Showcasing the work on integrated yolk-shell 3D nanocomposite electrodes by Dr. Wei Ni, Dr. Bin Wang et al. at Institute of Chemical Materials, China Academy of Engineering Physics and co-workers at College of Polymer Science and Engineering, Sichuan University, China.

Title: Integration of Sn/C yolk-shell nanostructures into free-standing conductive networks as hierarchical composite 3D electrodes and the Li-ion insertion/extraction properties in a gel-type lithium-ion battery thereof

Three-dimensional electrodes offer great advantages including enhanced ion and electron transport, improved mechanical stability, and next-generation wearable electronic devices. Here, a novel kind of Sn/C yolk-shell hollow nanospheres integrated into nanofibrous 3D electric conducting structures as free-standing materials were designed for related potential applications.

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A novel style of Sn/C yolk–shell nanospheres integrated into nanofibrous 3D electric conducting structures as free-standing materials for potential applications such as new-generation anode structures for gel-type lithium-ion batteries via the design principle of inhibiting the aggregation of tin nanoparticles, buffering the occurring volume strain, and the flexible conductive networks.

Introduction

New materials, particularly nanostructured materials, have attracted tremendous interest in recent years, due to their unusual properties for a potential new generation of energy devices as well as the environmental concerns. Hierarchical three-dimensional (3D) electric conducting networks on the nano- and micro-scale, such as the nanocable-like structure and graphene-based networks have offered great advantages and became ideal candidates for the structural backbone and current collector. The application of 3D electrode structures has made the future of lithium-ion batteries quite bright in view of the higher specific capacity, much improved rate performance, as well as superior cycling stability brought by the powerful nanotechnology tool in the design of new electrode materials for lithium-ion batteries, especially for high-capacity electrode materials with large volume variations and low electrical conductivities.

For lithium-ion batteries, as a main power source for portable electronic devices and the promising fields of electric grids and electric vehicles, a great deal of effort has been made to develop new electrode materials with exquisitely designed structures to meet the demand for batteries of higher energy density and improved cycle performances. Among the anode materials, such as silicon (Si), germanium (Ge), tin (Sn), etc., elementary substances provide promising alternatives to conventional carbonaceous ones, due to their much higher capacity density via alloying reversibly with more lithium, such that tin has a theoretical specific capacity of 992 mA h g⁻¹ (Li₄.₄Sn) over that of conventional graphite of 372 mA h g⁻¹ (LiC₆), as well as the eliminated irreversible charge losses caused by solvent intercalation. In the meantime, to overcome the huge challenges arising from large volume variation during lithium-ion insertion/extraction cycles (ca. 260% based on the densities of bulk Sn and fully lithiated tin) which will lead to very rapid capacity decay due to severe pulverization or agglomeration in the anode electrode, many kinds of appropriate structure designs based on tin materials have been exploited for relatively higher specific capacity as well as better cycle performances. As we know that yolk–shell or ‘rattle-type’ nanomaterials with nanoparticle cores inside hollow shells are of special interest among the complex hollow nanostructures, which are promising functional candidates for a variety of applications such as selective catalysis, controlled delivery, advanced lithium-ion batteries and biosensors due to their tailorability and functionality in both cores and hollow shells. Based on this principle, some pioneering research studies such as ones into tin-encapsulated spherical hollow carbon structures by pyrolysis of tin-containing organic precursors or by a colloid template assisted pyrolysis process have been done for better electrochemical performances. The carbon shell for the above yolk–shell or rattle-type structures has itself good electric conductivity and prevents the aggregation of active materials via excellent elasticity to effectively accommodate the strain of volume change during Li⁺ insertion/extraction just like some other hollow transition metal oxide/carbon nanocomposites reported with high capacity and capacity retention as anode materials.
However, one of the main drawbacks that need to be pointed out is that the classical or traditional yolk–shell structures are typically of particulate morphology and are usually cohered by additives such as polymer binders and conductive carbon. The gaps between the particles may eventually deteriorate the structural integrity and may pose more challenges in applications of next-generation flexible or wearable electric devices. The fabrication of complex hollow nanostructures into 3D electrodes would be of great interest and may show potential in optimized Li-ion anodes. Since the optimized design principle has been primarily introduced into the fabrication of electrochemical capacitors, for instance, cobalt oxide hollow nanoparticles incorporated into a flexible carbon nanofiber film as self-supported electrodes have been explored for supercapacitors.29

Here we further design a strategy to integrate the Sn/C yolk–shell structures and the concept of ‘hierarchical 3D electric conducting networks’ to fabricate novel free-standing 3D nanostructures as lithium-ion anodes, which eliminate the use of polymer binders, conducting carbon black and copper current collectors, to meet the aim of more cost-effective and environmentally friendly batteries of the future.

Results and discussion

Scheme 1 shows the in situ formation of Sn nanoparticle/buffering carbon shell (Sn@C yolk–shell) nanospheres integrated into carbon nanofibers by the one-step pyrolysis–reduction process of electrosprun SnO2 hollow sphere/polyacrylonitrile (PAN) core–shell fibers. The process is depicted briefly as follows: a well dispersed composite slurry was firstly electrosprun to generate the SnO2 hollow sphere/PAN sub-microfibers, which were then pyrolyzed at 800 °C under a hydrogen atmosphere to obtain the Sn/C yolk–shell structures embedded in carbon nanofiber backbones via an in situ reduction process (for experimental details see the Experimental section).

Pristine SnO2 hollow spheres (SnO2HSs) were first prepared by a facile one-pot hydrothermal method according to literature recipes shown in the Experimental section. As shown in our previous study, relatively uniform SnO2 nanospheres with a diameter of ~200 nm and a shell thickness of ~30 nm were obtained.29 By electrosprning the as-prepared SnO2 hollow spheres into a polymer substrate (e.g. PAN), the necklace-like ‘SnO2HSs stringed by PAN nanofibers’ structure was fabricated. The scanning electron microscopy (SEM) images in Fig. 1 reveal the morphology of the as-prepared hierarchical SnO2HSs@PAN fibers, which displays a uniform diameter distribution of ca. 600 nm for the PAN backbone, and a main size distribution of ca. 450–550 nm for the SnO2HSs@PAN core–shell microsphere subsystem structure.

The as-collected SnO2@PAN free-standing paper-like composites were first stabilized in air (pre-oxidation) at 200 °C for 10 h, beneficial for a well preserved morphology after carbonization. The carbonization was conducted under a hydrogen atmosphere, and the composite fibers were finally transformed into Sn@C yolk–shell nanospheres integrated into carbon nanofibers, with the carbon backbone average diameter of ~400 nm and the carbon-shell size in the range of 430–820 nm with embedded nanopores of mainly 1–2 nm, and the tin yolkds show a typical diameter of ca. 270–470 nm, as representatively shown in Fig. 2. As shown above, the SnO2@PAN can alternatively be transformed into a Sn@C yolk–shell subsystem structure by an in situ self-sacrificing reduction process in a nitrogen atmosphere, which could be regarded as a reverse
process of Sn@C oxidation, and the resulted Sn@C structures may further reversibly transform into SnO2@C hybrid hollow spheres by a self-templating methodology via the nanoscale Kirkendall effect. Compared with some reported studies on Sn nanoparticles inside/at the surface of electrospun fibers, where the precursors of the Sn component are mostly restricted to tin salts, the yolk–shell integrated 3D nanofibrous structure may be endowed with better tailored buffering space as well as electric conductivity.

The XRD analysis confirmed the composition and crystal structures of the above-mentioned SnO2@PAN and Sn@C free-standing nanofibrous composite materials. As shown in Fig. 3a, the XRD diffraction peaks shown in the ‘SnO2@PAN’ sample can be assigned undisputedly to the tetragonal rutile SnO2 phase (cassiterite, JCPDS file no. 41-1445; space group: $P4_2/mnm$, $a_0 = 4.738$ Å, $c_0 = 3.187$ Å). The sharp XRD peaks of the ‘Sn@C’ sample can be well indexed to the tetragonal metallic Sn phase (JCPDS file no. 86-2265) of high crystallinity and no SnO2 residue was found. Furthermore, an additional weak and broad peak appeared at $2\theta$ of about 24.5–27.5° in the Sn@C sample comes from the carbon backbones.

The graphitic structure of the carbon shells of the Sn@C composite could be further revealed by Raman spectroscopy (Fig. 3b). Two characteristic peaks of ca. 1340 and 1600 cm$^{-1}$ can be attributed to the D band arising from the defects and disorders in carbonaceous solid and the G band from the stretching mode of C–C bonds of typical graphite, respectively. The intensity ratio of ($I_D/I_G$) of the two bands is about 0.91 (G-band peak intensity higher than that of the D-band), further indicating the relatively low graphitization degree of the as-obtained carbon shell structures over the tin cores. The discontinuous carbonaceous layers and numerous defects in
the shells of the composite structures may be propitious to the diffusion of Li-ions. The specific surface area, mainly contributed by the carbon shell, calculated with the Brunauer–Emmett–Teller (BET) model by the nitrogen adsorption–desorption isotherms of the Sn/C composite is 151 m² g⁻¹. The average pore size calculated from the desorption data is 5.4 nm, and the total pore volume is 1.04 cm³ g⁻¹ by the Barrett–Joyner–Halenda (BJH) method from the desorption branch of the nitrogen isotherm (Fig. S3 in the ESI†). The nitrogen sorption analysis and the higher resolution SEM images of the Sn@C nanocomposite showed that the carbon shell frameworks possessed a bimodal nanoporous structure; the presence of large pores will enable the buffering of volume strain and the suppression of aggregation of the Sn component, while small pores will benefit rapid electrolyte transport. These small pores are primarily responsible for the surface area determined for the composite. On the other hand, thermogravimetric analysis (TGA) results of the Sn/C structures under an air atmosphere were recorded to determine the mass composition of Sn/C structures derived from varied chemical reduction conditions including temperature and time (as shown in Fig. S4 in the ESI†). The mass of the samples basically was kept stable below 200 °C, and with the increase of temperature, the following reactions occurred:

\[
C + O_2 \rightarrow CO_2 \text{ (gas)}
\]

\[
Sn + O_2 \rightarrow SnO \rightarrow SnO_2
\]

The chemical oxidation of C to CO₂ resulted in a mass decrease while the oxidation of Sn to SnO and SnO₂ resulted in a mass increase, so the TGA curves exhibited a first mass increase then a decreasing trend related to these actions. After the temperature rose to 800 °C, the total oxidation reactions completed and all carbon and tin in the Sn@C composite structures were converted to CO₂ and SnO₂, respectively.¹⁷ It can be accordingly determined that the Sn@C composite has a chemical composition of ca. 44 wt% tin and 56 wt% carbon for the sample shown in Fig. 2. And the Sn content may be
regulated by the control of pyrolysis conditions for a wide range from 44 to 78 wt%, for example.

Taking the safety factors into consideration, we herein adopted the semi-solid electrolytes. Since the unconventional electrolytes, including solid electrolytes (ceramic, polymeric and composite) and polymer electrolytes, such as poly(vinylidene fluoride) (PVDF)-based fibrous polymer electrolytes, microporous PVDF gels play an important role in lithium-ion batteries. For example, PVDF has a good electrochemical and temperature stability and it plays an advantageous role as polymer-based electrolytes.\textsuperscript{48-52} The following test data of electrochemical performances are based on cells equipped with a PVDF microporous separator (see Fig. S5 in the ESI†). The cyclic voltammetry (CV) profile of the Sn/C yolk–shell free-standing electrode within a potential window of 3–0 V vs. Li/Li\textsuperscript{+} at a scan rate of 0.05 mV s\textsuperscript{-1} is shown in Fig. 4a. There is a pronounced decrease of cathodic current between the first and the second CV for the Sn/C-Li half cell. Similar phenomena were reported in previous Sn-based anode materials and can be attributed to the irreversible reaction and the formation of the solid electrolyte interface (SEI) layer.\textsuperscript{53} Furthermore, it can be seen that three major smooth anodic peaks exist in the stabilized CV curve, which match with that given in other reports (see Note S1 in the ESI† for illustration in detail),\textsuperscript{54-56} and are corresponding to the Li\textsuperscript{+} extraction profiles and to the galvanostatic plateaus in Fig. 4b (galvanostatic half-cell cycling, see Fig. S6 in the ESI†). The novel Sn@C nanocomposite shows an initial capacity of 979 mA h g\textsuperscript{-1}, for Li storage in the potential window of 2–0.01 V at 50 mA g\textsuperscript{-1} (i.e. \sim 100 mA cm\textsuperscript{2}). The electric potential during the alloying and dealloying of lithium from the Sn@C composite negative electrode material varied as the phases of Li–Sn present in the electrode change, where the Sn component was subjected to the subsequent conversion reactions (Li\textsubscript{2}Sn ↔ Sn\textsuperscript{3}). This potential profile matches well with that of a tin negative electrode calculated and measured by Courtney et al. for the lithiation of tin.\textsuperscript{57} And the large irreversible capacity for the oxygen containing materials, e.g. SnO\textsubscript{2}, is partly eliminated. Fig. S7 in the ESI† shows the Nyquist plots via electrochemical impedance spectroscopy (EIS). In the middle-to-low frequency region, a 45° line can be associated with diffusion in the presence of a block electrode. And at intermediate frequencies, it is deduced that the diffusion takes place through a porous and heterogeneous carbon shell. A high-frequency feature commonly describes Li\textsuperscript{+} migration through a conductive passivation. The charge-transfer resistance ($R_{ct}$), which is believed to be one of the important factors in electrochemical reactions, is reflected in the diameter of the semicircle along the Z' axis. The $R_{ct}$ of the activated Sn@C yolk–shell free-standing anode (after 5 cycles) is estimated to be reduced by 76% in contrast to that of the pristine Sn@C anode. The decreasing of resistance may be attributed to a catalytic action of the encapsulated Sn nanoparticles toward the Li\textsuperscript{+} desolvation step at the carbon/electrolyte interface, thus enhancing the lithium insertion rate and reducing the polarization related to the charge-transfer process.\textsuperscript{51,56,59}

The Sn/C composite as a single electrode in a half cell is usually not sufficient to claim its practical relevance as a novel anode material in a lithium-ion battery. Herein a full cell where the Sn@C yolk–shell free-standing composite electrode (binder-free anode) was coupled with a most commercialized LiCoO\textsubscript{2} cathode in a 1 M LiPF\textsubscript{6} EC–DMC gel-type electrolyte (PVDF microporous separator). For the LiCoO\textsubscript{2}–acetylene black cathode, it delivered a stable potential of \~3.8 V and a capacity of \~130 mA h g\textsuperscript{-1} with a cut-off voltage range of 4.2–2 V and a current density of 50 mA g\textsuperscript{-1} (Fig. S8 in the ESI†), though the acetylene black powder may agglomerate and is separated from LiCoO\textsubscript{2} particles by the binder PTFE.\textsuperscript{48} Although it could reach up to a capacity of \~150 mA h g\textsuperscript{-1} with a wider cut-off voltage range of 4.5–2 V, the capacity dropped sharply mainly due to a fatal structural failure.\textsuperscript{48}

The performances of the full battery cells in terms of capacity (referred to the anode) versus the potential cut-off window and/or cycle number are illustrated in Fig. 4c and d. The theoretical specific capacity of tin and carbon is 992 mA h g\textsuperscript{-1} and 372 mA h g\textsuperscript{-1}, respectively, so the Sn@C (with Sn mass fraction of ca. 44%) has a theoretically calculated specific capacity of 645 mA h g\textsuperscript{-1}. The electrochemical characteristics of the Sn/C
composite are maintained in the full cell, and it delivered an initial charge and discharge capacity of 893 and 599 mA h g\(^{-1}\) in the potential cut-off window of 4.0–1.5 V with a mid-value discharge potential of 3.15 V and a Coulombic efficiency (CE) of 67%, and the CE increased from 81% to 95% during the following few cycles, and cycled with a specific capacity higher than 440 mA h g\(^{-1}\) in the initial 10 cycles. The Sn/C composite electrode suffered from an irreversible capacity loss in the first cycle which largely results from the electrolyte decomposition on the carbon surface. By subtracting the capacity of the carbon shell (372 mA h g\(^{-1}\)), the discharge specific capacity in a full cell by the Sn component (44 wt%) was estimated to be 889 mA h g\(^{-1}\), which amounts to about 90% of the theoretical value (992 mA h g\(^{-1}\)). With a widened potential cut-off window, e.g. 4.2–1.2 V, the capacity of the full cell shows an increase of ca. 29%, i.e. from 440 to 567 mA h g\(^{-1}\). The increase in discharge capacity can be ascribed to the further enhanced delithiation effect for the Sn/C anode in the Li\(^+\) insertion/extraction process. However, a further higher charge potential (e.g. 4.5 V) would lead to the destruction of the LiCoO\(_2\) cathode and the capacity of the full cell dropped drastically in the following cycles after an eruption. Nevertheless, the coulombic efficiency may be further improved by a pre-lithiation process of the Sn@C anode for better long-term performance upon electrochemical charge/discharge cycling.

In addition, it may be stressed that when the Sn/C composites were derived by the pyrolysis of SnO\(_2\)@PAN under a nitrogen atmosphere instead of a hydrogen atmosphere, the carbon shells might offer a self-sacrificing reduction effect for the SnO\(_2\) cores, and would usually render the Sn/C composite with a higher Sn content. The difference is that there were four separate peaks at 0.5–0.8 V for the anodic scanning loop, which are related to the dealloying reaction of the Sn component (i.e., Li\(^+\) extraction from Li\(_x\)Sn alloys), and these phenomena are also revealed in Sn@graphene structures with exposed tin nanoparticles. Fig. S9–S11 in the ESI† show the features of the Sn/C hierarchical nanocomposites with partly exposed tin nanoparticles and the differential current density versus potential curves, where the sharp peaks appearing in the Sn/C–Li cell well match those in a Sn–Li cell. For most Li/tin-oxide anode materials, sharp features may not be noted due to the absence of the formation of two phase regions. Relatively sharp peaks were alternatively appeared as charge or discharge plateaus in tiers for a galvanostatic mode, which would also be revealed in
the full cell of the LiCoO$_2$–Sn/C system. The phenomena might be basically ascribed to the unrestricted Li$^+$ insertion/extraction processes. Furthermore, the freestanding Sn/C composite with exposed tin microspheres derived from higher SnO$_2$ content in the electrospinning slurry (i.e., 75 wt% in SnO$_2$/PAN precursor) showed similar electrochemical characteristics and the specific capacity faded faster as well (Fig. S12 in the ESI$^+$), and the analogous phenomena were reported elsewhere in the literature.$^{48}$

Conclusions

In summary, a novel approach was designed to prepare a kind of 3D electrode of integrated Sn/C yolk–shell composite structures. The tin nanoparticles encapsulated in the elastic hollow carbon spheres, which were integrated into a porous electron-conductive network, may have great potential for the next-generation flexible or wearable electronic devices. Not only is this approach a further example of the directed nanostructure design of freestanding networks with elastic hollow carbon spheres as buffers and containers for lithium-ion batteries, but also the strategy could be extended to other anode and cathode materials or as novel substrates for applications in nanoreactors, controlled release and selective adsorption fields.

Experimental section

Materials

A polyacrylonitrile (PAN, average $M_w$ 150 000 (typical); Aldrich) solution with a concentration of ca. 10–14 wt%, prepared by dissolving SnO$_2$ hollow spheres and PAN powder (with a mass ratio of 0.200 g/0.264 g, or 0.737 g/0.243 g) in N,N-dimethylformamide (DMF, 1.94 g or 2.42 g) at room temperature with vigorous stirring overnight, was used for the electrospinning process. The LiCoO$_2$ particles (99.8% metals basis, Aladdin Reagent, China) were used directly without post-treatment as cathode materials for a LiCoO$_2$–Sn/C full cell.

Sample preparation

SnO$_2$ hollow spheres were synthesized via a classic one-pot, template-free, hydrothermal route by Prof. Lou et al. in the literature.$^{44}$ Typically, a fixed amount of potassium stannate trihydrate (0.384 g, K$_2$SnO$_3$·3H$_2$O, 99.5% metal basis; Aladdin) and urea (0.48 g, $\approx$99.0%; Chengdu Kelong Chemical Reagent Co., China) was dissolved in a mixture solution of deionized water (50 mL) and ethanol (30 mL, $\approx$99.7%) under continuous stirring. The clear solution was then swiftly transferred into a Teflon-lined stainless steel autoclave (with a volume of ca. 100 mL), followed by heating at 200 °C for 24 h in an electric oven. Afterwards, the autoclave was cooled naturally to room temperature. The white precipitate was collected by centrifugation, washed with ethanol several times, and then dried at 60 °C overnight. For the preparation of a classical cathode electrode, a slurry mixture of LiCoO$_2$ power, acetylene black (AB), and poly(vinylidene fluoride) (PVDF) with a weight ratio of 8 : 1 : 1 was spread on a piece of Al foil, and dried at 80 °C in a vacuum overnight.

A piece of grounded aluminum foil was placed 20 cm below the single-nozzle spinneret to collect the nanofibers. A high voltage of 20 kV was supplied at the spinneret by a direct-current power supply, and the typical feeding rate was set at ca. 30 μL min$^{-1}$. All the samples were collected at room temperature in an air atmosphere. The collected electrospun paper of SnO$_2$/HS/PAN nanofibers was tailored and transferred to a tube furnace and calcined typically at 800 °C in a hydrogen or nitrogen atmosphere for 5 min or 0.5 h with a heating rate of 20 °C min$^{-1}$ to obtain Sn/C yolk–shell composite nanofiber paper.

Characterization

The composition and crystal structures of the samples were obtained by X-ray diffraction analysis (XRD, PANalytical X’Pert Pro, Cu Kz radiation, $\lambda = 1.5418 \text{Å}$) over a 2θ range of 10 to 90°. The surface morphology was investigated using scanning electron microscopes (FE-SEM, ZEISS Ultra 55; TESCAN VEGA3) operating at 15–20 kV after Pt coating. Transmission electron microscopy (TEM) was performed using a JEOL JEM-100CX operating at 80 kV. Thermogravimetric analysis (TGA) was conducted on a TGA 1, STARe System (Mettler Toledo) to determine the thermal decomposition process and the weight ratio of Sn in the composite at a heating rate of 20 °C min$^{-1}$ between 50 and 1000 °C. Raman spectra were collected on a Jobin-Yvon LabRam HR800 spectrometer with excitation from a Torus 50 mW diode-pumped solid-state laser (532 nm). Nitrogen adsorption and desorption isotherms were carried out at 77 K on a surface area and pore size analyzer (BK300, Beijing JWGB Sci&Tech Co., Ltd.) after degassing at 200 °C for 3 h under vacuum in the degas port.

Electrochemical characterization

The obtained Sn/C nanofibrous paper was cut into squares of ca. 1 × 1 cm$^2$ weighed $\approx$2.0 mg, and used as free-standing electrodes with a lithium plate as the counter electrode and the reference electrode, with 1 M LiPF$_6$ in EC–DMC (v/v = 1 : 1) as the electrolyte, with porous PVDF (pore size 0.45 μm) as a gel-type polymer separator membrane. For the full Li-ion battery, the classic LiCoO$_2$–AB (acetylene black) cathode was used as the cathode and the as-prepared Sn@C 3D nanostucture as a freestanding anode.

The CR2032 coin cells were assembled in an argon-filled glovebox (Vigor, with SOTA Standard), where moisture and oxygen levels were kept below 1 ppm. Electrochemical experiments were carried out on the LANHE CT2001A battery testing system (Wuhan Land Electronic Co., China) for cycling characteristics, and the VSP ultimate electrochemical workstation (BioLogic Science Instruments, France) for CV and PEIS profiles.

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Notes and references