



Development of novel mesoporous C–TiO₂–SnO₂ nanocomposites and their application to anode materials in lithium ion secondary batteries

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ARTICLE INFO

Article history:

Received 9 August 2011

Received in revised form 4 October 2011

Accepted 23 October 2011

Available online 3 November 2011

Keywords:

Ordered mesoporous materials

TiO₂

SnO₂

Anode

Lithium ion batteries

ABSTRACT

Herein, we employed the tetra-constituent co-assembly method based on the acid–base pair of Sn and Ti precursors. Using this method, novel mesoporous carbon–TiO₂–SnO₂ nanocomposite materials were prepared and their structural change with an increase of SnO₂ amount was investigated. In low amount of SnO₂, an ordered mesoporous structure was observed but it became collapsed at 64 wt.% SnO₂, while crystal size of anatase TiO₂ embedded within amorphous SnO₂ and carbon matrix became larger. When applied to anode materials in lithium ion batteries, an increase of the reaction peaks of Li⁺ in SnO₂ was observed and peak associated with discharging in TiO₂ nano-crystal increased in spite of lower amount of TiO₂. This indicated that TiO₂ was highly utilized for lithium storage (275 mAh g⁻¹ in 19.9 wt.% TiO₂ case). In the nanocomposite electrode with 28.8% TiO₂, however, a high rate performance and a very stable cycle performance (95.3% retention at 40th cycles) were observed, which was attributed to the stable nanostructure.

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1. Introduction

Recently, the investigation about ordered mesoporous carbon (OMC) composite materials containing electrochemically active metal oxides has been vastly tried in order to apply into the anodes in lithium ion batteries (LIBs) [1–5]. It has been clarified that they have the beneficial features as anode materials. First, the high rate capability was attainable due to the fast diffusion of lithium ions within the nanosized pore walls and the easy transport of electrolyte through the ordered mesopores. Also, the charge accumulation at charge storage sites was facile due to the high surface area [1–6]. Among various metal oxides which can store lithium ions as anodes, several candidates such as CoO, SnO₂ and TiO₂ have been investigated as the nanocomposites with OMC [1–5]. Although it has been reported that OMC–TiO₂ nanocomposite electrodes have exhibited an improved anode performance, their intrinsically low capacity (~200 mAh g⁻¹) can be one of the shortcomings of their anode application [2,6]. In order to overcome this, the nanocomposite with other metal oxides such as SnO₂, SbO₂ and SiO₂ was investigated, where a larger charge storage was observed due to its alloying reaction with lithium ion. Most research on OMC/TiO₂ or SnO₂ has employed a post-addition of Sn or Ti sources into

the pores of OMC materials, which can give rise to the formation of inhomogeneous and bulky metal oxide crystals after thermal treatment of those composites [1,5].

In the typical preparation of carbon–TiO₂–SnO₂ nanocomposite (C–TiO₂–SnO₂), it has been reported that the crystal growth of TiO₂ and SnO₂ was severe due to the high carbonization temperature [1,5]. As for the crystal structure of TiO₂, various crystalline phases exist as rutile [7,8], anatase [9,10], TiO₂-B [11,12], brookite [13] and ramsdellite [14], which were applied as anode materials in lithium ion batteries. When they were prepared as nanostructures, high capacity from 200 to 300 mAh g⁻¹ was observed. Due to their structural instability, however, the high capacity above 200 mAh g⁻¹ was hard to maintain after long cycles. Although SnO₂ has a high theoretical capacity of 780 mAh g⁻¹, furthermore, the cycle performance was not satisfactory even after the nanostructure formation by the post-addition of Sn precursor into the OMC matrix, which was attributed to the large volume change of SnO₂ during charging–discharging [5]. In order to overcome these obstacles, it is highly required to prepare a complete C–TiO₂–SnO₂ nanocomposite by one-step process using carbon, Ti and Sn precursors. With this in mind, the tetra-constituent co-assembly (Tetra-CCA) method using Ti-citrate precursor was reported in our previous paper [3]. In this method, a block copolymer surfactant, oligomeric resol and silicate source were reacted with Ti-citrate solution. After aging and calcination, the C–TiO₂–SiO₂ nanocomposite containing ordered mesopores was obtained.

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In order to prepare a mesoporous nanocomposite of carbon–TiO₂ and SnO₂ via one-step synthesis, herein, the tetra-constituent co-assembly (Tetra-CCA) method based on the acid–base pair concept is employed. It is expected that carbon skeleton which is helpful in maintaining an ordered structure makes a high electrical percolation network. An acid–base pair between Ti alkoxide and Sn chloride is added in order to avoid a formation of inhomogeneous metal oxide phase and make a stable nanostructure. Using the evaporation-induced self-assembly (EISA), a homogeneous film-type gel is obtained and heat-treated to produce an ordered mesoporous C–TiO₂–SnO₂ nanocomposites.

2. Experimental section

2.1. Preparation of composites

The resol as carbon precursor was prepared according to the literature [17]. The final resol precursors were dissolved in ethanol (20 wt.% ethanolic solution) for direct use. For Tetra-CCA preparation of C–TiO₂–SnO₂ nanocomposite, typically, 1 g of P123 (EO₂₀-PO₇₀EO₂₀, Aldrich, *Mw* = 5800) was dissolved in 20 g of ethanol under stirring until a clear solution was acquired. Then 0.973 g (3.6 mmol) of SnCl₄ (Aldrich) and 1.528 g (6.7 mmol) of Ti(OEt)₄ (Aldrich) was added dropwise under vigorous stirring separately. Upon stirring for 10 min, 2 g of 20 wt.% resol ethanolic solution was dropped slowly when the solution turned orange immediately. Upon further stirring for 2 h, the clear solution was poured into several Petri dishes and kept in a humidity-controlled ambient environment for full evaporation of ethanol. Afterwards the result film was polymerized at 100 °C for 24 h in an oven with a brittle transparent film forming. The as-prepared film was ground into fine powders, calcined at 450 °C for 2 h and further at 600 °C for 2 h under an inert atmosphere (N₂). After cooling down to the room temperature, the product was taken out, which produced Ti, Sn and carbon nanocomposite named as TSC-1. Similarly, a TSC-2 and a TSC-3 composite are prepared by adjusting the Sn/Ti molar ratio to 5:5 and 6.7:3.6 separately with the total molar amount of Ti and Sn maintained as 0.01 mol.

2.2. Characterization and anode performance investigation

The pore size distribution (PSD) was analyzed using an N₂ adsorption measurement (Micromeritics ASAP 2010). The external morphology of the carbon was examined using a scanning electron microscope (SEM, JEOL JSM-840A), whereas the pore image was scanned by a transmission electron microscope (TEM, JEOL JEM-2010). The energy dispersive X-ray analysis was conducted using the EDX analyzer equipped with the TEM in point mode and area mode. The X-ray diffraction (XRD) patterns were obtained with a Rigaku D/Max-3C diffractometer equipped with a rotating anode and Cu K_α radiation ($\lambda = 0.15418$ nm). X-ray photoelectron spectroscopy (XPS) experiments were carried out in an ultrahigh vacuum using the Scienta ESCA-300 high-resolution X-ray photoelectron spectrometer (HR-XPS).

For the preparation of composite anodes, the prepared materials were mixed with a conducting agent (Super P) and PVDF (polyvinylidene fluoride) binder with a weight ratio of 8:1:1. The mixture was then dispersed in NMP and spread on Cu foil (apparent areas of 1 cm²), followed by pressing and drying at 120 °C for 12 h. The half-cell characteristics was analyzed with a coin-type (CR2016) two electrode cell in which lithium foil (Cyprus Co.) was used. The electrolyte was 1.0 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 volume ratio) (Technosemi Chem.). To investigate the anode performance in a lithium ion battery, a galvanostatic charge–discharge test in a voltage range of

2.5–0 V vs. Li/Li⁺ was conducted. For the rate performance measurement, the current was varied from 30 mA g⁻¹ to 300 mA g⁻¹. The cycle performance for 40 cycles was recorded at 30 mA g⁻¹. All of the electrochemical measurements were conducted using a WBCS-3000 battery cycler (Xeno Co.) at ambient temperature in a glove box filled with argon. For cyclic voltammetry measurement, a voltage range of 2.5–0 V vs. Li/Li⁺ was applied with scan rate of 0.2 mV s⁻¹. For the electrochemical impedance spectroscopy (EIS) measurement, a frequency range of 10⁶ Hz to 5 mHz was used with an ac amplitude of 10 mV (Ivium potentiostat) at 2 V vs. Li/Li⁺.

3. Results and discussion

In Fig. 1, the schematic explanation of the overall preparation is summarized. In this approach, Tetra-CCA method was employed in order to obtain a mesoporous nanocomposite that was composed of TiO₂, SnO₂ and carbon. As carbon precursor, PF resol was added for the purpose of increasing the structural strength of mesoporous structure forming an amorphous glue-like background for the controlled in situ crystallization of metal oxides and making a high electrical percolation within mesostructure [1,3,15,16]. As Ti and Sn precursor, Ti(OEt)₄ and SnCl₄ were utilized because an acid–base pair can be formed between them, which can have an interaction with P123 surfactant and also prevent isolated phases formation of metal oxides after high temperature sintering [17]. After the evaporation induced self-assembly (EISA) procedure, the composite was carbonized at 600 °C. During this step, an ordered mesoporous nanocomposite composed of C–TiO₂–SnO₂ was prepared. To the best of our knowledge, this is the first preparation of ordered mesoporous nanocomposite materials composed of carbon, TiO₂ and SnO₂ using simple one-step synthesis. In general, multi-step procedures have been utilized for the preparation of similar nanocomposites. In addition, the prepared materials were applied as anode materials in lithium ion batteries. The weight fraction of TiO₂, SnO₂ and carbon was calculated by ICP methods, which was listed at Table 1.

Fig. 2 displays the small angle and wide angle X-ray diffraction (XRD) patterns. In TSC-1 material, a broad peak was observed at $2\theta = 0.7^\circ$, which was probably associated with a long-range ordering of mesopores. In TSC-2, the ordered peak became sharper and moved to a lower angle, indicative of increasing cell parameter. However, the ordered structure was collapsed and no peak was observed in TSC-3, which reflected that higher addition of SnCl₄ resulted in a collapse of ordered structure. Fig. 2(b) displays the wide angle XRD patterns. Interestingly, only anatase phase TiO₂ was observed and, no crystal structure of SnO₂ and carbon appeared. Note that the peak intensity for [101] plane of TiO₂ crystal became higher as SnO₂ increased, in spite of a decrease of TiO₂ weight fraction. This implies that SnO₂ and carbon remained amorphous, but the crystallinity of TiO₂ became higher according to an increase of SnO₂. This observed tendency in crystal structure is possibly relevant to the mole ratio between Ti and Sn. It has been reported that crystallinity of anatase TiO₂ was less developed than our TSC-1 in the case of mesoporous material having 80% carbon and 20% TiO₂, indicating that carbon phase retarded a crystal growth of TiO₂. In our experiment, on the contrary, a high interaction between carbon and SnO₂ could accelerate crystal growth of TiO₂ or the lower concentration of titania source could promote its crystal growth, which require a further investigation. In addition, there are small bumps at around $2\theta = 31^\circ$ for all the three samples, which corresponded to the rutile TiO₂ phase. Small amount of rutile phase formed during high-temperature calcination because of its high thermodynamic stability. Because nanosized rutile TiO₂ shows excellent capacity retention and a high

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