

锂离子电池用 Sn/C 复合材料的碳热还原法制备

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摘要: 采用碳热还原法制备了 Sn/C 复合材料, 通过 XRD、SEM、恒流充放电循环、慢速扫描循环伏安(CV)等方法对材料以及其电化学嵌脱锂性能做了研究。结果表明: Sn 球均匀分散在絮状碳材料中, 加热时间越长, Sn 球粒径越大。加热 8 h 得到材料的首次嵌锂比容量可达 1 014 mAh·g⁻¹, 循环 15 周以后的嵌锂比容量为 406 mAh·g⁻¹。

关键词: 锂离子电池; 碳热还原; Sn/C 复合材料

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Carbon-Thermal Synthesis of Sn/C Composites for Secondary Lithium-ion Batteries

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Abstract: Electrochemical active Sn/C composites were synthesized by carbon-thermal reduction method from SnO₂ and C in Ar atmosphere at 950 °C. The obtained composites were characterized by XRD and SEM. Lithium insertion/ extraction characteristics of the composites were examined by constant current charge-discharge and cyclic voltammetry methods(CV). The results show that Sn metal spheres are embedded in excessive flocculent carbon matrix homogeneously. The average size of Sn spheres becomes larger after heating for a longer time. Sn/C composite heated for 8 h exhibits initial lithium insertion specific capacity of 1 014 mAh·g⁻¹ and the highest reversible lithium insertion specific capacity of 406 mAh·g⁻¹ after 15 cycles coupled with a reasonable capacity retention(4%loss/cycle).

Key words: lithium-ion battery; carbon-thermal synthesis; Sn/C composite

Lithium-ion batteries have been widely used, especially in the areas of portable computers and mobile telephones. The most popular choice of anode material for these batteries is graphite^[1~3]. Graphite-based anodes^[4,5] have a theoretical lithium insertion capacity of 372 mAh·g⁻¹ to form LiC₆ intercalation compound. However, the required capacity is rapidly increasing and graphite is insufficient to meet the further needs.

Thus metals able to reversibly alloy with lithium, such as Sn^[6,7], Al^[8], Sb^[9,10], Si^[11], have been proposed as an alternative anode material. Much work has been focused on Sn-based materials, since Sn possesses larger theoretical capacity of 994 mAh·g⁻¹, corresponding to the formation of Li₂₂Sn₅^[3,12,13]. However, it suffers from poor cycling stability due to large volume changes (~358%) during lithium insertion/ extraction^[14]. It has

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been demonstrated that these drawbacks can be partly overcome by alloys, such as Sn-Cu^[6,7,13-16], Sn-Sb^[17,18], Sn-Ni^[19-22] and so on.

Sn/C composites have been expected to provide a better compromise between large specific capacity of Sn and good reversible cycling behavior of carbon. Various approaches have been used to prepare Sn/C composites, such as pyrolysis^[23,24], high-energy ball-milling^[25], modified electroless plating technique^[26], chemical reduction method^[2,5,27] and so on.

In this work, carbon-thermal reduction was employed to obtain Sn/C composites as anode materials in lithium-ion batteries.

1 Experimental

According to our previous results^[28-30], it is possible to generate Sn/C composites by carbon-thermal reduction at 950 °C. SnO₂ (>99.5%, Chemical pure, China) and carbon powder (Vulcan xc-72r, Cabot, America) were mixed homogeneously and then heated at 950 °C in argon atmosphere for different time in a tube furnace(Linn High Therm GmbH, Germany) in this work. The chemical reaction for the synthesis of Sn/C composites is: $\text{SnO}_2 + \text{C} \rightarrow \text{Sn/C} + \text{CO} \uparrow$. Different composites were obtained by controlling the reaction time from 4 to 12 h. The heating time is designated as Sn/C-X, where X represents the heating time in hours. Carbon was also heated at 950 °C for 8 h in the same process and designated as C-8.

The crystal structure of the composites was characterized by X-ray diffraction (XRD, Dmax-2400, Rigaku, Japan) using the Cu K α radiation source ($\lambda = 0.154\ 06\ \text{nm}$) and with the following experimental conditions: 40 kV potential, 150 mA current, $8^\circ \cdot \text{min}^{-1}$ scan rate and 0.02° step width over a 2θ range from 10° to 90° . The morphology, size distribution and shape of particles were observed using scanning electron microscopy(SEM, S-3500N, Hitachi, Japan) operating at 20 kV.

The electrochemical performances of Sn/C composites were examined by two-electrode cells. A N-methyl-2-pyrrolidinone slurry was prepared with Sn/C composite, acetylene black and polyvinylidene fluoride

(PVDF) in a mass ratio of 85:10:5/95:0:5. The slurry was cast onto copper foil and then dried at 60 °C for 3 h, then pressed at 8 MPa, and cut to 8 mm×8 mm in size, and finally dried under vacuum at 55 °C for 8 h. After drying, the electrodes were moved into the Ar-filled glove box (Ar atmosphere, O₂ and moisture content <10 $\mu\text{L} \cdot \text{L}^{-1}$, Labmaster 130, Mbraun). Lithium metal plate served as counter and reference electrodes. The electrolyte was 1 mol·L⁻¹ LiPF₆ in EC/DMC(1:1 in mass ratio).

Cyclic voltammetry(CV) measurements were carried out on an IM6e electrochemical instrument(Zahner Elektrik, Germany) with a scan rate of 0.1 mV·s⁻¹ between 0.005 and 2.0 V (vs. Li⁺/Li). Charge/ discharge experiments were conducted with a Land cell tester (Wuhan, China). The cut-off voltage is 0.005~1.2 V(vs. Li⁺/Li) during charge/ discharge, and constant current density is 0.16 mA·cm⁻².

2 Results and discussion

2.1 X-ray diffraction and scanning electron microscopy characteristics

Fig.1 shows XRD patterns of all three kinds of composites obtained by carbon-thermal reduction at 950 °C for 4, 8 and 12 h. Only a trace of SnO₂ can be identified by XRD, the main peaks correspond to Sn phase with a tetragonal *I4₁/amd* structure, implying that SnO₂ was reduced by carbon at 950 °C effectively. The average crystal size of Sn spheres in Sn/C-4h sample was estimated to be about 54 nm from the value of the full width at half height of the(200) reflection, according

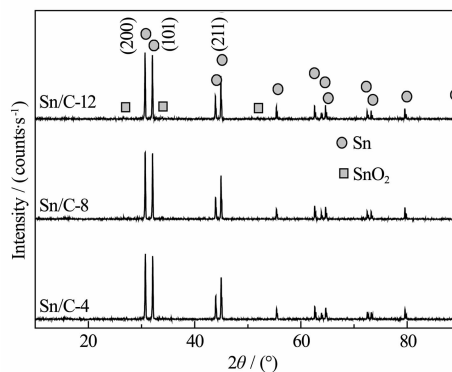


Fig.1 XRD patterns of Sn/C composites prepared by carbon-thermal reduction at 950 °C for 4, 8 and 12 h

to Scherrer formula. After heating for a longer time, aggregation and coalescence of Sn particles lead to Sn crystallites of about 65 nm and 66 nm in crystal size for Sn/C-8h and Sn/C-12h samples, respectively, but there is no significant difference in the intensity of the SnO_2 peaks among three kinds of composites. This is thought to be due to the lack of the connection between SnO_2 embedded in the Sn matrix with carbon.

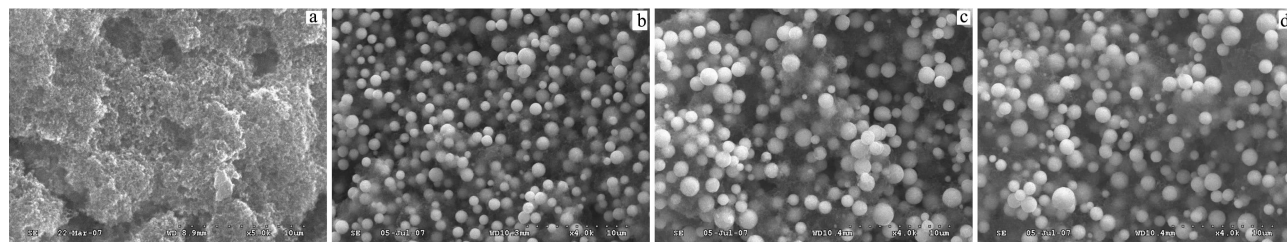


Fig.2 SEM images of carbon heated at 950 °C for 8 h and Sn/C composites prepared by carbon-thermal reduction at 950 °C for 4, 8 and 12 h: (a) C-8, (b) Sn/C-4, (c) Sn/C-8 and (d) Sn/C-12

2.2 Electrochemical characteristics

Table 1 summarizes the results of electrochemical performance for all five kinds of electrodes. The electrodes cast with Sn/C composites show much lower undesirable irreversible capacity in the first discharge than the electrode E, which makes Sn/C composites

meet one of the demands for practical use in commercial batteries. The electrode D composed of Sn/C-8h sample(85wt%), acetylene black(10wt%) and PVDF binder(5wt%) has the best cycle performance as it exhibits a moderately lower loss per cycle of ~4%.

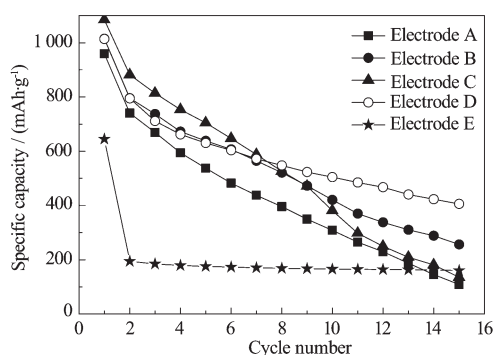
Table 1 Comparison of electrochemical characteristics of electrodes cast with Sn/C composites and with carbon

Electrode No.	Sample	Mass ratio of the composite, conductive agent and binder	Initial lithium extraction specific capacity / ($\text{mAh} \cdot \text{g}^{-1}$)	Initial irreversible loss / (%)	Loss per cycle / (%)
A	Sn/C-4	95:0:5	701	27	6
B	Sn/C-8	95:0:5	749	26	5
C	Sn/C-12	95:0:5	824	24	6
D	Sn/C-8	85:10:5	736	27	4
E	Carbon	95:0:5	141	78	5

The electrochemical performance of five kinds of electrodes is compared in Fig.3. After the first discharge, the electrode E cast with carbon sample shows slight fading of the reversible capacity with cycling, but lower reversible specific capacity. It is obvious that with the same mass ratio of 95:0:5, Sn/C composite prepared by heating for the longest time yields the largest initial lithium insertion specific capacity, but the electrode B cast with Sn/C-8h sample possesses the highest specific capacity of $257 \text{ mAh} \cdot \text{g}^{-1}$ after 15 cycles. Compared electrode B with D, it is

evident that mixing conductive agent here has no impact on the initial specific capacity of lithium insertion, but improves the electrode cycle performance significantly. The electrode D retains the highest reversible lithium insertion specific capacity of $406 \text{ mAh} \cdot \text{g}^{-1}$ after 15 cycles, which is higher than the theoretical lithium insertion capacity of graphite. It is possible that the conductive agent increases electronic contact among the Sn spheres interface.

Tin-graphite materials generated by chemical reduction yielded stable reversible capacity as high as



Charge/discharge current density $0.16 \text{ mA} \cdot \text{cm}^{-2}$, Potential range $0.005 \sim 1.2 \text{ V}$

Fig.3 Cycle performance of electrodes cast with carbon and with Sn/C composites in different mass ratios

$415 \text{ mAh} \cdot \text{g}^{-1}$ after 12 cycles^[5]. Tin-carbon composites prepared by adding 20% SnO_2 to a vacuum residue and following carbonization generated reversible capacity up to $400 \text{ mAh} \cdot \text{g}^{-1}$ after 25 cycles^[31]. When compared to these literatures^[5,31], the method employed by this study has the advantages of simple and safe operation and is suitable for mass production. According to our previous results^[28-30], Sn-carbon binary composites synthesized by selecting active carbon, mesocarbon microbeads(MCMB)

and graphite as reductant showed good performance. In this study, reversible capacity after 15 cycles of Sn/C composite is almost the same as those of forenamed composites, but the material is the most homogeneous one and the initial irreversible loss is smaller.

The electrode B(Fig.4a), after 1 cycle(Fig.4b) and 15 cycles(Fig.4c, d) were also observed by SEM. It is obvious that Sn spheres disperse inside the carbon rather than bind to carbon. Free Sn spheres are supposed to behave like massive elemental tin during lithium insertion^[5]. It is seen that the Sn spheres after 15 cycles(Fig.4c, d) shows much more cracks than the one after 1 cycle (Fig.4b), namely, the electrode has already experienced some structural failure, which will lead to a substantial change in the specific volume generating cracks and pulverization of the electrode with consequently a loss of inter-particle electronic contact and a capacity fade upon cycling. It is indicated that prolonged cycling continues to degrade the structural integrity of the electrode, which is conformed by the continual loss of capacity seen in Fig.3 for this electrode.

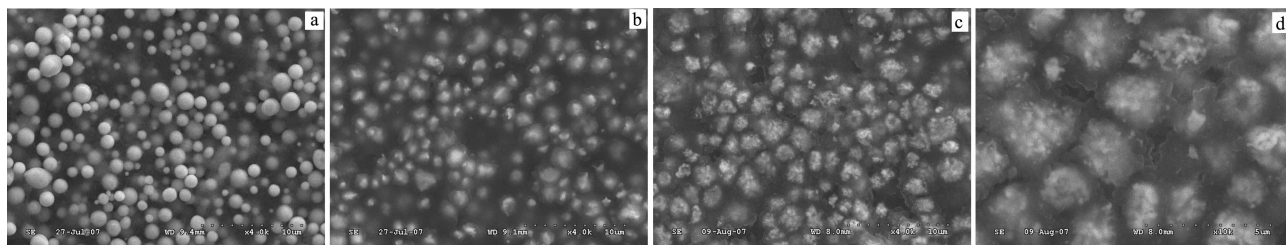


Fig.4 SEM images of electrode B cast with Sn/C-8h sample in the mass ratio of 95:0:5(a), after 1st cycle(b) and 15th cycle(d)

Fig.5 displays the first five cyclic voltammograms (CVs) of the electrode B. The broad peak observed between 1.6 and 1.4 V(vs. Li^+/Li) can be attributed to the irreversible formation of solid electrolyte interphase (SEI) on graphite and Sn surfaces, which contributes partly to the irreversible capacity of the electrode. The intensity of the peak related to the formation of SEI increases firstly during the first five cycles, and then decreases and disappears in the fifth reduction. This behavior is probably related to the structural factors of the composite. Sn spheres embedded in the carbon matrix are uncovered in the electrolyte after cycling and then SEI forms on the fresh Sn surfaces.

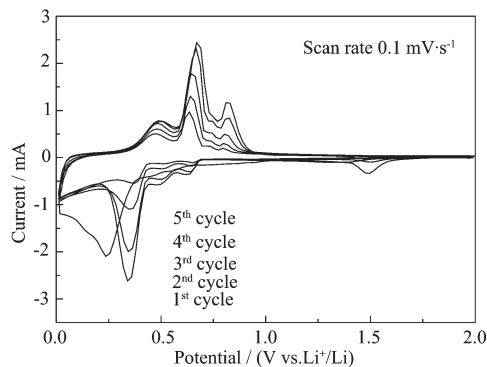


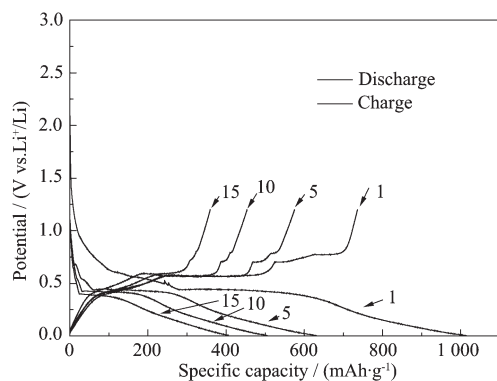
Fig.5 Cyclic voltammograms of electrode B cast with Sn/C-8h sample in the mass ratio of 95:0:5

The reduction peaks are related to the formation of the Li_xSn ($0 < x \leq 4.4$, Li_2Sn_5 , LiSn , Li_7Sn_3 , Li_5Sn_2 ,

$\text{Li}_{13}\text{Sn}_5$ and $\text{Li}_{22}\text{Sn}_5$) alloys between 0.8 and 0.2 V (vs. Li^+/Li) and corresponding peaks related to lithium de-alloying are present in the oxidation curve. According to the literature^[32] and to our previous results^[28-30], the reduction peaks are corresponding to the formation of Li_bSn ($b < 0.7$), Li_cSn ($c = 0.7 \sim 3.5$) and Li_dSn ($d = 3.5 \sim 4.4$) in turn. These peaks weaken greatly, which is consistent with the result of cycle performance curves shown in Fig.3.

The reduction peak below 0.1 V (vs. Li^+/Li) is related to the lithium insertion into carbon, but there is no corresponding peak related to the lithium extraction from carbon in the oxidation curve. Upon the first five cycling, the intensity of the peak below 0.1 V (vs. Li^+/Li) decreases and then to a stable value.

The insertion specific capacity close to $1\,015\text{ mAh}\cdot\text{g}^{-1}$ after 1 cycle decreases to a value of $406\text{ mAh}\cdot\text{g}^{-1}$ after 15 cycles, as presented in Fig.6. The potential plateaus are corresponding to the peaks present in cyclic voltammogram. The irreversible capacity observed during the first charge/discharge cycle is close to $278\text{ mAh}\cdot\text{g}^{-1}$. This value can be mainly related to lithium irreversible insertion into carbon and to the SEI formation on tin and carbon surfaces. In following cycles, the irreversible capacity decreases rapidly with cycle numbers and then decreases to a stable value of about $50\text{ mAh}\cdot\text{g}^{-1}$, likely in connection with less lithium irreversible insertion into carbon and the formation of the SEI on the tin surfaces.



Charge/discharge current density $0.16\text{ mA}\cdot\text{cm}^{-2}$, Potential range 0.005~1.2 V

Fig.6 Charge-discharge curves of electrode D cast with Sn/C-8h sample in the mass ratio of 85:10:5

3 Conclusion

Electrochemical active Sn/C composites as anode of lithium-ion batteries were synthesized by carbon-thermal reduction. The electrode composed of Sn/C composite heated for 8 h (85wt%), acetylene black (10wt%) and PVDF binder (5wt%) has the best performance. It exhibits initial lithium insertion specific capacity of $1\,014\text{ mAh}\cdot\text{g}^{-1}$, and initial coulombic efficiency of 73%. After 15 cycles, it possesses high reversible lithium insertion specific capacity of $406\text{ mAh}\cdot\text{g}^{-1}$ and an excellent cycle performance with only 4% capacity loss per cycle.

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