Short communication

A novel CuO-nanotube/SnO2 composite as the anode material for lithium ion batteries

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ARTICLE INFO

ABSTRACT

A novel CuO-nanotubes/SnO2 composite was prepared by a facile solution method and its electrochemical properties were investigated as the anode material for Li-ion battery. The as-prepared composite consisted of monoclinic-phase CuO-nanotubes and cassiterite structure SnO2 nanoparticles, in which SnO2 nanoparticles were dramatically decorated on the CuO-nanotubes. The composite showed higher reversible capacity, better durability and high rate performance than the pure SnO2. The better electrochemical performance could be attributed to the introducing of the CuO-nanotubes. It was found that the CuO-nanotubes were reduced to metallic Cu in the first discharge cycle, which can retain tube structure of the CuO-nanotubes as a tube buffer to alleviate the volume expansion of SnO2 during cycling and act as a good conductor to improve the electrical conductivity of the electrodes.

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1. Introduction

As an anode material for Li-ion batteries with a theoretical capacity of $782\,mAh\,g^{-1}$, SnO2 has been extensively studied as an alternate material to the commercially employed graphite with a theoretical capacity of $372\,mAh\,g^{-1}$. However, the practical use of this material has been hampered by its fast capacity fading upon cycling which is caused by the severe volume changes that occur during Li-ion insertion and extraction [1–4]. To minimize the mechanical stress in the electrode caused by the volume expansion, several strategies are mainly proposed in related literatures [1–11]. The first one is the use of SnO2 nanomaterials such as nanoparticles, nanotubes, nanowires, nanorods and hollow microspheres [1–2]. Those SnO2 nanomaterials with unique structure were expected to have improved electrochemical performance. The second one is the use of tin-based composite oxides (TCO) to replace pure SnO2. Tin-based composite oxides (TCO) can form a homogeneous matrix which serves as a buffer to accommodate the volume change of SnO2 electrode [5–10]. Although limited success has been achieved with the two strategies, considerable capacity fading still exists during charge–discharge cycling due to the still large volume change.

Recently, it was reported that the composite materials of the tin dioxide with other special-nanostructure carbon material, such as carbon nanotubes and carbon hollow spheres [5–8], exhibited higher specific capacity than graphite and improved fading characteristics relative to pristine tin oxide. For example, Wang et al. [9] reported that the good dispersion of SnO2 on MWCNT with small particle size is benefit to release the stress caused by the drastic volume variation during the lithium insertion/extraction process. It is believed that the combined material with unique nanostructure can greatly enhance the electrochemical property of the electrodes if the combined material has good electrical conductivity [10–11]. It is rationally expected that the use of the composite materials of the tin oxide with other special-structure nanomaterial that can alleviate the large volume expansion of tin oxide would be a promising way to minimize the mechanical stress in the electrode caused by the volume expansion. Herein we report, for the first time to our best knowledge, a novel CuO-nanotubes/nanosized-SnO2 composite prepared by a facile solution method, and its electrochemical properties as an anode material for Li-ion batteries. It was found that the CuO-nanotubes were reduced to metallic Cu in the first discharge cycle, which can retain tube structure of the CuO-nanotubes as a special buffer to alleviate the volume expansion of SnO2 during cycling and act as a good tube conductor to improve the electrical conductivity of the electrodes. The composite showed higher reversible capacity, better durability and high rate performance than the pure SnO2 due to the introducing effect of the CuO-nanotubes.

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2. Experimental

2.1. Preparation of materials

CuO-nanotube/nanosized-SnO$_2$ composites were prepared by a facile solution process. SnCl$_4$ and citric acid with a mole ratio of 2:1 were mixed together in distilled water, and the pH value of the result solution was adjusted at around 1.5 by NH$_3$·H$_2$O, and then a white gel appeared. After constant magnetic stirring for about 2 h, the gel was centrifuged, and washed thoroughly by distilled water until free of Cl$^-$. The sediment was redispersed by absolute ethanol, and then CuO-nanotubes (1:2 in mass ratio with calculational SnO$_2$) were added to the wet dispersoid. CuO-nanotubes were prepared by heating Cu nanowires for 3 h at 600 °C and the synthesis procedure of Cu nanowires has been reported elsewhere [12]. The mixture of dispersoid and CuO-nanotubes was dispersed with ultrasonic vibration, dried at 50 °C, and calcined at 600 °C for 2 h, the CuO-nanotube/nanosized-SnO$_2$ composite was obtained. The pure SnO$_2$ nanoparticles were obtained by the same procedure but without adding CuO-nanotubes. All the reagents used were analytical grade.

The crystal structure of the as-prepared samples was characterized by X-ray diffraction (XRD, Bruker D8) using Cu Kα (λ = 0.15418 nm) radiation at 40 kV and 60 mA in a 2θ range from 20° to 80° at room temperature. The morphology and microstructure were observed by scanning electron microscopy (SEM, JEM-5600) with energy dispersive spectroscopy (EDS) analysis, and transmission electron microscopy (TEM, FEITECNALG2).

2.2. Electrochemical performance

The electrochemical reactions of samples with lithium were investigated using a simple two-electrode cell: Li/LiPF$_6$(EC+DMC)/CuO–SnO$_2$. The working electrode consists of 80 wt.% as-prepared powders, 10 wt.% Super P carbon as the conducting agent, 10 wt.% polyvinylidene fluoride (PVDF) as binder, and Cu foil as substrate (current collector). A N-methyl pyrrolidinone (NMP) slurry consisting of 80 wt% of the active material powder, 10 wt.% of Super P carbon and 10 wt.% of PVDF was uniformly coated on a copper disk of 14 mm in diameter. The disk electrodes were dried overnight at 110 °C followed by compression at 1.0×10^6 Pa. The 2016 coin cells were assembled in an Ar-filled glove box using polypropylene (PP) micro-porous film as the separator, a solution of 1 M LiPF$_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v) as electrolyte and metallic lithium foil as counter electrode. The electrochemical tests were performed on a CT2001A Land battery testing systems (Hannuo Electronics Co. Ltd., China). The cells were charged and discharged at various current and a constant temperature of 25 °C in the voltage range of 0–1.5 V. Cyclic voltammogram (CV) was carried out at a scan rate of 0.1 mV s^{-1} on CHI660C electrochemical workstation (Shanghai Chenhua Co. Ltd., China). The electrochemical impedance measurements were also performed on CHI660C at an AC voltage of 5 mV amplitude in the 100 kHz to 0.01 Hz.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared CuO-nanotubes and CuO/SnO$_2$ composite. All the diffraction peaks of the as-prepared CuO-nanotubes are corresponding well with monoclinic-phase CuO (JCPDS 41-0254). The diffraction peak positions of the CuO/SnO$_2$ composite can be readily indexed to the monoclinic-phase CuO (JCPDS 41-0254) and SnO$_2$ with cassiterite structure (JCPDS 41-1445), no peak due to other phases are detected except for CuO and SnO$_2$.
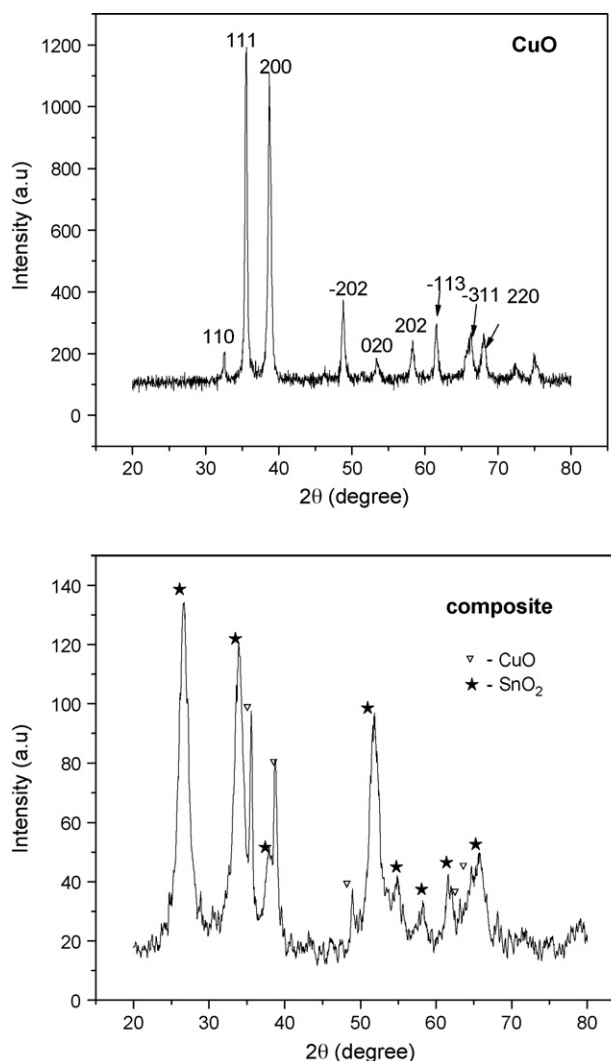

Fig. 1. XRD patterns of the samples.

The micrographs of samples have been investigated by SEM (Fig. 2). From Fig. 2(a), it is observed that the CuO-nanotubes were with smooth surface and diameters ranged from tens to two hundred nanometers. From Fig. 2(b), it can be observed that SnO$_2$ nanoparticles were coated on the surface of the CuO-nanotubes, which is confirmed by the EDS spot analysis (shown in Fig. 2c). Compared with CuO-nanotubes, the CuO/SnO$_2$ composite rods become with rougher surface and increased diameter about 1–2 μm. There are also some scattered SnO$_2$ particles on the side of the CuO/SnO$_2$ composite rods and not obvious conglomeration. To further analyze the microstructure of the composite, Fig. 3 gives TEM images with different magnified multiples of the CuO-nanotubes, the CuO/SnO$_2$ composite, and SnO$_2$ nanoparticles. Fig. 3(a)–(c) shows the typical TEM images of CuO-nanotubes, in which it can be seen that the wall-thickness of the nanotube is around 30 nm, the inner-diameter of the nanotube is around 100 nm. For the CuO/SnO$_2$ composite, it is found in the TEM images shown in Fig. 3(d)–(f) that the diameter of the CuO/SnO$_2$ composite rods increased because SnO$_2$ nanoparticles were uniformly coated on the surface of the CuO-nanotubes. The center of the CuO-nanotube in the CuO/SnO$_2$ composite is different with the central cavum of CuO-nanotube in Fig. 3(b) and (c), which was probably caused by the infiltration of SnO$_2$ nanoparticles. For comparison, the pure SnO$_2$ nanoparticles were prepared by the same procedure of the CuO/SnO$_2$ composite but without adding CuO-nanotube. Fig. 3(g)–(i) shows the typical
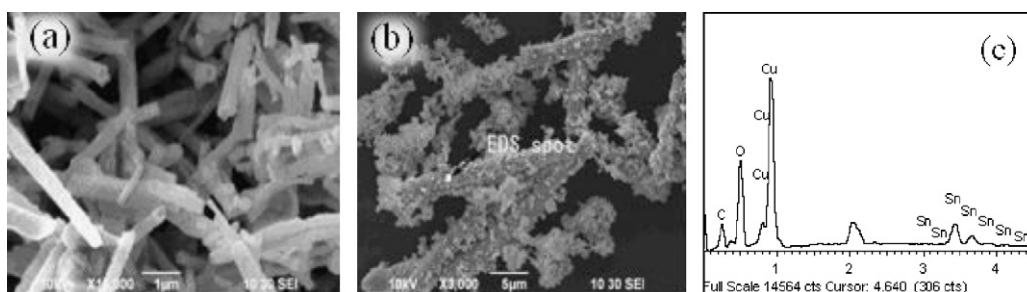
Fig. 2. SEM images of (a) the CuO-nanotubes, (b) the CuO/SnO₂ composite, and (c) the corresponding EDS spectra from the surface of the CuO/SnO₂ composite.

TEM images of the pure SnO₂ powders. It is observed that the SnO₂ powders are nanoparticle aggregations and the particles have an average size about 10–20 nm. Nanoparticle aggregations appeared in the pure SnO₂ powders while no obvious conglomeration in the CuO/SnO₂ composite. The result indicated that the good dispersion of SnO₂ nanoparticles on CuO-nanotubes with small particle size was obtained by introducing CuO-nanotubes in the composite.

Fig. 4 shows the discharge–charge curves of samples at the current of 50 mA g⁻¹. As shown in Fig. 4, the initial reversible capacities corresponding to the pure SnO₂ and the CuO/SnO₂ composite are 557.8 and 574.4 mAh g⁻¹, respectively. The initial coulombic efficiencies associated with pure SnO₂ and the CuO/SnO₂ composite are 31.65% and 41.85%, respectively. As shown in Fig. 4, the first discharge capacity of the CuO-nanotubes is 910.5 mAh g⁻¹, but the reversible capacity is negligible, only 120 mAh g⁻¹. Because CuO-nanotubes introduced into the CuO/SnO₂ composite showed a negligible reversible capacity compared with the pure SnO₂, the

initial reversible capacity of CuO/SnO₂ composite should be much lower than the pure SnO₂. However, experimental results were diametrically opposed. Why does the CuO/SnO₂ composite give the higher reversible capacity and initial efficiency?

As reported, CuO is also a potential candidate anode material for Li-ion battery with excellent cycling performance and high capacity [13–14], but its reversible voltage is as high as 2.5 V. In the voltage range of 0–3 V, CuO involves the following reversible reaction:

$$CuO + 2Li^+ + 2e^- \leftrightarrow Cu + Li_2O$$
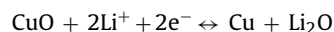
CuO was reduced to metallic Cu in the first discharge cycle as confirmed by the diffraction studies [13–16]. The recombination of Cu and Li₂O mainly occurs at the voltage of around 2.5 V [13–16]. In voltage window (0–1.5 V) of the present work, the reaction is irreversible. Fig. 5 shows the cyclic voltammograms of the electrodes composed of samples. For the pure CuO-nanotube electrode, only
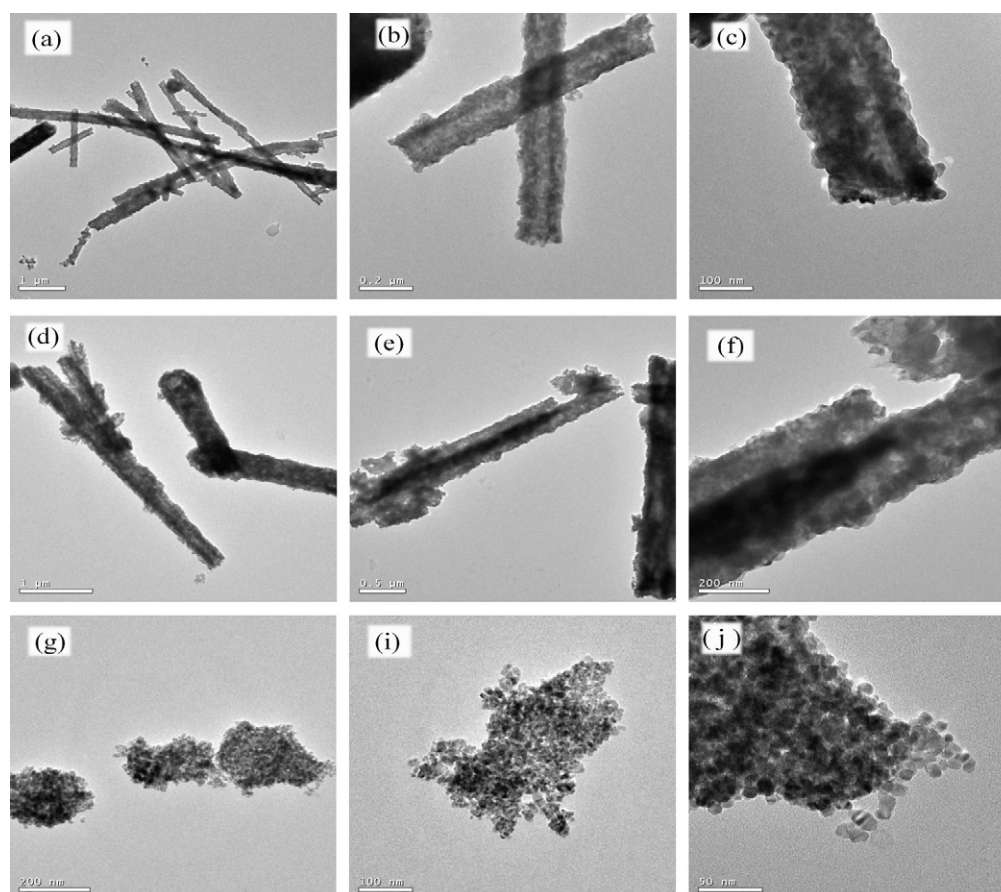

Fig. 3. TEM images of samples with different magnified multiples: (a–c) the CuO-nanotube; (d–f) the CuO/SnO₂ composite; (g–i) SnO₂ nanoparticles.
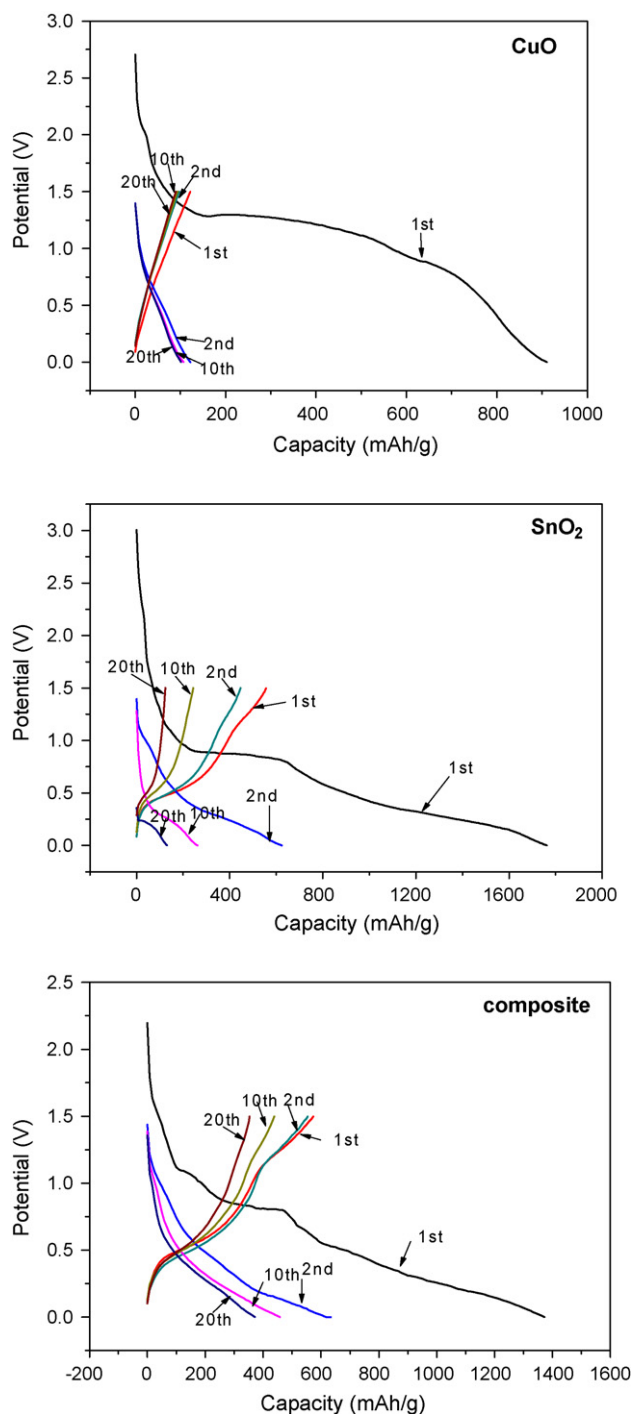
Fig. 4. The discharge–charge curves of samples at the current of $50\,mAh\,g^{-1}$.

Fig. 5. Cyclic voltammograms of the sample electrodes.

cathodic peaks can be observed and no reversible anodic peaks appeared, which confirmed the reaction is irreversible. For the pure SnO_2 curves, the cathodic peaks at around 0.2 V are related to the formation of Li–Sn alloys, and anodic peaks at around 0.5 V are the indication of de-alloying reaction of Li–Sn alloys. The curves of the SnO_2/CuO composite are very similar to the pure SnO_2. This implies the reduced metallic Cu was not acting as an active material contributing to the charge–discharge process.

Generally, the initial irreversible capacity loss of SnO_2 anode is mainly caused by the following factors: (1) the well-known and unavoidable phenomenon due to the irreversible appearance of Li_2O in the electrode reaction; (2) the severe side reaction of the
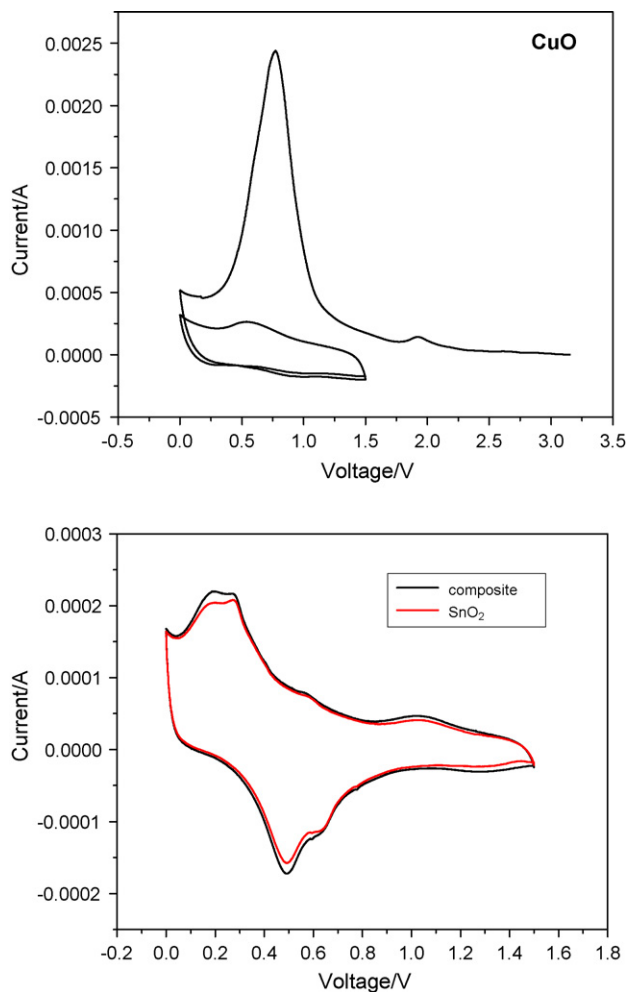
enlarged surface area of the nanosized-SnO_2 electrode with the electrolyte [17]. In order to improve the initial reversible capacity efficiency, two strategies are often employed. The first one is to reduce the side reaction of SnO_2 with the electrolyte. By choosing a narrow voltage window [18], surface coating, or additives [1] that can prevent the side reaction, the large irreversible capacity may be minimized. The second one is to improve the reversible capacity of the active material by the suitable combination with a conductivity additive [10–11,15,19]. In the present work, it was thought that the higher reversible capacity and initial efficiency of the SnO_2/CuO composite was mainly from the effects of the introduced CuO-nanotubes. As we know, the electrochemical performance of the SnO_2 nanomaterials has a dependence on their morphological characteristics. It was reported that the electronic conduction and charge transfer of SnO_2 nanowires and nanotubes along the length direction could be enhanced [11]. The one-dimensional structure of the CuO/SnO_2 composite features a high aspect ratio, which may provide better Li^+ transfer and more reaction sites [8,11]. As a result, the electronic conduction and the charge transfer of the composite along the length direction were enhanced [11]. On the other hand, the good dispersion of SnO_2 nanoparticles on CuO-nanotubes with small particle size was obtained by introducing CuO-nanotubes in the composite. Such a composite nanostructure can enhance the electrolyte/SnO_2 contact area, and lead to improved high current rate charge/discharge capacities [20,21]. Therefore, the CuO/SnO_2 composite gives the higher initial efficiency and reversible capacity.
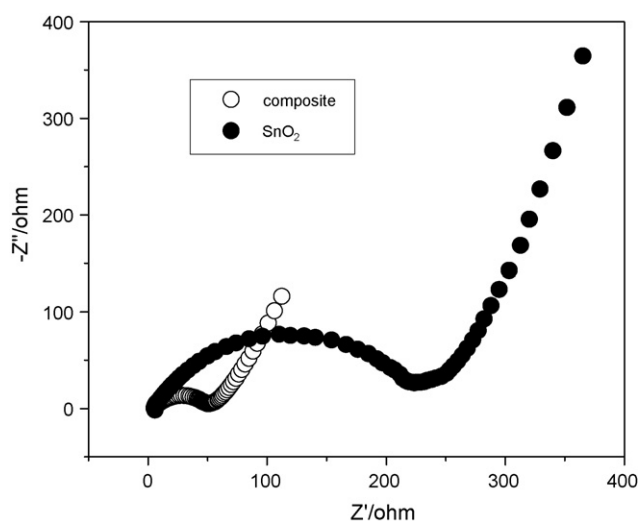
Fig. 6. AC impedance spectra of the sample electrodes measured at the open potential of 1.5 V (the 5th cycle).

Fig. 7. Discharge capacity vs. cycle number for the SnO_2/CuO composite and the bare SnO_2 anodes at different current.

Fig. 6 shows AC impedance spectra of the sample electrodes measured at the open potential of 1.5 V. The impedance spectra of the pure SnO_2 and SnO_2/CuO composite electrodes were obtained in the 5th cycle. The high-frequency semicircle is attributed to SEI film resistance, the semicircle in medium-frequency region is assigned to the charge-transfer impedance on electrode, and the inclined line corresponds to the lithium-diffusion process within electrodes [22]. From Fig. 6, it can be clearly seen that, in medium-frequency region the diameter of the semicircle for composite electrodes is smaller than that of pure SnO_2 electrodes. This result indicates that composite electrodes have lower charge-transfer impedances than pure SnO_2 electrodes when the surface area of both samples is same in the measurement of the impedance. Since the faradic reaction is determined by ion transfer and electron conduction, the reduction of the resistance can be attributed to the improved electronic conductivity of the composite electrodes induced by the metallic Cu. The electrochemical polarization of the composite electrode was greatly reduced compared with the pure electrode. The composite electrodes showed the higher reversible capacity close to theoretical reversible capacity taken out the factor of CuO-nanotubes in the CuO/SnO_2 composite. Fig. 7 shows the cycle number dependence of the extraction capacities of the CuO/SnO_2 composite and the pure SnO_2 electrodes at 50 and 200 mAh g^{-1}, respectively. The capacity of the pure SnO_2 electrode is rapidly decreased with the increasing cycle number, this is consistent with the results reported by literatures [1–10,16–17,20–24]. For the composite electrode, the capacity also decreased with the increasing cycle number. However, the latter produced a much
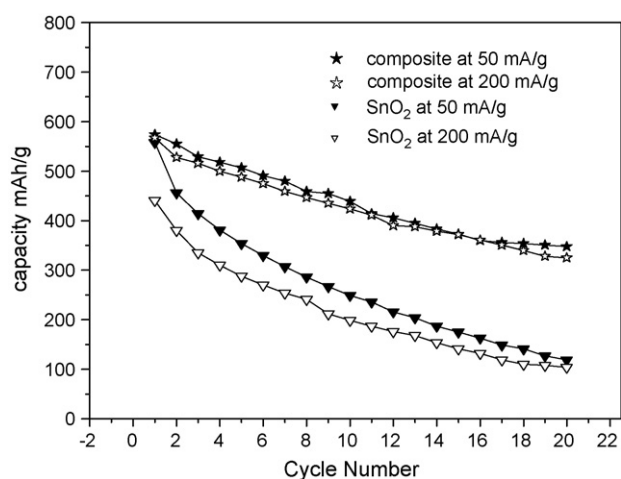
higher capacity retention than the former, up to 55.9% compared with only 21.3% after 20 cycles at 50 mAh g^{-1}. As shown in Fig. 7, even at a big current, the composite electrodes can maintain a higher extraction capacity and better cycle performance compared with the pure SnO_2 electrodes. The conclusion is supported by the SEM morphology of the electrodes after 20 cycles shown in Fig. 8. It is obviously that the pure SnO_2 electrode appeared the cracks after 20 cycles while the composite electrode did not appeared obvious cracks. The result implies the use of the CuO-nanotube is an effective way for enhancing the electrochemical performance of Li-ion battery.

It is believed that SnO_2 reacts with lithium in the following two step process [3,23]:

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

$$Sn + xLi^+ + ne^- \leftrightarrow Li_xSn, \quad 0 \leq x \leq 4.4 \tag{2}$$
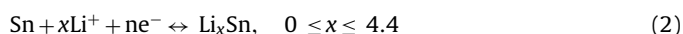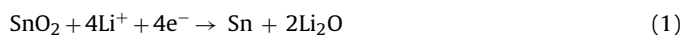
The irreversible process in Eq. (1) results in metallic tin dispersed in Li_2O matrix, then the alloying and de-alloying process of Li and Sn in Eq. (2) provides the reversible capacity of the material. But a large volume expansion occurs during the reversible step, even if the Li_2O matrix and small particle size SnO_2 can prevent Sn particles from aggregate, they cannot withstand the large volume change during the cycling process. So, the prevention or the minimization of the volume changes and the pulverization of the SnO_2 anode during the Li insertion and extraction process is important for improving the cycling ability of the electrodes. Fig. 9 shows SEM image of the CuO-nanotubes after 20th charge–discharge cycles at the current of 50 mAh g^{-1}. The XRD of CuO-nanotubes after the first discharge cycle was also given in Fig. 9, which shows the existence
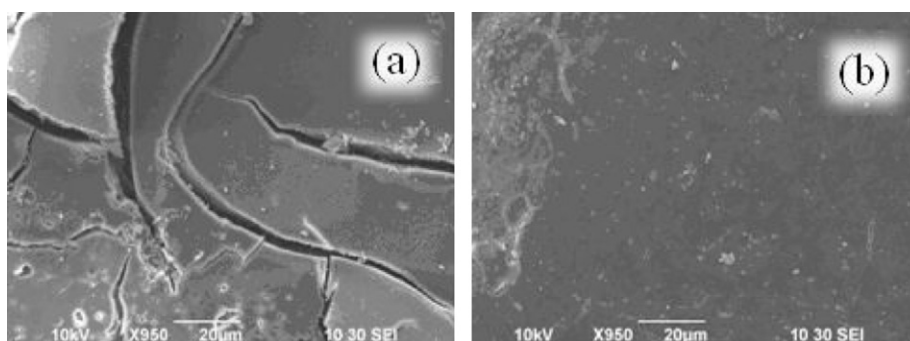

Fig. 8. SEM images of electrodes after 20 cycles: (a) the pure SnO_2 electrode and (b) the SnO_2/CuO composite electrode.
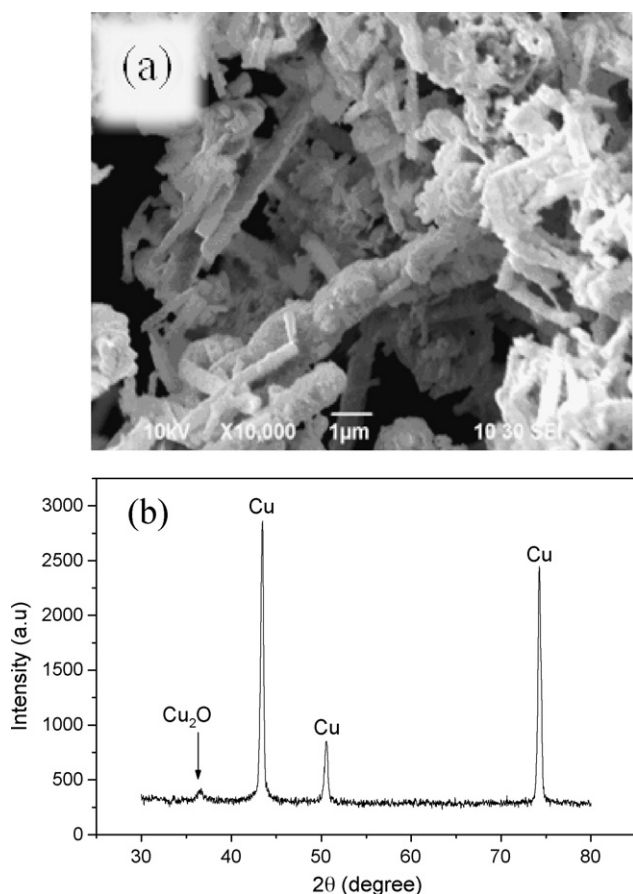
Fig. 9. (a) SEM imagine of the CuO-nanotubes after 20th charge–discharge cycles at the current of $50 \, mAh \, g^{-1}$, and (b) XRD patterns of the CuO-nanotubes after the first discharge cycle at the current of $50 \, mAh \, g^{-1}$.

size was obtained by introducing CuO-nanotubes in the composite. The cycling performance of SnO_2 nanomaterials of is extremely sensitive to their degree of aggregation [21,24].

4. Conclusion

A novel CuO-nanotubes/nanosized-SnO_2 composite was prepared and its electrochemical properties were investigated as the anode material for Li-ion battery. The composite as anode material for Li-ion battery showed higher reversible capacity, better durability and high rate performance than the pure SnO_2 powder. The better electrochemical performance can be attributed to the effect of CuO-nanotubes on SnO_2 nanoparticles in the composite. Due to the good electrical conductivity of the metallic Cu reduced from CuO, the lithium extraction reversibility was improved. On the other hand, the CuO-nanotubes as a tube structure buffer for the composite could effectively accommodate the volume variation of the Sn phase during cycling.

Acknowledgements

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of metallic Cu. The fact that CuO was reduced to metallic Cu in the first discharge cycle was also confirmed by the diffraction studies reported by Xiang et al. [15]. From the SEM image in Fig. 9, it is found that the reduced Cu still remained the original tubular structure. The one-dimensional structure and excellent flexibility of the composite was believed to lessen the effects caused by volume change during cycles and thus alleviate degrading of the electrodes [5]. The CuO-nanotubes have good mechanical strength and ductility, the central cavity of the nanotubes can also provide an extra space, and all of these can sustain the volume expansion caused by SnO_2. As noted above, all these advantages of CuO-nanotubes mentioned above can be remained for the CuO/SnO_2 composites during cycling because it was found that nanotube structure of the CuO-nanotubes was retained after 20th charge–discharge cycles at the current of $50 \, mAh \, g^{-1}$. On the other hand, it is also one of the reasons for the better cycle performance that the good dispersion of SnO_2 nanoparticles on CuO-nanotubes with small particle