Reversible and high-capacity SnO2/carbon cloth composite electrode materials prepared by magnetron sputtering for Li-ion batteries

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The flexible electrode material of SnO2/carbon cloth (SnO2/CC) is fabricated by RF magnetron sputtering method. As an anode material of lithium ion batteries, the SnO2/CC electrode exhibits more excellent cycling stability and rate capability than that of the pure carbon cloth and SnO2. The reversible capacity always maintain about 1.98 mAh/cm2 during 50 cycles, which is higher than that of the pure CC (about 1.61 mAh/cm2) and SnO2 (about 0.08 mAh/cm2). After 100 cycles, the capacity of SnO2/CC sample is 1.85 mAh/cm2, still retaining 89.4% of the initial capacity. The good electrochemical properties of SnO2/CC are mainly caused by the high surface area, porous structure and the intrinsic soft characteristics of CC, which can effectively accommodate the volume charge during charge and discharge process.

1. Introduction

Lithium ion batteries (LIBs) have attracted tremendous attention due to their advantages of high energy density, excellent cycle life and low environmental impact [1,2]. Graphite has been widely used as anode material for LIBs, however, the low capacity (372 mAh g⁻¹) of graphite can not satisfy the growing requirement for high energy and power density of next generation LIBs [3]. Among the numerous possible alternative anode materials, SnO2 has a high theoretical capacity (781 mAh g⁻¹) and low potential of lithium ion intercalation [4]. Therefore, it is considered to be one of the most promising candidates in the future. However, the severe volume change (over 300%) issue in the process of charging and discharging results in pulverization of active material [5] and loss of electrical contact at the anode [6,7]. Up to now, series of approaches have been adopted to overcome the above-mentioned problems. These methods include (i) reducing the size of particles, or preparing SnO2 material with special morphology [8], (ii) forming tin-base alloy [9], (iii) doping some substance, (iv) synthesizing composite material [10]. However, the traditional electrode materials prepared by aforementioned measures were mainly fabricated by coating method. Videlicet, the mixtures of the active material, conductive material (carbon black) and binder were coated on the current collector. Not only the process is complex, but also the active material can not be fully utilized. Therefore, if SnO2 can be synthesized directly on the flexible CC, which would make it have a good mechanical contact between the active material and the current collector, additionally, the energy density of the anode material has been greatly improved due to avoiding utilizing conductive additive and binder. However, that the SnO2 direct grown on CC by magnetron sputtering method as the anode material of LIBs has not been realized.

In this paper, the SnO2 is grown directly on the flexible CC by magnetron sputtering method as the anode material. The electrochemical performance of the sample was obviously improved.

2. Experimental

2.1. Preparation of SnO2/CC

The composite SnO2/CC was synthesized by RF magnetron sputtering. Firstly, the CC (WOS 1002, CeTech, the thickness is 360 µm, Fig. S1 shows the external photo and the low magnification SEM image of pure CC in the supplementary material) was cut into a circle with a diameter of 12 mm, cleaned with acetone, deionized water and absolute ethyl alcohol for about 30 min using supersonic wave apparatus, respectively. Then the CC was transferred into
bake oven at 80 °C for 12 h. After that, the CC was introduced into the magnetron sputter apparatus. Subsequently, the sputtering system was evacuated to a pressure of 5.0 × 10⁻⁴ Pa, then substrate was heated to 250 °C and the Ar/O₂ gas (both 99.999% in purity) mixture was adjusted at a flux ratio of 32:8. The pre-sputtering was carried out for 20 min to ensure a clean SnO₂ target surface. Next, the working pressure was adjusted to 0.5 Pa, sputtering power was setted to 100 W. After the CC was sputtered for two hours, the composite SnO₂/CC was prepared successfully.

2.2. Characterization

The prepared samples were characterized by using X-ray powder diffraction (XRD, SHIMADZU 6100) and scanning electron microscope (SEM, Phenom Prox). The energy dispersive spectrometer (EDS) and elemental mapping studies were performed under the SEM.

2.3. Electrochemical measurements

The electrochemical measurements were performed at 25 °C using coin cells (CR2025) with pure lithium foil as the counter and reference electrode. The prepared SnO₂/CC composite were used directly as the working electrode. Cells were constructed in a glove box in argon atmosphere under a dew point below -65 °C. The cells were performed by galvanostatic charge/discharge tests. The charge/discharge tests were carried out on a LAND battery program-control test system (CT2001A, Wuhan Jinnuo Electronic Co. Ltd. of China) at a constant current of 200 µA in a cut-off potential window of 0–3.0 V. Cyclic voltammetry (CV) measurements were carried out on a CHI660D electrochemical workstation at a scan rate of 0.2 mV s⁻¹ in a potential range of 0–3.0 V.

3. Results and discussion

3.1. Microstructure and morphology

Fig. 1a demonstrates the structural characteristics of the CC sample before magnetron sputtering investigated by XRD. The sharp peak at around 26° and the weak peak at around 44° are agreed with the carbon material (JCPDS file No. 65-6212) [11]. The XRD patterns of SnO₂/CC composite is shown in Fig. 1b, the major diffraction peaks are in accordance with the rutile SnO₂ (JCPDS file No. 41-1445), which suggests that high-purity SnO₂ products have been synthesized.

The typical SEM images of pure CC and the SnO₂/CC products are shown in Fig. 2a and b, respectively. As shown, every single carbon fiber is closely wrapped by nanometer-sized SnO₂. The inset in Fig. 2b shows that there are some fault sections on the surface of CC, which verify that the SnO₂ was grown on the CC successfully. Fig. 2c–f show the EDS mapping of the SnO₂/CC for the detected elements C, O and Sn, respectively. The C, O and Sn elements are uniformly distributed across the whole SnO₂/CC product.

In order to further analyze the stoichiometric proportion of the comprised elements in the as-prepared product, the EDS spectrum of SnO₂/CC has been carried out, and the results are shown in Fig. S2 in the supplementary material. The values of the atomic ratio among C, O and Sn are 45.9:35.5:18.6, which means the stoichiometric phase of SnO₂ has been obtained.

3.2. Electrochemical performance

In order to clarify the electrochemical reactions of the SnO₂/CC electrode, CV test in a potential range of 0–3.0 V versus Li/Li⁺ was implemented. And the result is shown in Fig. 3a. In the first cathodic scan, there is one weak peak at 0.95 V, which can be ascribed to the formation of the solid electrolyte interphase layer on the active materials, and the reduction of SnO₂ to Sn and the synchronous formation of LixSn as described in Eq. (1). The strong peak at about 0.25 V should be related to the formation of Li₂O as described in Eq. (2).
which is attested to be highly reversible during the charge and discharge process [12]. In the first anodic scan, the peaks at 0.65 and 1.85 V can be attributed to Li dealloying from Li$_x$Sn [13] and partly reversible reaction [14] of the Eq. (1), respectively. Meanwhile, it
quite obvious that the CV curves of the second and the third cycles were nearly overlapped, implying that the reactions in Eqs. (1) and (2) are highly reversible. The major reactions can be summarized as follows:

\[
\text{SnO}_2 + 4\text{Li}^+ + 4e^- \rightarrow \text{Sn} + 2\text{Li}_2\text{O} \quad (1)
\]

\[
\text{Sn} + x\text{Li} + xe^- \rightarrow \text{Li}_x\text{Sn}(0 \leq x \leq 4.4) \quad (2)
\]

The cycling performance of SnO\(_2\)/CC, pure CC and the SnO\(_2\) electrodes were investigated by galvanostatic charge and discharge between 0 and 3.0 V at the constant current of 200 \(\mu\)A, and the results are shown in Fig. 3b. The SnO\(_2\)/CC electrode displays a high reversible capacity and good cyclic retention. The reversible capacity always maintain at about 1.98 mAh/cm\(^2\) during 50 cycles, which is higher than the pure CC (about 1.61 mAh/cm\(^2\)) and SnO\(_2\) (about 0.08 mAh/cm\(^2\)). After 100 cycles, the capacity of SnO\(_2\)/CC sample was 1.85 mAh/cm\(^2\), still retaining 89.4% of the initial capacity. It is obvious that the SnO\(_2\)/CC sample demonstrates much better reversible capacity and cycle stability than the pure SnO\(_2\).

The SnO\(_2\)/CC sample also shows significantly enhanced rate performance than pure CC and SnO\(_2\). The comparison of the rate results of the three samples was shown in Fig. 3c. As can be seen, after the electrodes cycled at 200 \(\mu\)A for 10 cycles, the applied current densities were increased stepwise to 3200 \(\mu\)A. The average reversible capacities of the SnO\(_2\)/CC electrode are 1.83, 1.53, 1.22, and 0.86 mAh/cm\(^2\) at the constant current of 400, 800, 1600, and 3200 \(\mu\)A. However, the average reversible capacities of the pure CC electrode are 1.65, 1.36, 1.07, 0.78, and the average reversible capacities of the pure SnO\(_2\) electrode are 0.59, 0.41, 0.21, 0.11 mAh/cm\(^2\) under the same test program respectively. Most notably, it can be seen from Table S1 [15–20] in the supplementary material that the capacity of SnO\(_2\)/CC composite is much better than most of the previously reported SnO\(_2\)-based anode materials for LIBs. The improvement of lithium storage properties is mainly caused by synergistic effect of SnO\(_2\) and flexible CC. Firstly, compared with the traditional methods (hydrothermal method, molten salt method, etc.), the SnO\(_2\) prepared by magnetron sputtering method has better homogeneity and higher purity. Additionally, the SnO\(_2\) is grown directly on the flexible CC, the energy density of the anode material has been greatly improved due to avoiding utilizing conductive additive and binder. Secondly, CC with a three-dimensional structure has a good electronic transmission efficiency, which can greatly improve the rate performance of the battery. Thirdly, the high surface area, porous structure and the intrinsic soft characteristics of CC can effectively accommodate the volume change during charge and discharge process [21], which can enhance the cycle performance of the battery.

4. Conclusions

The SnO\(_2\)/CC composite was successfully fabricated by magnetron sputtering method. From the phase and morphology characterization results, it can be seen clearly that the sample has a high purity and uniformity. When used as anode materials for lithium-ion batteries, the SnO\(_2\)/CC electrode exhibits better electrochemical performance than the pure CC and SnO\(_2\), which is mainly because the high surface area, porous structure and the intrinsic soft characteristics of CC can effectively accommodate the volume change during charge and discharge process. The results of this work proposed a method for preparing flexible electrode material and enhancing the electric performance of SnO\(_2\) as anode materials in lithium-ion batteries.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.matlet.2016.12.071.

References