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Al-doped SnO_2 hollow sphere as a novel anode material for lithium ion battery

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ABSTRACT

SnO_2 hollow spheres are doped with different contents of Al (1, 1.5, 2 at.%) by a one-step hydrothermal reaction. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM) and Brunauer–Emmett–Teller (BET) are utilized to characterize the structures, components, chemical environments, morphologies and specific areas of the as-prepared samples. The investigation in cycling performances demonstrates that 1.5 at.% Al-doped SnO_2 hollow spheres exhibit the best cycling stability, with a specific capacity of 443 mAh g^{-1} and coulombic efficiency of 99.1% after 50 cycles at 0.1 C, much higher than those of the pristine SnO_2 hollow spheres and the other Al-doped samples. The improved electrochemical performances of Al-doped SnO_2 hollow spheres are attributed to the increase of electronic conductivity and lithium ion diffusion coefficient, and therefore, enhance the reversible capacity and cycling properties.

1. Introduction

Rechargeable lithium ion battery (LIB) represents a well-established technology for energy storage, being nowadays the most popular power source in portable electronics. The increasing miniaturization of microelectronic devices continuously challenges the performances of conventional LIB based on bulk, micrometer-sized materials. Nowadays, even much higher requirements are raised to power electric and hybrid-electric vehicles, in terms of both energy and power densities. The development of alternative routes towards higher storage capacities relies on the application of metals and transition metal oxides that can reversibly incorporate more Li^+ than intercalation materials. Li-alloying with metals or semiconductors in various systems [1–5] as well as conversion reactions in interstitial-free 3d metal oxide structures [6–12] are feasible approaches to achieve large reversible capacities in anode electrodes. Amongst them, tin dioxide (SnO_2) is one of the most intensively studied anode material for its high theoretical capacity (1494 mAh g^{-1}), safe working potential and environmental benignity [13–16]. It is well established that two-step reactions are involved in the SnO_2-based electrodes:

$$SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O \tag{1}$$

$$Sn + xLi^+ + xe^- \rightleftarrows Li_xSn\ (0 \le x \le 4.4). \tag{2}$$

The first process is usually regarded to be irreversible for bulk Li_2O, however, it has been proved to be partly reversible when the conductivity has been somehow enhanced [15–17]. The second process is widely established to be reversible and mental Sn can be repeatedly alloyed and de-alloyed [18,19].

Despite the high theoretical capacity, the practical use of the SnO_2 anode is greatly hampered by its quick capacity fading upon extended number of cycles, which is believed to be derived from the huge volume change of SnO_2 during discharge/charge process [20]. Meanwhile, its electron conductivity is rather poor. To confront these drawbacks, several strategies have been proposed to improve its electrochemical performances. For example, one of the well-known methods is to design various SnO_2 nanostructures with large surface areas and high surface-to-volume ratios, such as nanotubes [21], nanoboxes [22], nanosheets [23] and hollow spheres [24], which exhibit increased capacities and improved cycling properties due to shortened diffusion distance of lithium ions and increased specific area [25–32]. Amongst these nanostructured materials, SnO_2 hollow spheres with larger specific areas, leading to soakage into the electrolyte more sufficiently, are beneficial to improve the electrochemical properties [24,33].

On the other hand, SnO_2 anode has intrinsically low electronic conductivity, which limits its application for high power output. Doping represents an important technique to effectively modify the mechanical, optical and electronic properties of SnO_2 bulk materials. An element with a higher charge state doping will lead to the reduction of a fraction of tin ion, while an element with a lower charge state creates vacancies in the oxygen sublattice [34–36]. In this way, *n*- or *p*-doped materials are obtained, respectively. The creation of vacancies can also enhance

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the electronic conductivity. Ravichandran et al. reported that Al-doping effectively increased the electron conductibility of SnO_2 thin film, which shows attractive potential in transparent electronics applications [37].

In our study, SnO_2 hollow spheres were prepared by a simple one-step hydrothermal method for the first time, which is more controllable and repeatable, compared with the intensively utilized template method in the synthesis of nano-sized SnO_2 for LIB. As another feature of this work, Al is doped into the lattice of SnO_2 hollow spheres in the same one-step hydrothermal process. Interestingly, it is found that the 1.5 at.% Al-doped SnO_2 hollow spheres demonstrate the optimal electrochemical performances compared with its pristine material, which can be attributed to the increase of electronic conductivity and lithium ion diffusion coefficient.

2. Experimental

SnO_2 hollow spheres were synthesized by a one-step hydrothermal reaction. In a typical synthesis, 4.3 g of $SnCl_4 \cdot 5H_2O$ was dissolved in 80 ml of deionized water, then 2.7 g of NaOH was added into the solution under mechanical stirring. The obtained solution was then transferred into a 100 ml of Teflon-lined stainless steel autoclave and kept in an oven at 200 °C for 16 h. The autoclave was then taken out of the oven and cooled naturally to room temperature. Finally, the precipitate was harvested via centrifugation, washed thoroughly with ethanol, and dried at 80 °C overnight to obtain the SnO_2 hollow spheres. To be strict, the preparation processes of 1, 1.5 and 2 at.% Al-doped SnO_2 hollow spheres were the same as described above except different contents of $Al(NO)_3 \cdot 9H_2O$ added in.

Surface morphologies of the samples were characterized by field-emission scanning electron microscopy (FESEM, JSM-7001F, JEOL). The specific surface areas were evaluated with a BELSORP-mini surface analyzer (V-Sorb2800, Beijing, Gold App) based on the Brunauer–Emmett–Teller (BET) multipoint method and N_2 physisorption at room temperature. X-ray diffraction (XRD) measurements were performed on a diffractometer (DX-2700, Fangyuan) with Cu $K\alpha$ radiation ($\lambda = 1.54145$ Å). Raman spectra were recorded on a Raman Spectrometer (RM-1000, Renishaw) with a 632.8 nm He–Ne laser as an irradiation source. The X-ray photoelectron spectroscopy (XPS) analysis was carried out on Kratos Axis Ultra using a monochromatic Al $K\alpha$ radiation and the binding energies (BEs) were calibrated with that of C1s at 284.8 eV as the reference.

The electrochemical measurements were carried out using two-electrode button-type cells with pure lithium metal as the counter electrode at room temperature. The working electrode was fabricated by compressing the mixture of 70 wt.% active material, 15 wt.% acetylene black (Super-P, MMM Carbon), and 15 wt.% binder (polyvinylidene fluoride, PVDF) dissolved in N-methyl-pyrolline (NMP) on a copper foil. Then the slurry was dried in a vacuum oven at 100 °C overnight and finally cut into square electrode sheets (8×8 mm^2). Celgard 2400 and 1 M $LiPF_6$ dissolved in a mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) with 1:1 volume ratio were used as the separator membrane and the electrolyte. The test cells were assembled in a purified Ar-filled glovebox (Super1220/750, Mikrouna) with concentrations of oxygen and moisture below 1.0 ppm. Cyclic voltammetry (CV) was performed using an electrochemical workstation (CHI660C, Shanghai Chenhua). The CV curves were recorded between 0 and 3.0 V at a scan rate of 0.1 mV s^{-1} at room temperature. The charge/discharge tests were performed using a battery tester (Neware CT-2001A, China) at 0.1 C cycled between 0 and 3.0 V versus. Li^+/Li unless otherwise specified.

3. Results and discussion

The surface morphologies of pristine and Al-doped SnO_2 hollow spheres with different contents of Al (1, 1.5, 2 at.%) are illustrated in Fig. 1. It can be clearly observed that pristine, 1 and 1.5 at.% Al-doped SnO_2 present the similar morphology of hollow sphere structure in a large field of view (Fig. 1(a)–(c)). More carefully observation indicates that the hollow spheres are compacted with small nanometer particles with an average size of about 50 nm. As clearly observed in Fig. 1(a), the particles are homogeneously distributed with an average particle size of 2 μm. Another important feature is that pristine SnO_2 presents a unique hollow sphere structure with truncated particles. Clearly, the diameter of the cave leaves by the truncation is about 400 nm. As the Al doping content increases to 1 and 1.5 at.%, the general morphology of hollow spheres remains unchanged. Nevertheless, the diameters of the caves experience prominent growth, which increase to about 500 and 700 nm for 1 and 1.5 at.% Al-doped SnO_2, respectively (Fig. 1(b)–(c)). Markedly, the 2 at.% Al-doped SnO_2 totally loses the morphology of hollow sphere (Fig. 1(d)), which may be originated from the influence of high content of Al doping. Furthermore, the element mapping images of 1.5 at.% Al-doped SnO_2 hollow spheres are demonstrated in Fig. 1(e) and (f), which prove the homogeneous distribution of Al in the hollow spheres.

The specific areas are determined to be 98, 104, 117 and 93 m^2 g^{-1} for pristine, 1, 1.5 and 2 at.% Al-doped SnO_2, respectively, based on BET multipoint analysis. Obviously, 1.5 at.% Al-doped SnO_2 exhibits the largest specific area, which may benefit from the optimal doping content. This will presumably facilitate the rapid diffusion of Li^+ during the electrochemical discharge/charge reactions and therefore, lead to enhanced electrode kinetics in cycling.

Fig. 2 illustrates the XRD patterns of as-prepared pure and Al-doped SnO_2. It can be observed that the samples are well-crystallized, and all the diffraction peaks in the figure can be indexed to crystalline SnO_2, consistent with JCPDS card 01-0657. In addition, no diffraction peak from impurity can be observed after Al doping, suggesting that the doping process has no influence on the main structure of pure SnO_2. The grain sizes of pure and Al-doped SnO_2 are calculated using Scherrer's formula, $D = K\lambda/\beta\cos\theta$, where K is a constant (shape factor, about 0.89), λ is the X-ray wavelength, β is the full width at half maximum (FWHM) in radians obtained using Jade software, and θ is the scattering angle [38]. As shown in Table 1, the calculated grain size of pure SnO_2 is 18.5 nm, and those of the other three Al-doped samples are 16.7, 14.7 and 15.7 nm, for the doping ratios of 1, 1.5 and 2 at.%, respectively. It is obvious that the grain size of SnO_2 decreases with Al-doping, when the doping content is lower than 2 at.%. After that, it increases in the opposite direction. The lattice parameters of the four samples are also compared in Table 1. Interestingly, the evolution of lattice constants demonstrates the similar tendency. Generally, they shrink first when the doping content is less than 2 at.%, and then exhibits a sharp increase along a direction and a decrease along c direction. Taken the different ionic radii of Sn^{4+} (0.081 nm) and Al^{3+} (0.054 nm) into account [39], it is easy to understand the initial decrease of lattice parameters, involving a partial substitution of Sn^{4+} by Al^{3+}. It is worth mentioning that, nevertheless, when the doping content reaches 2 at.%, different situation occurs. The lattice parameters and grain size all change differently. This trend coincides with the BET analysis data, which could be attributed to the structure collapse of hollow spheres, as can be observed in Fig. 1(d).

Fig. 3(a) shows the XPS survey spectra of 1.5 at.% Al-doped SnO_2 hollow spheres, in which the strong signals of Sn and a small amount of Al can be observed. Double peaks with binding energies (BEs) at 485.5 and 495.5 eV are shown in Fig. 3(a), which correspond to Sn $3d_{5/2}$ and $3d_{3/2}$, respectively, indicating the quadrivalent oxidation state of this element [40]. Besides, a small amount of Al can also be observed in Fig. 3(a). For clarity, the smoothed profile of Al 2p is illustrated in Fig. 3(b), in which the fitted BE is at 74.2 eV [40], implying the trivalent oxidation state of doped Al. The above analysis indicates that Al^{3+} ions have successfully doped into the lattice of SnO_2, consisting with the XRD results. The absence of Al^0 (72.7 eV) confirms that Al element only exists in the form of trivalent ions.