Cu₆Sn₅@SnO₂-C nanocomposite with stable core/shell structure as a high reversible anode for Li-ion batteries

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Abstract: Tin-based electrodes have attracted much attention because of their potential to offer high energy and power density while maintaining excellent cycling stability. Here we report our findings from the rational design and synthesis of a high-performance $\text{Cu}_6\text{Sn}_5@ \text{SnO}_2\text{-C}$ electrode, a tin-based anode with a unique core/shell structure consisting of a tin-copper intermetallic (Cu_6Sn_5) core and a tin dioxide (SnO_2)/carbon (C) shell. The hybrid structure was synthesized by a simple and cost-effective two-step process. When used as an electrode, the $\text{Cu}_6\text{Sn}_5@ \text{SnO}_2\text{-C}$ hybrid nanocomposite demonstrated a reversible capacity of 619 mAh/g after 500 cycles between 0.05 and 3.0 V vs. Li/Li^+ at 0.2A/g, with stable capacities of ~300 mAh/g from the reversible conversion reaction of SnO_2 in a potential range of 1.1-2.0V. Results suggest that the maximum volume change of the $\text{Cu}_6\text{Sn}_5@ \text{SnO}_2\text{-C}$ electrode during cycling was relatively small (~12.7%) so that the Cu_6Sn_5 core components and the core/shell structure remained relatively stable over many cycles, leading to significantly enhanced reaction reversibility and cycling stability.

TOC Graphic

1. Introduction

The development of rechargeable Li-ion batteries (LIBs) with higher energy density and longer cycle life is of great importance to many emerging technologies such as electric vehicles and portable devices. However, the limited gravimetric capacity of commercial graphite anodes (372 mAh/g for LiC_6) has stimulated an intense interest in alloy-based anodes with higher capacities and energy density for a new generation of LIBs. Significant efforts have been devoted to the development of Sn-based anode materials¹⁻³ because metallic Sn has not only high theoretical capacity (993 mAh/g or 7,262 mAh/cm³ for $\text{Li}_{4.4}\text{Sn}$) but also excellent electronic conductivity (greater than those of semiconductor-based anodes such as Si and Ge). However, the key challenge for Sn electrodes is how to overcome the rapid capacity decay associated with large volume expansion (e.g. $V \approx 260\%$ for the $\text{Sn} \rightarrow \text{Li}_{4.4}\text{Sn}$ transition) induced by the insertion of $\text{Li}^{3, 4}$, leading to serious cracking and eventual pulverization of the Sn anodes.

Two important Sn-based derivatives, namely Sn-based intermetallic (Cu_6Sn_5) and Sn-oxide (SnO_2), have been intensively studied^{5, 6} to alleviate capacity decay because they are expected to buffer the large volume change during cycling by the *in situ* formation of two host matrixes, Cu in Cu_6Sn_5 ⁷ and Li_2O in lithiated SnO_2 ⁸, respectively. The intermetallic Cu_6Sn_5 has a theoretical capacity of 605 mAh/g by forming Cu and $\text{Li}_{4.4}\text{Sn}$ upon discharge,⁷ while that of SnO_2 is as high as 1,494 mAh/g but involves a two-step process: a conversion step ($\text{Li} + \text{SnO}_2 \rightarrow \text{Li}_2\text{O} + \text{Sn}$) followed by an alloying reaction ($\text{Li} + \text{Sn} \rightarrow \text{Li}_{4.4}\text{Sn}$)⁹. In comparison to pure Sn, the Cu_6Sn_5 can maintain enhanced cycleability due to a reduced volume expansion (140%, while 260% for pure Sn) associated with Li^+ insertion and an improved retention of the initial crystalline structure after Li^+ extraction¹⁰. However, Cu_6Sn_5 anodes have been reported to yield relatively low capacity (around 400 mAh/g), attributed to a lower maximum lithium content of $\text{Li}_{3.5}\text{Sn}$ for lithiated Sn-intermetallics compared to $\text{Li}_{4.4}\text{Sn}$ for pure Sn¹¹. In

contrast, SnO₂ based anodes usually yield higher capacities^{12, 13}, but they suffer from inferior electronic conductivity and poor reversibility of the conversion step due to the formation of thermodynamically stable Li₂O and the coarsening of Sn^{14, 15}. Furthermore, like pure Sn electrodes, SnO₂ still exhibits serious structural degradation and instability of the solid-electrolyte interphase (SEI) accompanied by undesirable capacity fading with each charge/discharge cycle.

Significant efforts have been devoted to improving structural stability and reaction reversibility to minimize capacity fading of SnO₂ anodes. One strategy was to prepare different kinds of SnO₂ nanostructures, including SnO₂ nanoparticles^{16, 17}, nanowires^{18, 19}, nanotubes²⁰⁻²³, and nanocrystalline /amorphous SnO₂ thin films^{14, 24, 25} which could accelerate Li⁺ ion diffusion kinetics and accommodate the volume change to some extent during the lithiation /delithiation process. Another effective strategy was the combination of SnO₂ with carbon²⁶⁻²⁹, which was introduced to improve electrical conductivity and act as a buffer layer to suppress the large volume change of SnO₂ anodes. Indeed, SnO₂/C composite anodes have shown good improvement in overall electrochemical performance by combining the advantages of different carbon networks and SnO₂⁶. Lou et al. reported that 6–10 nm SnO₂/C nanoparticles with 8% carbon delivered an initial capacity of 1,100 mAh/g and retained a capacity as high as 631 mAh/g after 100 cycles³⁰. Zhang et al. developed a strategy in which SnO₂ nanoparticles were uniformly loaded onto cross-stacked carbon nanotube sheets, achieving improved performance³¹. Recently, by introducing graphene supporting materials with high specific surface area and superior electronic conductivity the cycling life of SnO₂ has been greatly extended to several hundred cycles^{32, 33}. Guo et al. reported that a hybrid anode consisting of SnO₂ nanocrystals (4-5 nm) and N-doped graphene sheets exhibited a reversible capacity of 1,346 mAh/g after 500 cycles at a current of 0.5A/g between 0.005 and 3V³⁴. These studies suggest that maintaining a high dispersion state of ultrafine SnO₂

particles within a carbon nanostructure is of great importance to enhancing the reversibility and cycleability of SnO₂-based electrodes.

Unfortunately, many of these SnO₂-C nanostructures were prepared by complex chemical synthesis methods, which are difficult to scale up for production. In contrast, by simple ball-milling, Liu et al. synthesized a SnO₂-SiC/graphene core-shell structure in which nanosized SnO₂ particles were uniformly dispersed on SiC and encapsulated with coatings of graphene³⁵. When charged to a potential of 3.0 V, the SnO₂ phase in the hybrid delivered a reversible capacity of 97% of its theoretical value. It was proposed that the enhanced reversibility of SnO₂ was attributed mainly to the structural stability; the nano-SiC cores acted as a rigid structural framework to hinder Sn agglomeration and maintain good contact between Sn and Li₂O in the nanoscale matrix, which resulted in improved mutual reactivity between Sn and Li₂O. However, in these nanocomposites^{21, 35-37} the large amount of additives (such as SiC) are electrochemically inactive and cannot contribute to the reversible capacity, lowering the overall specific capacity and energy density of the hybrid electrodes when the weight of inactive additives is included. From this point of view, replacing the inert SiC, Cu³⁸, Ni^{37, 39}, or TiO₂^{40, 41} components with a highly active Sn-based intermetallics such as Cu₆Sn₅ may greatly increase the overall gravimetric and volumetric capacity of electrode while still providing good reversibility and cycleability of SnO₂-C hybrid anodes.

Here we report a core/shell ternary-composite as schematically illustrated in **Figure 1**, where nanosized SnO₂ grains are uniformly dispersed in an amorphous carbon matrix, which is coated on agglomerates consisting of Cu₆Sn₅ particles. This Cu₆Sn₅@SnO₂-C composite was prepared using a scalable two-step process: boiling micro-sized Sn and Cu powders together with sucrose followed by a heat treatment in Argon. We discovered that, within this unique architecture, nanosized SnO₂ was fixed between the Cu₆Sn₅ and the amorphous carbon, while the Cu₆Sn₅ cores were mechanically reinforced by the carbonaceous shells, resulting in excellent electrochemical performance.

2. Experimental

Materials Fabrication: In a typical experiment, an aqueous mixture consisting of 20g elemental Sn (~100mesh, 99.9% purity) and 10.8g Cu (~150mesh, 99.9% purity) powders, 19.2g sucrose (edible grade), and 200ml deionized water was boiled in a stainless steel pot in air using an electric oven (2kW) until all water was evaporated and a brown charred product was obtained (hereafter referred to as the coking mixture). The sucrose was used as a water soluble carbon precursor to introduce carbon to a desired hybrid with $\text{Cu}_6\text{Sn}_5/\text{SnO}_2$ in mole ratio of 1/1. The obtained coking mixture was transferred to an alumina crucible and kept in a tube furnace at 400°C for 4h in flowing Ar atmosphere, resulting in brown powders (hereafter referred to as $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$). A control sample ($\text{SnO}_2\text{-C}$) using similar procedures but without Cu powder was also prepared. Both of these materials were prepared for testing as electrode materials after the carbonizing heat treatment by grinding with a mortar and pestle. Pure nanosized SnO_2 (nano- SnO_2 , with average diameters of 50nm) was also tested as an electrode for comparison.

Materials characterization: The structure and morphology of the samples were characterized using a Philips X-ray diffractometer (XRD) with Cu-K α radiation, a Carl Zeiss Supra 40 field emission scanning electron microscope (SEM), and a JEOL JEM-2100 transmission electron microscope (TEM) operating at 200kV. The electronic states of Sn and Cu in the electrodes were determined by an AXIS Ultra DLD X-ray photoelectron spectrometer (XPS) using Al-K α radiation. Raman spectra were obtained using a Renishaw RM 1000 spectromicroscopy system using an air-cooled Ar laser with a 446nm wavelength. Differential scanning calorimetry (DSC) and Thermogravimetric (TG) analysis was conducted under O_2 on NETZSCH STA409 with a heating rate of 10°C/min.

The $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ electrodes at different lithiated states were prepared by discharging/charging to a controlled cutoff voltage. These electrodes were then removed from the electrochemical cells, rinsed with DMC and absolute ethanol, and dried under vacuum in

the ante-chamber of an argon filled glove box. For XRD analysis, the sample electrodes were sealed inside Kapton tape to minimize air exposure during the XRD measurement. For TEM and XPS analysis, the samples were transferred from the ante-chamber to the analysis chamber using a small box filled with argon to minimize air exposure.

Electrochemical measurements: The discharge–charge cycling performance of the samples was investigated using a cell test system (LAND-CT2001A) with CR2016 coin-type cells assembled in an argon-filled glove box. The working electrodes consisted of 80 wt% of the active materials ($\text{Cu}_6\text{Sn}_5@ \text{SnO}_2\text{-C}$, $\text{SnO}_2\text{-C}$, and nano- SnO_2 powders), 10 wt% conductive additive (Super-P), and 10 wt% binder polyvinyl difluoride. Lithium foil was used both as counter electrode and as reference electrode in the half cells. The electrolyte was LiPF_6 (1 mol/L) in a mixture of ethylene carbonate (EC)/diethyl carbonate (DEC)/ethyl methyl carbonate (EMC) with volume ratio EC/DEC/EMC=1:1:1 (Shanshan Tech Co., Ltd.). The cells were tested at various current densities in a potential range between 0.05 and 3V at room temperature. Impedance spectra were acquired at ac voltage of 5 mV in the frequency range of 1MHz to 0.05 Hz using a Gamry Interface 1000 Electrochemical System.

3. Results and Discussions

The $\text{Cu}_6\text{Sn}_5@ \text{SnO}_2\text{-C}$ composite was fabricated by a simple boiling and subsequent heat treatment of micro-sized Sn and Cu elemental powders together with sucrose, as schematically shown in **Figure 1a**. In our previous work we reported that large micro-sized Sn particles were dramatically refined by boiling with sucrose to form a coking mixture⁴². It is expected that during boiling and subsequent heating, some portion of the molten Sn can alloy with Cu to form Cu_6Sn_5 (reaction 1), while the remainder was oxidized by sucrose to form SnO_2 (reaction 2) and loaded onto the outside of the agglomerates consisting of Cu_6Sn_5 particles. The decomposed sucrose remained as amorphous carbon in the final product after annealing at 400°C for 4 hours in an inert atmosphere. When reacting with lithium, the integration of

Cu_6Sn_5 and amorphous carbon is expected to maintain a good integrity of the core-shell structure (**Figure 1b**) and result in enhanced cycleability.

Figure 1 (a) A schematic two-step process for synthesis of a Cu_6Sn_5 @ SnO_2 -C core/shell composite electrode; **(b)** schematic microstructure evolution of a Cu_6Sn_5 @ SnO_2 -C core/shell agglomerate during long-term discharge-charge cycling. The reversible Cu_6Sn_5 cores maintain good structural integrity of the agglomerate, which leads to a stable SEI layer formation.

X-ray diffraction (XRD) analyses (**Figure 2a**) reveal that, after boiling with the sucrose for 1h, the main phases in the product are Cu_6Sn_5 and SnO_2 , with a small amount of elemental Sn. This is quite different from the SnO_2 -C nanocomposite obtained by boiling sucrose and Sn without Cu. In this case Sn is maintained in the elemental state. (**Supporting Information, Figure S1**). After calcining the dried Sn/Cu/sucrose composite at 400°C, almost all the diffraction peaks for pure Sn disappear while the diffraction peaks of Cu_6Sn_5 (melting point at 415°C) become more prominent after undergoing significant crystallite coarsening during annealing. Moreover, the increased background intensity in the range of 20~35°2θ can be attributed to the amorphous carbon content in the sample. We did not detect any elemental Cu,

other Cu-Sn intermetallic phase, or Cu oxide in the final products, suggesting that all the Cu was contained in the observed Cu_6Sn_5 alloy or an unidentified amorphous phase. Accordingly, the ratio of Cu_6Sn_5 to SnO_2 in the as-prepared composite is expected to reach the desired value of 1:1. **Figure 2b** shows the differential scanning calorimeter (DSC) together with thermal gravimetric (TG) curve of the composite recorded under O_2 , in which the two separated exothermic peaks around 400°C are attributed to combustion of amorphous carbon and the subsequent partial oxidation of Cu_6Sn_5 . The calculated weight percent of carbon in the sample is about 13%, which is lower than that in the SnO_2 -C nanocomposite (20wt%, **Supporting Information, Figure S2**). The XRD and TG/DSC results suggest that a ternary-composite, containing Cu_6Sn_5 , SnO_2 , and carbon, has been successfully produced by a simple two-step process. It should be noted that this method is facile, and easy to scale up for large-quantity production. **Figure 2c** shows the typical morphology of the final product consisting of multiscale particles with spherical shape, forming agglomerates. **Figure 2d** shows the X-ray photoelectron spectroscopy (XPS) survey scan of the as-prepared hybrid, revealing that the near surface layer mainly contains C, Sn and O elements, while the Cu signal is very weak, consistent with our hypothesis that the Cu_6Sn_5 phase is within the interior of the agglomerates. Furthermore, the XPS $\text{Sn}3d$ spectrum indicates that the dominant signal at 487.3 eV is assigned to Sn^{4+} , while the peaks at 486.3 eV is ascribed to Sn^{2+} and the weakest peaks at 484.9 eV corresponds to metallic Sn^0 . Raman spectroscopy studies (see **Supporting Information, Figure S3**) also support the existence of above-stated SnO_2 and carbon, confirming that a large amount of SnO_2 is formed in the carbonaceous surface layer of the agglomerates, while the Cu_6Sn_5 intermetallic phase is completely encapsulated inside the agglomerates.

Figure 2 (a) XRD patterns of the coking product (bottom) obtained by boiling a mixture of Cu, Sn, and sucrose for 1 h and the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ (top) obtained by annealing the coking product at 400°C for 4h in flowing Ar; (b) DSC and TG curves of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ under O_2 with a heating rate of 10°C/min; (c) an SEM image of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ composite; (d) XPS survey scan of the as-prepared $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ (top) and high-resolution XPS Sn 3d spectrum (bottom).

The phase composition and detailed morphology of the as-prepared $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ were further studied using transmission electron microscopy (TEM). The low-magnification TEM image shown in **Figure 3a** reveals that the composite consists of a large amount of multiscale spherical particles, which should be derived from the melting of Sn during heating. **Figure 3b** shows an enlarged image of three core/shell particles, in which the Cu_6Sn_5 particle is encapsulated by a mixture layer of SnO_2 nano-grains and amorphous carbon. Both the

Cu₆Sn₅ core and SnO₂ shell were confirmed by their corresponding selected-area electron diffraction (SAED) patterns in **Figure 3c**. The SAED pattern indicates that the nano-sized Cu₆Sn₅ particle is a single crystal. The high resolution TEM image in **Figure 3d** shows that a mixture nano-SnO₂ layer (with thickness about 10nm) coats outside the Cu₆Sn₅ single crystal. The lattice fringes (inset of Figure 3d) with a basal distance of 0.33nm can be observed from the mixture SnO₂ layer, which is consistent with the (110) lattice spacing of tetragonal SnO₂. The above analyses suggest that the fabricated agglomerates (a ternary-composite) have a core-shell structure with a cluster of Cu₆Sn₅ grains encapsulated by a SnO₂-C nanocomposite coating. In contrast, the mixture of only Sn and sucrose produced a final composite with a quite different microstructure, consisting of uniform ultrafine SnO₂ nanoparticles dispersed in an amorphous carbon matrix (**Supporting Information, Figure S4**). The results suggest that the addition of Cu to the Sn/sucrose mixture induced *in situ* formation of the multiscale Cu₆Sn₅ and SnO₂ in carbonaceous hybrids (Figure 3). It is noted that the Cu₆Sn₅ particles in the final electrodes have a spherical shape, due largely to the immiscibility between the Sn/Cu phase and the carbon matrix. During the first-step boiling, the Sn with low melting point was melted and dispersed inside the carbonaceous mixture. Due to the high surface tension of Sn and the immiscibility of Sn with the carbon, the Sn liquid would tend to have spherical shape to minimize the surface/interface energy. Further, as the Cu alloyed with the molten Sn, the product Cu₆Sn₅ phase tends to form spherical particles because the Cu₆Sn₅ is also immiscible with the carbon. The unique architecture of this Cu₆Sn₅@SnO₂-C is helpful to accommodate the volume change of SnO₂ and thus can maintain the structural integrity of the electrode during repeated reactions with Li.

Figure 3 (a) Low magnification TEM image of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ composite; (b) a closer viewer of the zone framed in (a), showing three core/shell particles; (c) SAED patterns of the Cu_6Sn_5 in core (top) and the SnO_2 (bottom) for the particle C marked in (b); (d) High-resolution TEM image of core/shell particle D marked in (b), inset is a lattice image of SnO_2 in the shell layer.

Figure 4a shows the initial three voltage profiles of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ anode material. The initial discharge and charge capacities were 1,636 and 1,062 mAh/g, respectively, which are higher than the theoretical capacity of a mixture of Cu_6Sn_5 and SnO_2 [$(605 \times 50\% + 1494 \times 50\%) \times (100 - 13\%) = 910 \text{ mAh/g}$], suggesting that a considerable amount of the initial capacities come from the amorphous carbon. The initial Coulombic efficiency (ICE) was ~65%, which is higher than that of the nano- SnO_2 (43%) and $\text{SnO}_2\text{-C}$ (42%) with initial discharge and charge capacities of 1,991 and 830 mAh/g (inset in Figure 4a), respectively. **Figure 4b** shows the differential capacity plots (DCPs) for the first three cycles of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$, indicating that the anode behaviors are dominated by the conversion

reaction of SnO_2 and subsequent alloying/dealloying between Li and Sn or Cu_6Sn_5 . It is known that the conversion reaction of SnO_2 takes place at a potential range of $\sim 1.2\text{-}0.3\text{V}$ (vs. Li/Li^+)^{43, 44} while the lithiation of Cu_6Sn_5 occurs mainly at potentials below 0.4V ¹⁰. Accordingly, the DCP peak with onset at 0.9V in the first discharge corresponds to conversion of SnO_2 to Li_2O and Sn, and the subsequent peaks in the potential range of 0.4 to 0.05 V are attributed mainly to Li-ion insertion into Cu_6Sn_5 and the alloying of Sn. With respect to the charge process, in addition to the sharp peaks for the dealloying of Li-Sn and recovery of Cu_6Sn_5 , a broad peak emerges at 1.3V (**inset in Figure 4b**) which can be attributed to the regeneration of SnO_x by the reaction of Sn and Li_2O ^{34, 35, 45}. During subsequent discharge cycles, the SnO_x phase could again react reversibly with Li and a consistent DCP signature was observed at around 1.0V , suggesting that the conversion reaction of SnO_2 could be partially reversible in this core-shell $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ composite. Furthermore, it is well known³ that, in a multi-phase electrode, each phase may react sequentially because of the difference in reaction potential. Hence, while one component is active (expanding or contracting) at a given time period during cycling, the other inactive phase(s) can function as a buffer for the reacting phase to enhance the structural integrity of the multi-phase electrode.

The cycling performance of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ electrode was compared directly with those of the $\text{SnO}_2\text{-C}$ and the nano- SnO_2 electrodes in **Figure 4c**. When cycled at a current density of 0.2A/g , the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ electrode displayed much larger reversible capacities and better capacity retention than the $\text{SnO}_2\text{-C}$ nanocomposite and pure nano- SnO_2 electrodes, retaining 619 mAh/g after 500 cycles. Specifically, the capacity loss within the first 200 cycles was $\sim 1.9\text{ mAh/g}$ per cycle, which decreased to $\sim 0.2\text{ mAh/g}$ per cycle during the subsequent 300 cycles. Furthermore, the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ electrode also exhibited enhanced rate capability, as shown in **Figure 4d**. A reversible capacity of $\sim 1,235\text{ mAh/g}$ was demonstrated at the end of the fifth charge/discharge cycles at current of 0.05 A/g with an ICE

of ~69%. The capacity at 0.8A/g was ~644 mAh/g, and decreased to ~390 mAh/g at a rate of 2A/g. As the current returned to 0.8A/g, a very stable capacity of ~670 mAh/g was observed after 80 cycles. These results indicate that the intermetallic Cu_6Sn_5 cores and the carbonaceous shells promote the rate of electron / Li^+ transfer in the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ and thereby improve the electrochemical performance of the hybrid electrode.

Figure 4 (a) Galvanostatic voltage profiles and (b) corresponding DCPs of $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ half-cell during the first three cycles. The inset in (a) shows the voltage profiles for the first three cycles of the $\text{SnO}_2\text{-C}$ nanocomposite, while that in (b) is the enlarged DCPs in the voltage region of 1.1-2.4V; (c) Capacity-cycle number plot of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$, $\text{SnO}_2\text{-C}$ and nano- SnO_2 electrodes cycled between 0.05 and 3.0 V at a current density of 0.2A/g; (d) Rate performance of $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$.

Figure 5 Comparison of capacity retention (a) and initial Coulombic efficiency (b) of $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ with $\text{Sn}@\text{SnO}_2/\text{C}$ ⁴⁶, $\text{Sn-SnO}_2/\text{C}$ ⁴⁷, $\text{TiO}_2/\text{SnO}_2/\text{C}$ ⁴⁰, $\text{Cu}_2\text{O}/\text{SnO}_2@\text{C}$ ⁴⁸, $\text{NiO-SnO}_2\text{-C}$ ³⁶, and $\text{Fe}_2\text{O}_3@\text{SnO}_2@\text{C}$ ⁴⁹ ternary-composite anodes. (c) Reversible capacities vs. cycle number of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ separated into potential ranges of 0.05-1.1V, 1.1-2.0V, and 2.0-3.0V; (d) DCPs of $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ half-cell during charge at different numbers of cycle; (e) Reversible capacity vs. cycle number of the cells cycled at different voltage regions, namely 0.05-1.1V, 1.1-2.0V, 2.0-3.0V, and 0.05-2.0V, respectively. All cells were firstly cycled one time between 0.05 and 3.0 V at a current density of 0.2A/g.

As shown in **Figure 5a**, the superior capacity retention of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ electrode is comparable to those of the $\text{SnO}_2\text{-Sn-C}$ and $\text{SnO}_2\text{-MO}_x\text{-C}$ ternary composite electrodes fabricated by more complex methods, which also contain additional active components such as Sn, NiO, Cu_2O , Fe_2O_3 , and TiO_2 ^{35, 40, 46, 50-52}. Furthermore, the ICEs of this core/shell $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ is better than those of other hybrid electrodes highlighted in **Figure 5b**. Since all three phases of this core-shell hybrid electrode (i.e. SnO_2 , Cu_6Sn_5 , and C) may react with Li at different potentials, the reversible capacities (charge capacities in Figure 4c) in each

cycle are separated into three parts according to the three potential zones and presented in **Figure 5c**. The three potential zones, namely 0.05-1.1V, 1.1-2.0V, and 2.0-3.0V, were determined from the DCP curves shown in Figure 4b. The capacity between 1.1-2.0V is attributed mainly to the reversible reaction between Sn and Li_2O to form SnO_x ⁴⁵. It has been reported that the charging capacities above 2.0V could come from the reversible formation of polymeric gel-like film and pseudo-capacitive type storage on the surface of amorphous carbon^{53, 54}. Accordingly, it can be seen that capacities of ~300 mAh/g are obtained in both potential ranges of 0.05-1.1V and the subsequent 1.1-2.0V, while a stable capacity around 200 mAh/g is delivered among 2.0-3.0V. These suggest that all the three active phases could contribute to the total capacity of the hybrid electrode. However, the capacity in the 0.05-1.1V range declined most rapidly and the variation of capacity in this region during cycling is quite similar to the total capacity shown in Figure 4c, indicating that the capacity fading of the hybrid electrode occurred mainly in the potential range of 0.05-1.1V, as reflected by the DCP curves (**Figure 5d**) in which the height of the peaks for Li-Sn dealloying and recovery of Cu_6Sn_5 diminish gradually with each cycle. In contrast, the height of the peaks (1.1-2.0V) for regenerating SnO_x remains quite stable, indicating good stability for reversible reformation of SnO_x for over 300 cycles. The good reversibility of SnO_2 and good capacity retention of the $\text{Cu}_6\text{Sn}_5@ \text{SnO}_2\text{-C}$ should be attributed to the core-shell structure and robust Cu_6Sn_5 cores.

The $\text{Cu}_6\text{Sn}_5@ \text{SnO}_2\text{-C}$ electrode was also cycled at different voltage regions, including 0.05-1.1V, 1.1-2.0V, 2.0-3.0V, and 0.05-2.0V. As shown in **Figure 5e**, the cell cycled between 0.05 and 1.1V yielded reversible capacity of ~300mAh/g, which is close to the capacity at potential region of 0.05-1.1V separated from the cell cycled between 0.05-3.0V. However, when the cells were cycled with a discharge cut-off voltage above 1.1V, the reversible capacities are much lower than those corresponding to the same potential range when the cell was cycled in the range of 0.05-3.0V. There is only ~20 mAh/g for the cell cycled in the potential range of 1.1-2.0V while ~5mAh/g for the cell cycled in the potential

range of 2.0-3.0V, suggesting that little lithiation took place above 1.1V during discharge⁵⁴. With respect to cell cycled between 0.05 and 2.0V, the first reversible capacity of ~1050 mAh/g obtained between 0.05-3.0V dropped to ~814mAh/g when the charge cut-off potential was restricted at 2.0V at the second cycles. Subsequently, the capacity degraded gradually and remained ~72% after 100 cycles, a bit lower than ~76% of that for the cell cycled in the potential range of 0.05-3.0V. In addition, the cells cycled in different potential ranges (i.e., 0.05-1.1V, 0.05-2.0V, and 0.05-3.0V) showed some variation in capacity with cycles. However, the cell cycled over the full voltage range (0.05-3.0V) has the highest reversible capacity and the best capacity retention, suggesting that the high-voltage for charge not only contribute to high reversible capacities, but also affect the microstructure variation of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ electrode during long-term cycling.

Figure 6 (a) Evolution of the XRD patterns of $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ during the first cycle : (1) the fresh electrode before cycling, (2) discharged to 0.5 V (vs. Li/Li^+), (3) discharged to 0.05 V, (4) charged to 3.0 V; Typical cross-sectional images (SEM) of $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ electrode (b) before and (c) after the first cycle (charge state). The observed expansion ratio was ~12.7%. TEM image of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ discharged to 0.05 V (d) and recharged to 3.0V (e) at the first cycle.

The phase evolution of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ hybrid during lithiation /extraction at different potentials was identified by *ex situ* XRD analysis, as shown in **Figure 6a**. When the hybrid is lithiated to 0.5V, the corresponding XRD pattern shows no obvious change from the as-prepared electrode, except for a decrease in the relative intensity of diffraction peaks attributed to SnO_2 . Further lithation down to 0.05V leads to the complete disappearance of the SnO_2 phase and appearance of Li_xSn alloy phases. However, even at a completely discharged state the Cu_6Sn_5 diffraction peaks are still observable, suggesting that a part of the core component Cu_6Sn_5 could not react with Li and still remained. The reduction of SnO_2 had also been confirmed by XPS (**Supporting Information, Figure S5**), in which the two Sn 3d peaks became much weaker after the electrode was discharged to 0.05V. However, we could not see the obvious XPS signal of the Sn (~484.5eV) and Li_xSn (~482.5eV) phases in the fully lithiated electrode. This should be attributed to the inability of Sn photoelectrons to escape from the Li_xSn phase embedded in an amorphous Li_2O matrix as well as the coverage of the SEI layer and polymeric film⁵⁴. On the reverse charge in the first cycle to 3.0V, the characteristic XPS peaks for SnO_2 became stronger with the same binding energies for Sn 3d_{5/2} and 3d_{3/2} as in the as-prepared electrode. These confirm that the reversed conversion reaction could take place to reform SnO_2 during charge. The XRD pattern also reveals the existence of some irreversible Li_xSn phase, together with a stronger diffraction of Cu_6Sn_5 in the electrode as it recharged to 3.0V. The residual Cu_6Sn_5 should be still encapsulated inside the shell as indicated by the TEM image in Figure 6e. **Figure 6b** and **c** show the SEM images for the cross-section of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ electrode before and after the first cycle (charge to 3.0V). The microscopy analysis indicates that the thickness of the as-coated $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ electrode is about 8.7 μm , within which there are many voids and free-space among the particles. After the first cycle the active material coating becomes dense and its thickness increases to 9.8 μm , suggesting that the expansion ratio of the electrode is 12.7%, which is comparable to graphite anode materials (~10%)⁵⁵. **Figure 6d** shows a magnified

TEM image of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ hybrid after the first discharge to 0.05V, revealing that there are cracks generated in the active nanoparticles due to volume expansion. However, when the electrode is recharged to 3V, as clearly revealed in **Figure 6e**, the core-shell structure is recovered with an integrated shell layer.

Figure 7 (a) and (b) Nyquist plots of the half cells with $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ electrodes after discharged to 0.05V in different cycles; (c) The proposed equivalent circuit used to fit the impedance data; (d) The fitted R_e , R_f , and R_{ct} in different cycles.

It is expected that the good integrity of $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ core/shell structure could also benefit the formation of a stable SEI film on the surface of the active particles. To investigate this, the resistance variations of the SEI film and others in the hybrid were also inspected. Nyquist plots of the electrodes are reported at a fully discharge state. The spectra evolutions at the desired cycles are summarized in **Figure 7a** and **b**. Typically, the Nyquist plot of Li/anode half-cell consists of a high-frequency arc related to the resistance of SEI film (R_f), and a

second arc in the medium-frequency region corresponding to charge transfer resistance (R_{ct}), followed by a 45 degree straight line originated from Warburg diffusion. In this $\text{Cu}_6\text{Sn}_5@ \text{SnO}_2/\text{C}$ half-cell, the Nyquist plots collected at some cycles, including OCP, the 1st cycle, from 80 to 100 cycles, contain the three parts as mentioned above. However, in the 2nd cycle and the subsequent cycles such as the 10th, 20th, 40th, 60th cycle, the impedance spectrum appears to contain an inductive loop in the medium to low frequency region, which masks the sloping line of Warburg diffusion at low frequency region. A plausible explanation for the inductive loop since from the 2nd cycle could be the formation of an electromotive force superimposed on the Li ion insertion, which was contributed from the concentration cells established between lithiated SnO_2 and Cu_6Sn_5 phases (**Figure S6, Supporting Information**)^{56, 57}.

In general, an inductive loop may occur in impedance spectra when there are local current loops in a heterogeneous electrode during the impedance measurement. Thus, a plausible explanation for the inductive loops in some of our impedance spectra is due most likely to inhomogeneous insertion of Li ions during cycling. Our $\text{Cu}_6\text{Sn}_5@ \text{SnO}_2/\text{C}$ electrode consists of two main active phase, Cu_6Sn_5 and SnO_2 , which are lithiated at different potentials with different Li storage capability. When Li ions are inserted into a ternary $\text{Cu}_6\text{Sn}_5@ \text{SnO}_2/\text{C}$ composite electrode, separation of a Li-rich ($x\text{Li-SnO}_2$) region from a Li-poor ($y\text{Li-Cu}_6\text{Sn}_5$) region in the electrode by an SEI film (due to local non-equilibrium with respect to electronic continuity) could create local concentration cells. The Li ion diffusion between $x\text{Li-SnO}_2$ and $y\text{Li-Cu}_6\text{Sn}_5$ ($x > y$) separated by the SEI film formed in the interfaces between the changeable Cu_6Sn_5 and SnO_2 phases (**Figure S6**) may induce local current loops. Because these SEI films are imperfect (leaky) due to the dramatic volume change (as illustrated in Figure 1b), the local diffusional current due to inhomogeneity in the ternary $\text{Cu}_6\text{Sn}_5@ \text{SnO}_2/\text{C}$ electrode could oppose the current flow of the charging/discharging electrode, thus inducing small inductive loops in the impedance spectra. Since the as-prepared electrodes have a relatively

uniform composition, the impedance of the first cycle did not show any inductive loops, although they do occur in the subsequent cycles. Also, as the microstructures of the electrodes evolve and SEI films develop during cycling, the occurrence of this local phenomenon diminishes. Overall, this effect is relatively small; the sizes of the inductive loops are quite small. They have little effect on the overall performance of the electrodes.

In order to evaluate the variations of the R_f and R_{ct} as a function of cycling, our analysis focuses on the two semi-circles in the high and medium-frequency regions. Thus, the Nyquist plots can be fitted using the equivalent circuit seen in **Figure 7c**, where R_e represents the electrolyte solution resistance, and Q_f and Q_{ct} are constant-phase elements (CPE) associated with R_f and R_{ct} , respectively. A cell geometric CPE (Q_g) is also taken into account. By comparison (**Supporting Information, Figure S7**), it has been found that the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ electrode has much lower R_f and R_{ct} than the $\text{SnO}_2\text{-C}$ nanocomposite. **Figure 7d** presents the R_e , R_f and R_{ct} obtained by fitting the impedance spectrum. These data show that the R_f remains very small and constant (around 4Ω) throughout the cycling. This suggests that the structure of surface SEI film in the electrode is quite stable during repeated discharge and charge, which benefits from the spherical particle geometry and mechanical reinforcement from the carbonaceous shell that can ensure good structural integrity for the SEI layer. The slight increase of R_e during cycling (from 5 to 10Ω) could be due to the gradual consumption of the electrolyte in the cell, which is one reason for the capacity fading as shown in Figure 5a. A dramatic variation is found for the R_{ct} . During the initial forty cycles, the R_{ct} is first dramatically increased from 73Ω before cycling to 307Ω at the tenth cycle and then gradually declines to 137Ω after 40 cycles. It should be noted that the variations in R_{ct} for this core-shell hybrid electrode could be related to the structural evolutions of the core component Cu_6Sn_5 during cycling. As schematically shown in **Figure 1b**, during the initial cycles the multiscale Cu_6Sn_5 would suffer from a large volume change ($\sim 150\%$)¹⁰ as Li is inserted into or extracted from the electrode, resulting in decomposition of Cu_6Sn_5 to Cu and Li_xSn alloys. This may

lead to cracking of the Cu_6Sn_5 particles and formation of smaller grains, as observed by TEM examination (Figure 6d). These cracks and the large amount of boundaries among the nanograins could block charge transfer and thus lead to increasing R_{ct} . However, as cycling continues the cracks are refilled by the ultrafine recovered Cu_6Sn_5 particles and the electrolyte, resulting in declined charge transfer resistance. As shown in Figure 6d, after 40 cycles the charge-transfer resistance remained stable around 100Ω , indicating that the core components (Cu_6Sn_5 , could be observed after 100cycles, see **Supporting Information, Figure S8**) remained stable during the subsequent cycles. This further demonstrates that the integration of Cu_6Sn_5 and C in the core-shell structure suppresses the possible structural collapse associated with the volume change of Cu_6Sn_5 and SnO_2 during cycling, resulting in enhanced structural stability and thus good performance of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ hybrid electrode.

4. Conclusions

In summary, a unique $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ ternary composite electrode was produced using a simple and scalable method by heating elemental Cu and Sn together with sucrose, during which nanosized SnO_2 particles were uniformly dispersed in an amorphous carbon matrix, which was coated on the agglomerates of multiscale Cu_6Sn_5 particles to form a core-shell structure. The three constituent phases of the $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ are all active for lithium storage and contribute to the total capacities of the electrode. The $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ core-shell structure greatly reduced the maximum volume change (12.7%) of the electrode during cycling; both the Cu_6Sn_5 core and the $\text{SnO}_2\text{-C}$ shell remained mostly intact over many cycles, leading to a stable and relatively low charge-transfer resistance. The hybrid electrode demonstrated a reversible capacity of 619 mAh/g after 500 cycles at 0.2A/g in a potential range of 0.05 to 3.0 V. Furthermore, a stable capacity ~300 mAh/g was obtained by the reversible conversion reaction of SnO_2 in the potential range of 1.1 to 2.0V, a significant improvement over the reversible capacity and cycling stability for the nano- SnO_2 and $\text{SnO}_2\text{-C}$

nanocomposite anode produced in this study and others.

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Supporting Information

Supporting Information associated with this article can be available from the online version or from the author.

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TOC Graphic for manuscript of “ $\text{Cu}_6\text{Sn}_5@\text{SnO}_2\text{-C}$ nanocomposite with stable core/shell structure as a high reversible anode for Li-ion batteries”