



Short communication

A facile synthesis of $\text{SO}_4^{2-}/\text{SnO}_2$ solid superacid nanoparticles as anode materials for lithium-ion batteries

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ABSTRACT

This paper presents a study of SnO_2 and $\text{SO}_4^{2-}/\text{SnO}_2$ solid superacid nanoparticles, synthesized by a facile sol-gel route, as anode materials for lithium-ion batteries (LIBs). A possible reversible reaction mechanism is proposed for the $\text{SO}_4^{2-}/\text{SnO}_2$ solid superacid nanoparticles used as an anode material. The $\text{SO}_4^{2-}/\text{SnO}_2$ exhibits a reversible lithium storage capacity of 925 mAh g^{-1} at a low charge-discharge rate of 0.2 C (156 mA g^{-1}). Furthermore, it exhibits a stable cycling performance over 50 cycles at the rate of 0.2 C , maintaining the specific capacity of 310 mAh g^{-1} , whereas SO_4^{2-} -free SnO_2 only delivers a capacity retention of 126 mAh g^{-1} .

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1. Introduction

Lithium-ion batteries (LIBs) are among the prime candidates for electrical energy storage because of their reasonably high energy densities and good cyclability [1,2]. Many transition metal oxides have been investigated for use as anode materials for LIBs. Among them, SnO_2 has attracted particular attention due to its high theoretical specific capacity (782 mAh g^{-1} based on 4.4 Li per formula unit) and low potential for lithium alloying [3]. However, a dramatic volume change ($>300\%$) commonly occurs in SnO_2 -based anodes during lithium-ion alloying/dealloying, leading to rapid capacity decay and poor cyclability [4]. To overcome this problem, we report a novel, simple and low-cost synthetic route to prepare the $\text{SO}_4^{2-}/\text{SnO}_2$ solid superacid, which improves the electrochemical activity of SnO_2 nanoparticles as anode materials for LIBs. To the best of our knowledge, this is the first report of the $\text{SO}_4^{2-}/\text{SnO}_2$ solid superacid applied to LIBs.

2. Experimental

A total of 10 mL of a solution containing 0.4 mmol of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in N,N -dimethylformamide (DMF) was sealed in a 25 mL Teflon-lined autoclave. The autoclave was heated at $110 \text{ }^\circ\text{C}$ for 16 h . The resulting sol was washed four times with ethanol and dried under vacuum at $80 \text{ }^\circ\text{C}$. Finally, a yellow solid powder of SnO_2 was obtained. The obtained SnO_2 was immersed in sulfuric acid (3 M , 15 mL of acid solution per 1 g of solid) at room temperature for 1 h . Subsequently, the solid was filtered,

dried, and calcined in air at $500 \text{ }^\circ\text{C}$ for 4 h to afford the $\text{SO}_4^{2-}/\text{SnO}_2$ superacid.

A common method to confirm the presence and the type of acid sites in a solid acid is pyridine absorption-IR spectroscopy, which focuses on specific vibrational bands of pyridine that shift in position when the pyridine adsorbs to Lewis or Brønsted acid sites. FT-IR spectra were recorded on a Nicolet AVATAR 380 infrared spectrometer. The detailed procedure of preparation of electrodes is similar with the previous report [4]. The C rate was set so that $1 \text{ C} = 782 \text{ mA}$ per gram of active material in the electrode, which corresponds to the theoretical capacity of SnO_2 .

3. Results and discussion

XRD patterns of SnO_2 and $\text{SO}_4^{2-}/\text{SnO}_2$ nanoparticles are shown in Fig. 1a. For both materials, the pattern corresponds to the crystalline phase of SnO_2 (JCPDS: 41-1445). The diffraction peaks at $2\theta = 27^\circ$, 34° , and 52° can be indexed to the (110), (101), and (221) reflections of tetragonal structure of SnO_2 . In addition, the broadness of the peaks indicates that the crystalline SnO_2 and $\text{SO}_4^{2-}/\text{SnO}_2$ particles are very small. According to the Scherrer equation, the average crystallite sizes of SnO_2 and $\text{SO}_4^{2-}/\text{SnO}_2$ were calculated to be similar for the two materials, 2.5 and 3.4 nm , respectively. A magnified TEM image (Fig. 1b) reveals that the typical diameter of SnO_2 nanoparticles is $3\text{--}5 \text{ nm}$, consistent with the XRD data. Even though the $\text{SO}_4^{2-}/\text{SnO}_2$ nanoparticles were synthesized at a high temperature of $500 \text{ }^\circ\text{C}$, at which agglomeration and sintering might be expected, the nanoparticles of $\text{SO}_4^{2-}/\text{SnO}_2$ remained very fine with particle sizes between 3 and 5 nm , and they formed a looser network (Fig. 1c). The reason may be the negative

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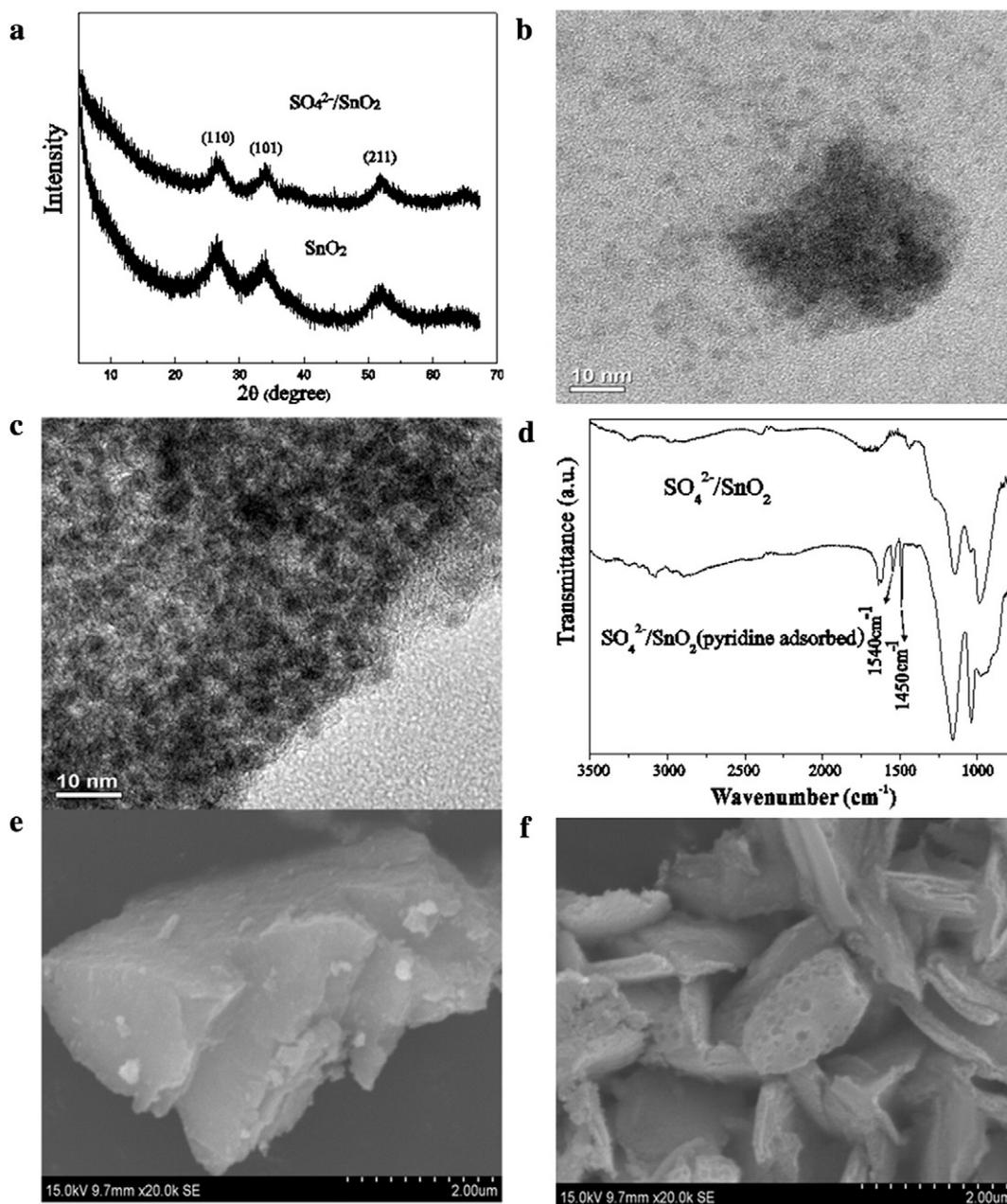


Fig. 1. (a) XRD patterns of SnO₂ and SO₄²⁻/SnO₂; TEM images of (b) SnO₂ and (c) SO₄²⁻/SnO₂. (d) Infrared spectra of SO₄²⁻/SnO₂ without and with adsorbed pyridine; SEM images of (e) SnO₂ and (f) SO₄²⁻/SnO₂.

surface charge introduced to the SO₄²⁻/SnO₂ particles by the SO₄²⁻ groups.

The IR spectra of SO₄²⁻/SnO₂ samples before and after pyridine adsorption are given in Fig. 1d. Four obvious adsorption peaks in the 900–1300 cm⁻¹ range can be observed, which are respectively located at ca. 990, 1037, 1157, and 1272 cm⁻¹. The IR peak at 990 cm⁻¹ can be attributed to the ν_1 vibrational mode of the sulfate group. In the free ion, this is not IR active, but here it becomes active due to the decrease in symmetry when the sulfate group complexes with Sn. The other three peaks are due to the splitting of the ν_3 peak of the sulfate group in the reduced symmetry environment [5]. Therefore, the IR data confirm that the sulfate groups have been combined mainly with Sn on the SO₄²⁻/SnO₂ surface. The type of acidity of these nanoparticles can be distinguished from infrared spectra of adsorbed molecules, especially pyridine. The infrared spectra of the pyridine-adsorbed SO₄²⁻/SnO₂ (Fig. 1d) reveals two peaks at ca. 1450 and 1540 cm⁻¹ due to pyridine adsorbed on Lewis and Brønsted acid sites [6], respectively. Evidently,

sulfate modification not only increased the number of strong Lewis acid sites but also induced a significant amount of strong Brønsted acidic sites on the surface of SnO₂. The IR spectra therefore demonstrate that the SO₄²⁻/SnO₂ nanoparticles possess the characteristics of a solid superacid. In addition, the results obtained from SEM images (Fig. 1e and f) are consistent with a previous report [7], the surfaces of SO₄²⁻/SnO₂ particles show greater pore structures, which are beneficial for the electrochemical reaction.

Fig. 2a shows the cyclic voltammograms of SnO₂ for the initial three cycles at a scan rate of 0.1 mV s⁻¹ in the potential window of 0.01 to 3.0 V vs. Li/Li⁺. During the cathodic sweeps, two reduction peaks occur at 0.76 V and 0.07 V, respectively. The former peak could be assigned to the reduction reaction between SnO₂ and Li⁺ to form Sn and Li₂O (Eq. (1)) and the formation of a solid electrolyte interface (SEI) [8], while the latter is due to the alloying process of Sn with additional Li uptake (Eq. (2)) [9]. Usually, the alloying reaction 2 is thought to be highly reversible, giving a theoretical lithium storage capacity of

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