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Improved Coulombic efficiency and cycleability of SnO$_2$-Cu-Graphite composite anode with dual scale embedding structure

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Abstract

To improve the Coulombic efficiency (CE) and cycle life of SnO$_2$ anode in lithium ion batteries, SnO$_2$-Cu-Graphite composites with dual scale embedding structure are synthesized by ball milling. The SnO$_2$-Cu composite, in which SnO$_2$ nanoparticles with grain size less than 10 nm are uniformly dispersed in inactive nanocrystalline Cu matrix, is firstly obtained by milling the mixture of SnO$_2$ and Cu nanopowders (molar ratio 1:2), and then further mill with graphite (C) to obtain SnO$_2$-Cu-C composite with microsized graphite sheets as matrix of SnO$_2$-Cu composite. The 50h-milled SnO$_2$-Cu composite exhibits higher initial CE (76.0±1.5%) and subsequent CE than 50h-milled SnO$_2$. Furthermore, the SnO$_2$-Cu-C composite anode is capable of retaining a maximum charge capacity of 450.8 mAh g$^{-1}$ at 100 mA g$^{-1}$ after 80 cycles with a capacity retention ratio of 74.4%, displaying superior cyclic stability to as-milled SnO$_2$, SnO$_2$-Cu and SnO$_2$-C composites. The improved CE and cycleability are attributed to the unique dual scale embedding structure that offers good conductivity of electron and lithium ion as well as the nanostructure stability of active materials. This unique composite structure might be extended to other high-capacity anode materials, to achieve high performance lithium ion batteries.

Keywords

Lithium ion batteries, Tin oxide anode, Dual scale embedding structure, Initial Coulombic efficiency, Lithium oxide
1. Introduction

The anode materials with high-energy density and long cycle life is one of keys for the development of lithium-ion batteries. \(^{1-3}\) SnO\(_2\) has been intensively investigated as alternative anode to commercially available graphite because of its high theoretical specific capacity of \(~1494\ \text{mAh g}^{-1}\), which is four times as that of graphite. The de-/lithiation mechanism of SnO\(_2\) could be described by the two-step reactions, \(^{4-8}\) i.e., the conversion reaction (SnO\(_2\) + 4Li\(^+\) + 4e\(^-\) ↔ Sn + 2Li\(_2\)O) and alloying reaction (Sn + xLi\(^+\) + xe\(^-\) ↔ Li\(_x\)Sn, 0 ≤ x ≤ 4.4), which could contribute theoretical capacity of 712 and 782 mAh g\(^{-1}\), respectively. However, the reversibility of the conversion reaction of SnO\(_2\) is rather poor, resulting in large initial irreversible capacity and low initial Coulombic efficiency (ICE), the theoretical ICE value is only 52.4% if the conversion reaction is fully irreversible.\(^{7-12}\) In addition, the huge volume variation (~300%) caused by lithium insertion and extraction of Sn results in the loss of active materials and rapid capacity fade, and thus the cyclic CE and reversible capacity are further decreased.\(^{13-15}\)

Extensive research efforts have been devoted to improving the electrochemical performances of SnO\(_2\) anode.\(^{7-12, 16-20}\) Undoubtedly, the nanosizing strategy is the most effective way to improve not only the reversibility of SnO\(_2\) but also ease the huge internal stress of Sn particles. It was found that Sn nanoparticles generated from ultrafine SnO\(_2\) readily reacted with Li\(_2\)O in the charging process, which was verified by the anodic peaks appearing above 1.3V in the cyclic voltammetry curve\(^{7-11}\) and the TEM observation of SnO and SnO\(_2\).\(^{12}\) Further, constructing nanostructured multiphase composite is shown to greatly improve the
ICE and cyclic performance of SnO$_2$ anode simultaneously.$^{10-12, 17-19}$ On the composition design of SnO$_2$ based composite, the light-weight carbon matrix is mostly used because of excellent electric conductivity and stress buffering effect.$^{18-20}$ For example, Lu et al.$^{10}$ prepared SnO$_2@$C composite by *in-situ* hydrolysis method, in which ultrafine SnO$_2$ was encapsulated in ordered tubular mesoporous carbon. The composite electrode showed a considerably high initial reversible capacity of 978 mAh g$^{-1}$ at a current density of 200 mA g$^{-1}$, which even increased up to 1039 mAh g$^{-1}$ after 100 cycles. However, the mechanism of those reported unusual high reversible capacity and Coulombic efficiency has not been fully revealed, and in particular, those synthetic processes usually include complicated steps and offer limited throughput.

Recently, conventional milling and plasma-assisted milling techniques have been used to synthesize various Sn-C, SnO$_2$-C composites with specific structure and enhanced electrochemical performances.$^{21, 22}$ Nevertheless, the previously reported ICE of SnO$_2$ based anodes prepared by the ball milling is normally low,$^{21-24}$ which needs further improvement. It is expected that the transition metals like Cu have the excellent electro-catalytic activity and conductivity, which should facilitate the Li$_2$O decomposition.$^{25}$ Also, the Cu additive is beneficial to not only the dispersion and refinement of SnO$_2$ particles in the milling process but also maintain the nanostructure of SnO$_2$ during cycling, which would promote the conversion and alloying reactions of SnO$_2$.

Herein, focusing on the improvement in CE and cyclic stability, the SnO$_2$-Cu composite was designed and prepared by ball milling. We prepared the SnO$_2$-Cu composite through ball
milling, aiming to obtain the soft Cu matrix embedded by nanosized SnO$_2$ particles. To further improve the cyclic performance of SnO$_2$-Cu composite, the graphite was added. The relationship between the microstructure and electrochemical performances of the as-milled SnO$_2$-Cu and SnO$_2$-Cu-C composites as well as the dependence on the preparing parameters and the composition were investigated in detail.

2. Experimental

2.1 Materials preparation

The raw materials are commercial natural graphite (99.9%; 38µm; Shanghai Colloid Chemical Plant, China), SnO$_2$ (99.99%, 50~70nm, Aladdin Industrial Inc., China) and Cu (99.9%, 80~100nm, Shanghai ST-nano Tech Co., Ltd., China) nanopowders. Firstly, the SnO$_2$ and Cu nanopowders with molar ratio of 1:2 were milled to form the SnO$_2$-Cu composite, the milling was performed on a planetary mill (QM-3SP4, China) with the weight ratio of ball-to-powder of 20:1 at 500 rpm for 10h and 50h, yielding the composites denoted as SnO$_2$-Cu-10h and SnO$_2$-Cu-50h, respectively. For comparison, a manually ground SnO$_2$-Cu mixture was prepared and denoted as SnO$_2$-Cu-0h, and the pure SnO$_2$ was milled for 50h using the same milling parameters and denoted as SnO$_2$-50h. Secondly, the SnO$_2$-Cu-50h composite was further milled with 10, 20, 30 wt.% graphite for 20h at 500rpm with ball-to-powder weight ratio of 30:1, yielding the composites termed as SnO$_2$-Cu-50h-10%C, SnO$_2$-Cu-50h-20%C, SnO$_2$-Cu-50h-30%C, respectively. Similarly, the SnO$_2$-Cu-10h composite and 50h-milled SnO$_2$ were also milled with 30 wt.% graphite for 20h, the resultant
composites were termed as SnO$_2$-Cu-10h-30%C and SnO$_2$-50h-30%C, respectively. The graphite was pre-milled for 10h at 500 rpm with the same ball-to-powder weight ratio. To prevent the Cu nanopowders from oxidation, all the powder mixtures were sealed in the stainless steel vial under pure argon atmosphere. After each 30 min of milling, the operation was suspended for 30 min to avoid temperature rising, and the milled powders were collected under pure argon atmosphere without heavy scraping.

2.2 Materials Characterization and Electrochemical measurement

The X-ray diffractometer (XRD, Philips X’Pert MPD) with Cu-K$_\alpha$ radiation, the field emission scanning electron microscope (SEM, Carl Zeiss supra40) and transmission electron microscope (TEM, JEOL-2100) operating at 200kV were used to characterize the phase structure, morphology and distribution of the composites. The milled SnO$_2$-Cu-10h and SnO$_2$-Cu-50h powders for SEM observation were compacted and followed by polishing process, while the other powder samples were dispersed and directly observed in the SEM experiments. As for the TEM specimen preparation, the powder was transferred out from the Ar-filled glove box and dispersed on a holey carbon film supported by a copper grid very quickly.

The electrochemical properties of the as-prepared composites were measured using coin-type half-cells (CR2016) assembled in an Ar-filled glove box with oxygen and moisture content less than 1 ppm. The working electrode was prepared by dissolving 80 wt.% active powders, 10 wt.% conductivity agent (Super-P), and 10 wt.% binder (polyvinylidene fluoride, PVdF) in solvent (N-methyl-2-pyrrolidone, NMP) with appropriate viscosity. Then the slurry
was coated onto copper foils by a spin coater and dried at 120°C in a vacuum oven for 10h. The loading of active materials was 1.5~1.8 mg cm$^{-2}$. Lithium metal foils were used as counter and reference electrodes and polyethylene membranes (Teklon@Gold LP) as separators. The electrolyte was LiPF$_6$ (1M) in a mixture of ethylene carbonate/diethyl carbonate/ethyl methyl carbonate (EC/DEC/EMC, 1:1:1, v/v/v, Shanshan Tech Co., Ltd.). Galvanostatic charge–discharge measurements were performed with battery testers (CT2001A, Land) at various current densities in the range of 0.01−3.0 V vs. Li/Li$^+$, and the current density and capacity were based on the weight of composite materials (such as SnO$_2$-C, SnO$_2$-Cu, SnO$_2$-Cu-C) without conductive agent and binder. Cyclic voltammetry (CV) test over the potential range of 0.0−3.0 V vs. Li/Li$^+$ at a scan rate of 0.2 mV s$^{-1}$ was performed on an electrochemical workstation (Interface 1000, Gamry). All the tests were carried out at ambient temperature.

3. Results and Discussion

3.1 SnO$_2$-Cu composites

Fig. 1a shows the XRD patterns of SnO$_2$-Cu composites milled for different times. Comparing with the sharp diffraction peaks in the un-milled SnO$_2$-Cu-0h sample, the peaks of SnO$_2$ and Cu become broadening and weakening with the increasing milling time, indicating the striking grain refinement of SnO$_2$ and Cu by milling. Based on the XRD peak profile analysis using the Scherer equation, the crystallite sizes of SnO$_2$ and Cu after 50h of milling are calculated as ca. 9 nm and 13 nm, respectively. It is observed in the 50-milled composite
that a weak Fe(110) reflection appears around 44.6°, which indicates small amount of Fe contamination caused by long time milling. Meanwhile, the Cu(111) peak shifts to the lower angle, which is an indication of the increase in the lattice constant of Cu. This might be owing to the formation of the Cu(Sn) solid solution by milling, because small amount of Sn is possibly formed via the mechanochemical reaction between Cu and SnO$_2$, and its relatively larger atomic radius ($r_{\text{Sn}}=0.158$ nm) than Cu ($r_{\text{Cu}}=0.128$ nm) results in the lattice expansion of Cu. The influence of the Fe contamination on the electrochemical performance of as-milled composites will be not further discussed due to its little amount.

Fig. 1b-e show the SEM images of pristine SnO$_2$, Cu nanopowders and SnO$_2$-Cu composites milled for different times, and Fig. S1 (see the ESI) shows the back-scattered electron SEM image of SnO$_2$-Cu-10h composite. Fig. 1b and Fig. 1c show that the pristine Cu and SnO$_2$ nanopowders have a particle size of 80 ~ 200 nm and 50 ~ 200 nm, respectively. For the SnO$_2$-Cu-10h (Fig. 1d and Fig. S1), the SnO$_2$ nanoparticles of 30 ~ 200 nm (white dots) are homogeneously distributed in the continuous Cu matrix (grey region), which experiences considerable agglomeration due to the drastic cold welding by mechanical impact of steel balls. As the milling time increases to 50h (Fig.1e), the disappearance of SnO$_2$ particles indicates the further grain refinement of SnO$_2$ and fully embedding of SnO$_2$ in the continuous Cu matrix.

To further investigate the distribution of SnO$_2$ in Cu matrix, the SnO$_2$-Cu-50h sample is characterized by TEM, and the results are shown in Fig. 1f-h. The bright-field TEM image (Fig. 1f) combined with the selected-area electron diffraction patterns (Fig. 1g) indicate the
homogeneous microstructure of SnO$_2$-Cu composite, while the high resolution TEM image (Fig. 1h) identifies the Cu and SnO$_2$ phases according to their characteristic planar distances. The measured Cu(111) inter-planar distance of 0.213 nm is slightly larger than the standard value (0.208 nm, JCPDS No. 03-065-9743) because of the formation of Cu(Sn) solid solution, which also agrees well with the XRD result (Fig. 1a). Importantly, it is clearly seen from Fig. 1h that the grain size of SnO$_2$ and Cu crystals are both about 10 nm, and the nanosized SnO$_2$ are homogeneously embedded in the nanocrystalline Cu matrix. The nanocrystalline structure of Cu matrix is formed due to the repeated cold welding and fracturing in the milling process.$^{27-29}$

Fig. 2a shows the initial discharge-charge profiles of the SnO$_2$-Cu-0h, SnO$_2$-Cu-10h, SnO$_2$-Cu-50h composite electrodes at a current density of 85 mA g$^{-1}$. The initial discharge and charge capacities of the SnO$_2$-Cu-0h, SnO$_2$-Cu-10h, SnO$_2$-Cu-50h electrodes are 716.4 and 231.2 mAh g$^{-1}$, 770.8 and 500.9 mAh g$^{-1}$, 752.4 and 566.5 mAh g$^{-1}$ respectively, corresponding to the ICE of 32.3%, 65.0%, 75.3% respectively. It is noted that the initial discharge capacity of SnO$_2$-Cu-50h is close to its theoretical value (1494 x 54.25% = 810.5 mAh g$^{-1}$) if only considering the contribution of the SnO$_2$ component in the SnO$_2$-Cu composite. To give a more accurate comparison of ICE between different SnO$_2$-Cu composite electrodes, the ICE statistics from six cells and the ICE values (mean ± standard deviation) for the SnO$_2$-Cu-0h, SnO$_2$-Cu-10h, SnO$_2$-Cu-50h composites are listed in Table 1. It is shown that the SnO$_2$-Cu-50h electrode has the highest ICE of 76.0±1.5%, which is much higher than the theoretical value 52.4% and those for the SnO$_2$-Cu-10h electrode (66.3±1.4%) and the
SnO$_2$-Cu-0h electrode (30.9±1.7%). This result is also much higher than previously reported ICE values of SnO$_2$ based anodes.\textsuperscript{21-24,30-33} Obviously, both the ICE and the initial reversible capacity increase with the milling time, which implies the improved reversibility of SnO$_2$.

The role of Cu additive is further confirmed by comparing the long-term Coulombic efficiency of the SnO$_2$-Cu-50h and SnO$_2$-50h electrodes. As shown in Fig. 2b, although the SnO$_2$-50h electrode shows high ICE of 74.4±1.9% (Table 1), its CE increases gradually up to 94.1% at the 15$^{th}$ cycle. Comparatively, the CE of SnO$_2$-Cu-50h electrode rapidly increases up to 95.6% at the second cycle and almost keeps stable in the subsequent cycles.

To understand the improvement in the Coulombic efficiency, the reaction mechanism of SnO$_2$ is investigated by CV analysis on the SnO$_2$-Cu-0h, SnO$_2$-50h and SnO$_2$-Cu-50h electrodes. Fig. 3 compares the initial five CV curves of these three electrodes. Two cathodic peaks $B$, $C$ and an anodic peak $C'$ appear in the first cycle for all three electrodes, which are respectively attributed to the reduction of SnO$_2$ to metallic Sn, the alloying of Li with Sn to form Li$_x$Sn during lithiation, and the Li$_x$Sn de-alloyed into metallic Sn during delithiation. For the SnO$_2$-Cu-50h electrode (Fig. 3a), the characteristic peak $B$ shows good reproducibility in the subsequent cycles, indicating the reversible formation of SnO$_2$ from the redox reaction of Li$_2$O in the charging process, which is also verified by two broad anodic peaks above 1.3V. To be specific, the anodic peak $B_1'$ at ca. 1.35V should be attributed to the redox reaction between Sn and Li$_2$O to form SnO (Sn + Li$_2$O $\rightarrow$ SnO + 2Li$^+$ + 2e$^-$), while the anodic peak $B_2'$ at ca. 1.80V should be ascribed to the further redox reaction between SnO and Li$_2$O to regenerate SnO$_2$ (SnO + Li$_2$O $\rightarrow$ SnO$_2$ + 2Li$^+$ + 2e$^-$), which is in agreement with the previous
CV results on the reversible formation of SnO$_2$.\textsuperscript{7-11} In addition, it is noted that there is no anodic peak of the redox reaction of Li$_2$O with Cu for these three electrodes, which should appear above 2.5V.\textsuperscript{34,35} These results demonstrate that the Cu additive is electrochemically inactive to react with Li$_2$O, but it promotes the reversible formation of SnO$_2$.

Comparatively, Fig. 3b shows no characteristics of redox reaction of Li$_2$O even at the first cycle, which explains the rather low ICE for the SnO$_2$-Cu-0h electrode. With respect to the SnO$_2$-50h electrode (Fig. 3c), the anodic peaks $B_1'$, $B_2'$ becomes rapid weakening with the cycling number, similar situation also occurs on the cathodic peak $B$, indicating the declined reversibility of SnO$_2$ in the SnO$_2$-50h electrode. This comparison among the CV results of SnO$_2$-Cu-0h, SnO$_2$-Cu-50h, SnO$_2$-50h electrodes clearly indicates that nanosized SnO$_2$ and the surrounding Cu nanocrystalline structure are beneficial to the reversible formation of SnO$_2$ from Li$_2$O and Sn, as previously reported for the Ni-Co$_3$O$_4$ anode.\textsuperscript{25}

Unfortunately, the SnO$_2$-Cu-50h electrode shows rapid capacity fade during cycling, as shown in Fig. 2b, where the cycling performance of SnO$_2$-50h is also compared. The charge capacity of the SnO$_2$-Cu-50h electrode decreases from 566.5 mAh g$^{-1}$ to 94.8 mAh g$^{-1}$ after 55 cycles, with the capacity retention ratio of only 16.7%. Comparatively, the SnO$_2$-Cu-50h electrode has better cyclic stability than the SnO$_2$-50h electrode, but relatively lower initial charge capacity, which is due to higher theoretical capacity (1494 mAh g$^{-1}$) for the SnO$_2$-50h electrode. The poor cyclic performance for the SnO$_2$-Cu composite electrode should be mainly due to the large volume variation during cycling, which causes the cracking and pulverization of microsized Cu matrix embedded with SnO$_2$ nanoparticles, finally leading to
the disconnection of active particles from the current collector. Therefore, to achieve better cyclic performance, the SnO$_2$-Cu composite is further milled with graphite to obtain SnO$_2$-Cu-C multiphase composite.

### 3.2 SnO$_2$-Cu-C composites

The cyclic performance of SnO$_2$-Cu-C composites with different amount of graphite and SnO$_2$-C composite are shown in Fig. 4a. The SnO$_2$-Cu-50h-10%C, SnO$_2$-Cu-50h-20%C, SnO$_2$-Cu-50h-30%C and SnO$_2$-50h-30%C composites have the theoretical capacity range of 419.0–766.6, 413.8–722.8, 408.5–678.9 and 659–1157.4 mAh g$^{-1}$, respectively. The former value in each composites based on the theoretical capacity of alloying/de-alloying reaction (782 mAh g$^{-1}$) of SnO$_2$, while the latter value is based on the theoretical capacity of both alloying/de-alloying and conversion reactions (1494 mAh g$^{-1}$) of SnO$_2$, the detailed calculation process is based on the method in Ref. [36] and shown in the ESI. As shown in Fig. 4a, the SnO$_2$-Cu-50h-10%C, SnO$_2$-Cu-50h-20%C, SnO$_2$-Cu-50h-30%C electrodes deliver the initial charge capacity of 753.3, 681.7, 605.8 mAh g$^{-1}$ at the current density of 100 mA g$^{-1}$, which retain 124.8, 306.5, 450.8 mAh g$^{-1}$ at 80$^{th}$ cycle, corresponding to the capacity retention ratio of 16.6%, 45.0%, 74.4%, respectively. On one side, as the graphite ratio increased from 10 wt. % to 30 wt. %, the initial charge capacity of the corresponding SnO$_2$-Cu-C composite decreased because of the reduced theoretical capacity. On the other side, it clearly demonstrates that the sufficient addition of graphite greatly improves the cyclic stability of SnO$_2$-Cu-C composite.

Fig. 4a further compares the cyclic performance of the SnO$_2$-Cu-50h-30%C electrode
with the SnO$_2$-Cu-10h-30%C and SnO$_2$-50h-30%C electrodes, which exhibit the initial charge capacity of 657.6, 807.9 mAh g$^{-1}$, and retain 258.2, 76.7 mAh g$^{-1}$ at the 80$^{th}$ cycle, with the capacity retention ratio being 39.3% and 9.5%, respectively. Apparently, the capacity retention of the SnO$_2$-Cu-50h-30%C electrode (74.4%) is much higher than those of the SnO$_2$-Cu-10h-30%C and SnO$_2$-50h-30%C electrodes, indicating the positive effect of nanocrystalline Cu matrix on the cyclic stability of SnO$_2$. In addition, the SnO$_2$-Cu-50h-30%C electrode shows the ICE of 79.1±2.1% (Table 1), implying the maintenance of the high reversibility of Li$_2$O after further milling with graphite, its reversible anodic peaks of Sn, SnO with Li$_2$O are also verified in the CV curves as shown in Fig.3d. Furthermore, the specific capacity and cycleability of present SnO$_2$-Cu-50h-30%C composite are better than previously reported SnO$_2$-based composite anodes.$^{22-24,32}$

As the SnO$_2$-Cu-50h-30%C composite has superior cyclic performance to other SnO$_2$-Cu-C composites, its rate capability is further investigated, and the result is shown in Fig. 4b. The SnO$_2$-Cu-50h-30%C electrode maintains a stable reversible capacity of about 335.0 mAh g$^{-1}$ at a high current density of 1.0 A g$^{-1}$, and a charge capacity of about 560.0 mAh g$^{-1}$ could be restored as the current density is back to 0.1 A g$^{-1}$. This result indicates the excellent rate performance for the SnO$_2$-Cu-50h-30%C composite electrode.

The enhanced electrochemical performances of the SnO$_2$-Cu-50h-30%C electrode are related to its carbon-matrix composite structure, as shown in the SEM image of Fig. 5a, and the back-scattered electron SEM image of Fig. S2 (see the ESI). It is clearly seen that the SnO$_2$-Cu particles of different particle size (50~500 nm) are embedded in the graphite layers,
forming the dual scale embedding structure in the SnO$_2$-Cu-50h-30%C composite. That is to say, the SnO$_2$ nanoparticles are embedded in nanocrystalline Cu matrix, meanwhile the SnO$_2$-Cu composite particles are embedded in microsized graphite matrix. The dual scale embedding structure is schematically shown in Fig. 5b, in which the role of the Cu and graphite additives on the electrochemical performances of SnO$_2$ are discussed as follows:

Firstly, in the aspect of electrical conductivity, both Cu and graphite act as good conductive media for electron transport, which is quite important for the redox reaction of the insulating oxide Li$_2$O. On one hand, the Cu nanocrystals surrounding the active SnO$_2$ nanoparticles allow the fast electron transport inside the SnO$_2$-Cu particles. On the other hand, the microsized graphite sheets construct a soft three-dimensional conductive network to bridge all of SnO$_2$-Cu particles, ensuring good electrical conductivity even the SnO$_2$-Cu particles are cracked and pulverized during cycling. Secondly, with respect to the enhancement of cyclic stability, the most important reason is that the three dimensional network of microsized graphite sheets could effectively buffer the volume change of Li insertion/extraction in the SnO$_2$-Cu composite embedded in the graphite matrix. It also avoids the disconnection of active SnO$_2$-Cu particles with the collector, and maintains the electrode integrity. Furthermore, the nanocrystalline Cu matrix could hinder the aggregation of nanosized SnO$_2$ and Sn particles, and maintain the nanostructure during cycling. All of these aspects are beneficial to reduce the loss of the active SnO$_2$ or Sn, and thus preserve the reversible capacity fade of the composite electrode. In summary, the overall enhancements in the conductivity of electron and the nanostructure stability due to dual scale embedding
structure of nanosized Cu and microsized graphite matrix are responsible for the greatly improved ICE and cycleability in the SnO$_2$-Cu-C composite anode.

4. Conclusions

The SnO$_2$-Cu and SnO$_2$-Cu-C composite anodes with improved ICE and cyclic stability have been produced by ball milling. For the SnO$_2$-Cu composite, the nanocrystalline Cu matrix and the resultant good electrical conductivity promoted the reversibility of nanoscale SnO$_2$ from Li$_2$O and Sn. The 50h-milled SnO$_2$-Cu composite electrode showed a high ICE of 76.0±1.5% at 85 mA g$^{-1}$, much higher than the theoretical value of 52.4% when the conversion reaction was irreversible. The further milling of SnO$_2$-Cu with graphite leaded to dual scale embedding structure, namely that nanosized SnO$_2$ were embedded in nanocrystalline Cu matrix, while the SnO$_2$-Cu composite particles were embedded in microsized graphite matrix. As a result, the SnO$_2$-Cu-50h-30%C composite delivered a higher ICE of 79.1±2.1%, and reversible charge capacity of 450.8 mAh g$^{-1}$ after 80 cycles at 100 mA g$^{-1}$, with the capacity retention ratio of 74.4%. This unique multiphase structure could be further optimized in the composition and adopted to other high-capacity anode materials.

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Table 1. The statistics, mean ($\mu$) and standard deviation ($\sigma$) of ICE for different composite electrodes

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Figures

Fig. 1 (a) XRD patterns of SnO$_2$-Cu-0h, SnO$_2$-Cu-10h, SnO$_2$-Cu-50h composites; SEM micrographs of raw materials and SnO$_2$-Cu composites for different milling time: (b) pristine Cu, (c) pristine SnO$_2$, (d) SnO$_2$-Cu-10h, (e) SnO$_2$-Cu-50h; (f) Bright-field TEM image, (g) selected electron diffraction pattern (inset
at the top right), and (h) high-resolution TEM image of the SnO$_2$-Cu-50h composite.

**Fig. 2** (a) Initial discharge-charge profiles of SnO$_2$-Cu-0h, SnO$_2$-Cu-10h, and SnO$_2$-Cu-50h electrodes between 0.01 and 3.0 V vs. Li$^+$/Li at 85 mA g$^{-1}$; (b) Comparative cycling performance for the SnO$_2$-Cu-50h and SnO$_2$-50h electrodes from 0.01V to 3.0V vs. Li/Li$^+$ at 85 mA g$^{-1}$. 
Fig. 3 CV curves for (a) SnO$_2$-Cu-50h, (b) SnO$_2$-Cu-0h, (c) SnO$_2$-50h and (d) SnO$_2$-Cu-50h-30%C electrodes in the potential range of 0.0V−3.0V vs. Li$^+/\text{Li}$ at scanning rate of 0.2 mv s$^{-1}$. 
Fig. 4 (a) Comparison of cyclic performance for the SnO$_2$-Cu-50h-10%C, SnO$_2$-Cu-50h-20%C, SnO$_2$-Cu-50h-30%C, SnO$_2$-Cu-10h-30%C and SnO$_2$-50h-30%C composites between 0.01 and 3.0 V vs. Li$^+$/Li at 100 mA g$^{-1}$; (b) Rate capability of SnO$_2$-Cu-50h-30%C electrode with a current density range from 0.1 A g$^{-1}$ to 1.0 A g$^{-1}$, cut off potential 0.01−3V vs. Li$^+$/Li.
Fig. 5 (a) SEM image of the SnO$_2$-Cu-50h-30%C composite; (b) Schematic diagram of dual scale embedding structure showing the enhanced electron transportation and lithium ion diffusion in the SnO$_2$-Cu-C composite.