mole ratio of 1:3 were prepared directly by ultrasonic spray pyrolysis from spray solution containing the carbon source material. The schematic diagram of the apparatus is shown in Fig. S1. A quartz reactor with length of 1200 mm and diameter of 50 mm was used. A 1.7-MHz ultrasonic spray generator with six vibrators was used to generate a large quantity of droplets. The total concentration of the Mn and Sn components dissolved in distilled water was 0.3 M. In this study, polyvinylpyrrolidone (PVP, $M_w = 40,000$) was used as carbon source material to prepare the Mn–Sn–O–C composite powders with yolk-shell structure. The amount of PVP dissolved in the spray solution of 250 mL was fixed at 10 g. The flow rate of N_2 used as carrier gas was fixed at 5 L min^{-1} . The reactor temperature during the spray pyrolysis process was changed from 300 to 900 °C.

2.2. Characterizations

The crystal structures of the resulting microspheres were investigated by X-ray diffractometry (XRD, X'pert PRO MPD) using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The morphologies of the microspheres were characterized using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4300) and high-resolution transmission electron microscopy (HR-TEM, JEM-2100F) operating at a working voltage of 200 kV. The specific surface areas of the powders were calculated by the Brunauer–Emmett–Teller (BET) analysis of nitrogen adsorption measurements (TriStar 3000). The carbon content of the Mn–Sn–O–C composite powders with yolk-shell structure was determined using thermogravimetric analysis (TGA, SDT Q600), which was performed in air at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

2.3. Electrochemical measurements

The capacities and cycling properties of the Mn–Sn–O–C composite powders were determined using a 2032-type coin cell. The electrode was prepared from a mixture containing 70 wt% of active material, 20 wt% of activated carbon (Super P), and 10 wt% of sodium carboxymethyl cellulose (CMC) binder. Lithium metal and microporous polypropylene film were used as counter electrode and separator, respectively. The electrolyte was a solution of 1 M LiPF_6 and a mixture of fluoroethylene carbonate–dimethyl carbonate (FEC–DMC) at the volume ratio of 1:1. The charge/discharge characteristics of the samples were determined through cycling in the potential range of 0.001–3 V at various fixed current densities. Cyclic voltammetry (CV) measurements were carried out at the scan rate of 0.07 mV s^{-1} .

3. Results and discussion

The XRD patterns of the Mn–Sn–O–C composite powders prepared by spray pyrolysis at various temperatures are shown in Fig. 1. The composite powders prepared at 300 °C showed broad amorphous peaks without sharp crystalline reflections. However, crystalline peaks of Sn metal and the MnO phase were observed in the XRD pattern of the powders prepared at 500 °C. The XRD pattern of the powders prepared at 700 °C showed main peaks of Sn metal, MnO, and Mn_2SnO_4 . The peak intensities of the Sn metal decreased at the preparation temperature of 900 °C, while the sharpness of the peaks of MnO and Mn_2SnO_4 increased.

Images of the morphologies and elemental mapping of the Mn–Sn–O–C composite powders prepared by spray pyrolysis at various temperatures are shown in Fig. 2–4. The SEM and TEM images of the powders prepared at the low temperature of 300 °C shown in Fig. 2 clearly reveal the core–shell structure. The dense core part corresponding to the white areas in the SEM image and dark areas in the TEM image was uniformly covered with material forming a porous shell. Powders with single cores were observed from the SEM and TEM images. The high resolution TEM image shown in Fig. 2d shows clear lattice fringes 0.49 and 0.26 nm apart, corresponding to the (200) and (111) crystal planes of MnO, respectively. The elemental-mapping image of the sample with single core is shown in Fig. 2e and revealed the distributions of Sn, Mn, C, and N over the composite powder. The Sn component was mainly observed in the single core part. However, Mn was observed in the core and shell parts of the powder. The size of the Mn-rich core part was slightly larger than that of the Sn-rich core part, as shown by the dotted lines in Fig. 2e. Therefore, we can estimate that the core part again had a core–shell sub-structure, in which Sn-related material is fully covered by Mn-related material. The C component originating from PVP was mainly observed in the shell part of the powder, as shown by the dotted circle. The distribution of N all over the powder revealed incomplete decomposition of PVP. The TEM images of the powders shown in Fig. S2 revealed melted and non-melted material. PVP is water soluble. Therefore, the spherical morphology of some specimens was destroyed by the dissolving of PVP into water during the sampling process of the powders on carbon-coated copper grid used for the TEM analysis. However, some of the samples maintained their spherical morphology even if dispersed in water. The partial decomposition

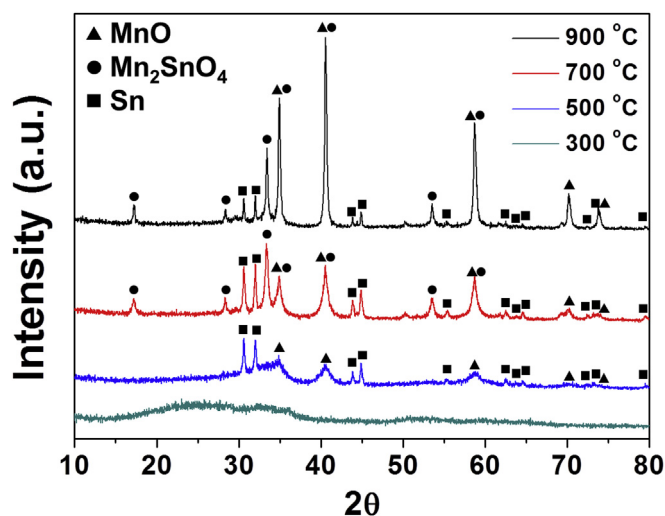


Fig. 1. - XRD patterns of the powders prepared by spray pyrolysis at various temperatures. (A color version of this figure can be viewed online.)

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