



Composites of tin oxide and different carbonaceous materials as negative electrodes in lithium-ion batteries

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Abstract

Tin and tin oxide have been considered as suitable materials with a high theoretical capacity for lithium ion batteries. Their low cost, high safety, and other technical benefits placed them as promising replacements for graphite negative electrodes. The problem to overcome with tin oxide, as well as with other metallic materials, is high volume changes during alloying/dealloying, subsequent pulverization, delamination from current collectors following continuous degradation of the anode. To solve these issues, different approaches have been applied. A number of various architectures from nanostructures to core-shell, porous, anchored, and encapsulated have been studied to improve cycling performance. Much attention was paid to incorporate carbonaceous materials. Here, summarized results regarding utilization of the tin oxide-carbonaceous negative electrode material are presented.

Keywords Tin oxide · Carbonaceous materials · Lithium ion batteries

Introduction

In 1991, Sony commercialized the first lithium-ion battery. Since that time during the next two decades, electronic devices have been rapidly developed. Nowadays, small portable electronic devices, that is, cellular phones, notebook computers, and cameras, are in common usage. This leads to increased demand for energy storage systems. Lithium-ion batteries can offer relatively high energy density, light design, long lifespan, and low environmental impact in comparison with other battery systems such as nickel-cadmium (NiCd), nickel-metal hydride (NiMH). A battery consists of negative (anode) and positive (cathode) electrodes separated with a solid or liquid electrolyte containing lithium ions. External connection of the electrodes causes a chemical reaction occurring at both electrodes and forces electron movement from the anode to cathode. At the same time, lithium ions migrate through the electrolyte. The obtained current flow can be utilized by the user. Thus, electrodes are key battery components to obtain

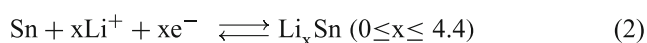
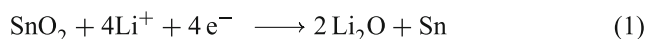
high energy/high power densities and better cycling stability and Coulombic efficiency [1].

Graphite has been an anode material in most commercialized batteries for more than 20 years now. It is due to its good mechanical stability, electric conductivity, and Li transport. Moreover, graphite exhibits a practical reversible capacity value of 350 mAh g⁻¹ [2] with low manufacturing cost and abundant availability. The problem with carbonaceous electrode materials is that they are not suitable for next-generation lithium-ion batteries, that is, smart electrical grid systems and electric vehicles [3]. Especially, the issue of all-electric vehicles is to overcome. A 500-km-range electric car needs a Li-ion cell with specific energy higher than 500 Wh kg⁻¹. Nowadays, the best Li-ion cells can deliver 250 Wh kg⁻¹, which is still below the requirements. Such a Li-ion battery is built from a transition metal oxide cathode material and graphite anode material. If the graphite negative electrode is replaced with silicon, the energy density is expected to reach 320 Wh kg⁻¹ [4]. Among many alternatives for replacement carbonaceous electrodes, Li alloys are considered as one of the most promising materials. Especially, silicon [5] and tin [6] are taken into consideration due to their high specific capacities and low operating potential. The theoretical specific capacity for lithium tin alloy (Li_{4.4}Sn) is 991 mAh g⁻¹ and is lower than the gravimetric capacity for the lithium silicon alloy (Li₁₅Si₄), 3579 mAh g⁻¹. However, comparison

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of volumetric capacities for Sn and Si alloys gives values of 1991 and 8340 mAh cm⁻³, respectively [7]. These Li-alloy systems suffer from volume changes, poor cycling performances due to pulverization leading to active material contact loss during the alloying and dealloying process. It is the reason why these metals are not used in practical applications. Metal oxides seem to be an alternative material for alloys as they also exhibit a high theoretical capacity (781 mAh g⁻¹ for SnO₂ and 1965 mAh g⁻¹ for SiO₂) [8, 9]. The electrochemical reaction of tin and lithium ions gives metallic tin and lithium oxide in the first step followed by lithium-tin alloy in the second step:



Metallic tin formation in reaction (1) causes volume changes for tin oxide-based electrodes as it is observed for pure metallic tin. This problem may be overcome by modification of the tin oxide electrode material in terms of morphology and structure. Tin oxide can be obtained in different forms of particle shape and size, e.g., nanorods [10, 11], nanosheets [12, 13], nanospheres [14, 15], nanowires [16, 17], nanotubes [18, 19], or nanoflowers [20]. The most common approach in nanomaterial preparation is hydrolysis of the tin salt followed by a special synthesis method. There are many types of these synthesis methods, i.e., hydrothermal or solvothermal processes, spray pyrolysis, annealing, thermal evaporation, or sol-gel. Among those methods, the hydrothermal process is widely used, especially when tin oxide nanoparticles are attached to carbon materials [21–26]. In general, the hydrothermal method is a synthesis method where crystal growth occurs under high pressure and elevated temperature. The advantages of hydrothermal synthesis are that one may obtain crystals of substances which are not stable near their melting point, and the possibility to synthesize large amount of crystals of high quality. It is also a simple and cost-efficient method of high efficiency yield with possibility of control over the sizes and morphologies of the desired product [27]. Moreover, the reaction takes place in an aqueous environment allowing to operate at high temperatures and high pressure conditions. Some examples of synthesis of nanosized-SnO₂ structures are given in Table 1.

Changing the size of the particles is one of the ways to improve electrochemical properties of negative electrodes based on tin-derived compounds [28, 29]. It is related with improving charge transport by shortening the lithium-ion diffusion length within the material. The diminutive particle size offers the existence of more electrochemically active sites which could enhance high rate performance due to curtailment of the diffusion pathway [30]. The other way

is to distribute tin oxide grains in a carbonaceous matrix of various origins as a stress-accommodating phase [31–49]. The origin of the carbon source can be very broad, e.g., graphite layers [50], disordered carbons [51], graphene [52], and carbon nanotubes [53]. It is very important to have the carbon matrix phase flexible and porous for the lithium-ion diffusion process, as well as suitable for limiting metallic phase volume changes. As an example of such an approach, a schematic illustration of the synthesis process of Sn/SnO₂ and SnO₂ in porous carbon (PC) is shown in Fig. 1. In their synthesis method, the authors designed a nanocomposite material via a simple reflux method. They used naturally occurring pine cones and SnCl₂·2H₂O as a source of porous carbon and a tin/tin oxide precursor, respectively [36]. Such an approach resulted in achieving a discharge capacity of over 140 mAh g⁻¹ at a current density equal to 400 mA g⁻¹ for the Sn/SnO₂/PC composite in a sodium-ion battery. It evidenced and confirmed that a porous carbon matrix acts as a buffer for volume expansion/shrinkage for tin and tin oxide-based electrode materials [36].

Carbon is known not to react with tin and does not form tin carbide [54]. It is very crucial in terms of utilizing carbon as a buffer in preventing electric contact loss of the tin negative electrode with the current collector [55]. The carbon phase, as a good electronic conductor, is known to improve electrical contact between the active material and the current collector [56]. This review is focused on the modification of tin oxide-carbon negative electrode materials in lithium-ion batteries. I wanted to show the strategies used to improve battery performance by incorporation of tin oxide into the carbonaceous matrix as a negative electrode in energy storage and energy conversion applications.

SnO₂ - based negative electrode materials modified with a carbonaceous matrix

The historical background for modification of tin oxides with carbonaceous material origins from Lee et al. who obtained synthetic graphite modified by a highly dispersed tin oxide [57]. Although results were better in comparison with unsupported tin oxide, the capacity fade was still very high. After only 30 cycles at a C/6 rate (note: a battery charging/discharging at a rate of C/6 (C-rate) will deliver its nominal evaluated capacity in 6h, and in the studied case, it was 90 mA g⁻¹), the capacity decreased by 12% and gave a value of 450 mAh g⁻¹. However, the authors showed that incorporation of tin oxide-based materials into the carbon matrix was the way to improve electrochemical cyclability of such an electrode due to prevention of tin agglomeration. This effect was achieved not only due to the presence of graphite but also thanks to the high dispersion of the tin

Table 1 Examples of synthesis of nanosized-SnO₂ material

Structure type	Synthesis	Chemicals	Reaction conditions	Reference
SnO ₂ nanorods	Hydrothermal method	SnCl ₄ , NaOH, H ₂ O	200 °C, 1h, autoclave	[10]
SnO ₂ nanosheets	Chemical precipitation	SnCl ₂ ·H ₂ O, NaOH, H ₂ O	800 °C in air, 8h, furnace	[12]
SnO ₂ nanospheres	Hydrothermal method	K ₂ SnO ₃ , C ₆ H ₁₂ O ₆ , H ₂ O	180 °C, 4h, autoclave	[14]
SnO ₂ nanowires	Vapor-Liquid-Solid (VLS) method	Sn powder	600 °C under O ₂ flow	[16]
SnO ₂ nanotubes	Electrospinning	PVP, SnCl ₄ ·5H ₂ O, C ₂ H ₅ OH	Voltage of 20 kV	[18]
SnO ₂ nanoflowers	Solvothermal method	SnCl ₂ ·2H ₂ O, C ₃ H ₆ O, H ₂ O, NaOH	180 °C, 15h, autoclave	[20]

oxide phase and the existence of a lithium oxide film formed during the first charging process:



The Li₂O layer was supposed to act a stabilizing barrier against Sn agglomeration.

Read et al. showed the possibility to use hard carbons as a diluent to embed metal oxides into the carbon matrix [58]. The tin oxide particles were trapped and separated by carbon. This method allowed to obtain a material with the specific capacity of 480 mAh g⁻¹ after the first cycle with capacity retention of 83% for the 40th cycle. The authors claimed that a significant part of the total capacity of the electrode material origins from the hard carbon part. The final conclusion was that to minimize capacity fade, one should perform additional studies in different configurations, i.e., variations in the SnO₂ to carbon ratio, the origin of carbon precursor, the particle size of the tin oxide, and the heat treatment procedure [58].

Another method utilizing hard carbon precursors was proposed by Molenda et al. in references [51, 59]. The authors used amorphous, pyrolytic carbon as a buffer matrix derived from a natural plant polymer. The idea was to encapsulate tin oxide-based grains in a flexible carbon framework in a one-step process simultaneously with the reduction of tin oxide to metallic tin. The source of the carbon matrix originated from pyrolysed potato starch. Starch was chosen due to its low cost, renewability, and showing a reversible capacity after being used as an anode material [60, 61]. The cyclic voltammetry curve of the 51% C/Sn-SnO₂@700 electrode material shown in Fig. 2 shows the voltage profile during the lithiation/delithiation process.

Electrode materials consisting of carbon and tin-tin oxide parts showed capacity values of 435 mAh g⁻¹ for the 30th cycle at C/2 — rate with coulombic efficiency equal to 98% [51]. The result evidences that modification of tin oxide nanoparticles improves electrochemical properties of the Sn/SnO₂-based electrode in terms of cycling

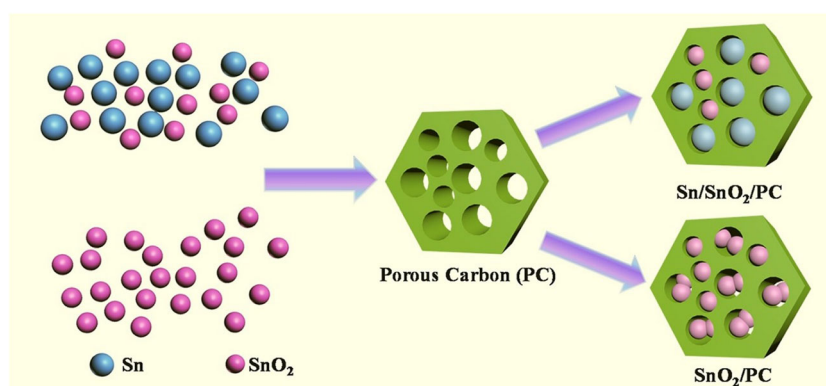


Fig. 1 Schematic illustration of the synthesis process of Sn/SnO₂/PC and SnO₂/PC reprinted from [36] with permission from Elsevier

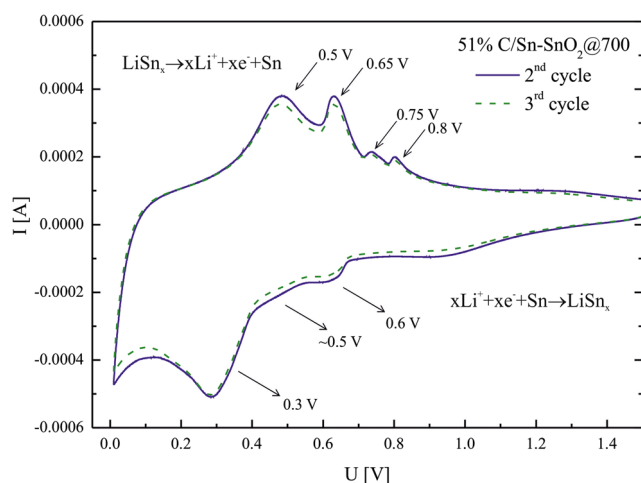
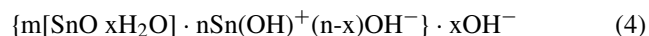


Fig. 2 CV curves of the cell containing 51% C/Sn-SnO₂@700 sample at 0.1 mV s⁻¹ scanning rate reprinted with permission from [51]. Copyright 2015, The Electrochemical Society

performances. However, the problem with high irreversible capacity loss for the first cycle (50%) may limit practical application of such electrode.

Nowak et al. studied tin oxide nanoparticles from laser ablation encapsulated in a carbonaceous matrix [32]. The authors used gelatine as a source of carbon. Metallic tin was used as a precursor. It was proposed that the laser ablation technique led to formation of colloidal species in the form of



The nuclei consisted of tin(II) hydroxide Sn(OH)₂ · (SnO_xH₂O) with adsorbed positively charged Sn(OH)⁺ at the first zone and negatively charged OH⁻ in the diffusional zone. The whole colloidal system was balanced and the charge was zero. In the next step, UV radiation was used to coagulate the colloidal system. After coagulation and mixing with gelatine, the SnO_x nanoparticles/gelatine mixture was pyrolysed at 900 °C. Encapsulation of the tin oxide nanoparticles into the carbonaceous matrix was confirmed by TEM and SEAD measurements (Fig. 3). The obtained electrode material showed first specific charge and discharge capacities of 1370 and 1070 mAh g⁻¹ at a current density equal to 25 mA g⁻¹ (C/20), respectively. It gave capacity retention of 78%, which was higher than that for results obtained by Molenda et al. in ref. [51]. It shows that changing the size of the inorganic part and utilization of the carbon matrix leads to improvement of electrochemical properties of the C/SnO₂ electrode material.

Recently, it was shown that graphene might be an excellent substrate for tin oxide nanoparticles [62]. Graphene is known to exhibit high electric conductivity and good mechanical flexibility and may diminish the volume changes of metal oxides [63]. Moreover, graphene is

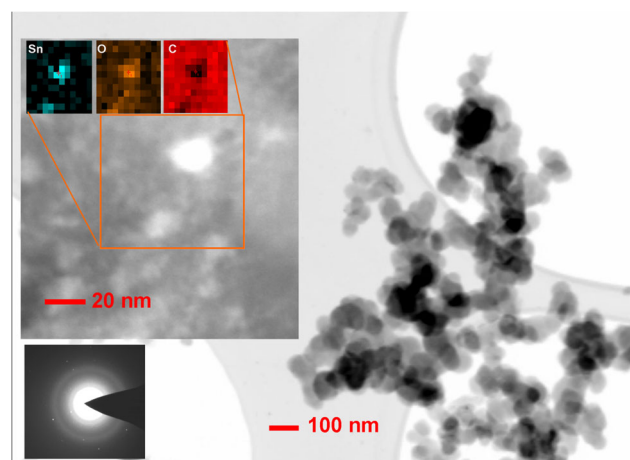


Fig. 3 TEM micrograph of the SnO@C_{gel} electrode material; inset: EDX analysis (upper left corner) and SEAD (bottom left corner) [32]. Reproduced by permission of The Royal Society of Chemistry

able to accommodate large amounts of lithium ions [64]. Chen et al. mixed 3-nm SnO₂ nanoparticles with graphene at a weight ratio close to 1:1. The synergistic effect of SnO₂/graphene was achieved, showing superior cycling performance with a very high rate performance equal to 574 mAh g⁻¹ at a current density of 10 A g⁻¹. Such results were obtainable due to the presence of ultra-small sizes of tin(IV) dioxide able to reversibly react with lithium ions to form an alloy, and were able to accommodate volume changes during the battery test. Additionally, the presence of the graphene phase was utilized as a material able to enhance electric conductivity and lithium diffusion. These phenomena were achieved due to reducing the size of SnO₂ nanoparticles and a shortened diffusion length within the particles and the graphene network. The authors claimed that the increase of capacity was also attributed to formation of a polymeric gel-like film at low potentials due to electrolyte decomposition [62], as well as simple lithium ion insertion/extraction on the graphene surface [65]. However, it seems that this polymeric gel-like film acted rather as a solid electrolyte interphase (SEI) which is known to affect performance of lithium ion cells in terms of its storage and cycling [66]. The ideal SEI film is expected to be thin, permeable for lithium ions and blocking for electrons. In general, the SEI layer influences initial capacity loss, battery cycle life, rate capability, and safety [67]. As a protective layer, SEI itself does not enhance nor diminish the capacity of the lithium ion cell. Carbon nanotubes (CNTs), similarly like graphene, exhibit high electrical conductivity. Their tubular structure and flexible matrix are widely used in lithium-ion battery applications [68, 69]. Particularly, filling the inner surface of nanotubes with tin oxide is an advantage [70]. In such situations, the carbonaceous matrix acts as a buffer for large volume

expansion of Sn during the lithium ion insertion/extraction process. The presence of CNTs improved the conductivity of the material due to the presence of electronic conductive channels, and although volume expansion was still observed, it did not lead to pulverization [70].

In the literature, one may find electrode materials consisting of SnO₂@CNTs core shell composites obtained by the wet chemical method [71]. It was shown that it was necessary to use KOH as the activation material. The base caused changes in the tubular structure of CNTs (see Fig. 4). Those changes affect creation of nanodefects which allowed to fill more tin oxide into the CNTs and enhance the insertion/extraction process of lithium ions. The electrode material exhibited reversible capacity of about 628 mAh g⁻¹ after 50 cycles at a current density of 0.2 mA g⁻¹, as is given in Fig. 5. This experiment showed that encapsulation of tin oxide into the carbonaceous matrix is important for such materials. Recent studies of ultrafine SnO₂ nanoparticles within multiwall carbon nanotube (MWCNTs) networks showed possibility to obtain electrode materials in non-solution synthesis [72]. In comparison with the widely used hydrothermal method [73–76], the proposed process does not require any solvent to be used. The electrode material exhibited a reversible capacity of 640 mAh g⁻¹ at a current density of 1 A g⁻¹ after 100

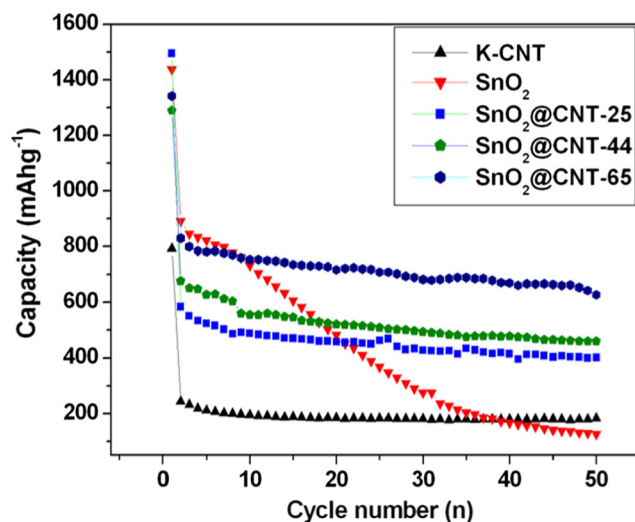
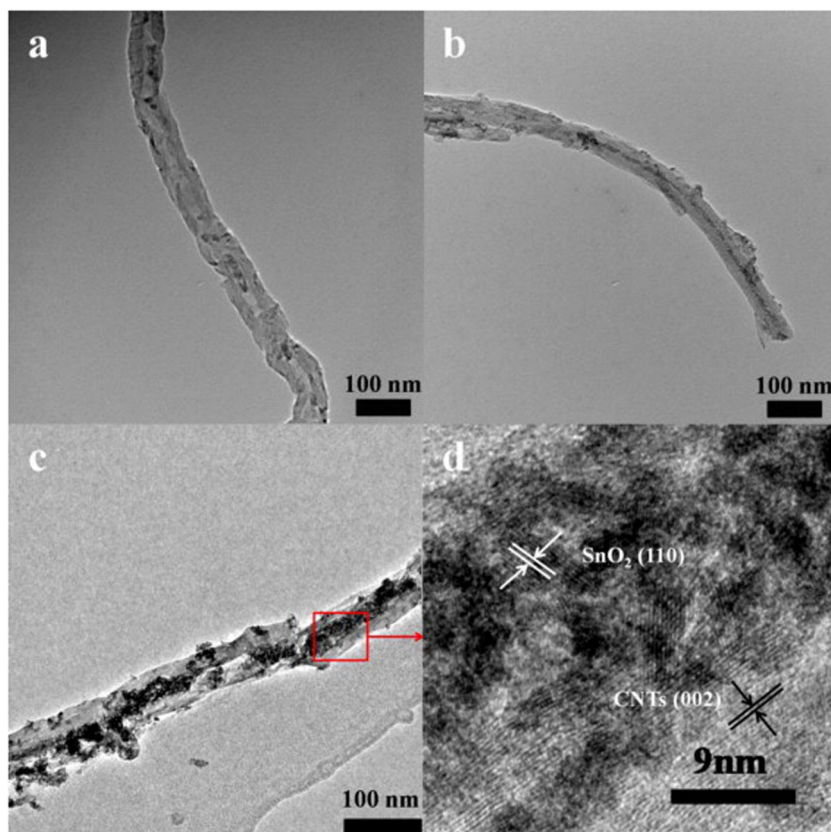


Fig. 5 Profiles of the discharge capacity vs cycle numbers at a current density of 0.2 mA cm⁻² reprinted from [71] with permission from Elsevier

cycles. The authors confirmed that a MWCNTs network may act as buffer against volume changes of tin oxide due to its flexibility and facilitate the charge transfer thanks to high electrical conductivity of MWCNTs.

Fig. 4 TEM images of SnO₂@CNT-25 (a), SnO₂@CNT-44 (b), SnO₂@CNT-65 (c), and HRTEM image of SnO₂@CNT-65 (d) reprinted from [71] with permission from Elsevier



Summary

The practical specific capacity of a graphite electrode of 350 mAh g⁻¹ is not attractive anymore for next-generation lithium-ion batteries. All tin oxide-based materials shown in this paper exhibited capacities higher than 430 mAh g⁻¹, and all those materials included usage of the carbonaceous matrix. This shows that the low cost and environmental benignity make tin oxides able to replace graphite anodes. The presence of the carbon phase is crucial for improved cycling performance of negative electrodes. The results showed that the major problem with huge volume changes of the tin oxide electrode may be successfully overcome by utilization of the carbonaceous matrix as a stress-accommodating phase, coupled with reducing the size of tin oxide particles. One should take into account that although the size of tin oxide-based electrode material can be reduced, it still itself undergoes volume changes. This one issue can not be overcome. Carbon is necessary to keep electric contact between tin and the current collector during alloying and dealloying of Sn. Although the engineering requirements and expectations regarding the capacity level were met, there are still two main problems to be solved: (1) transferring material preparation from the laboratory scale into the industrial scale. It is obvious that materials which are complicated to produce from the industrial point of view might not be attractive to manufacture. (2) reversibility and cycle stability need to be improved. The capacity retention in all cases was much lower than 80%. It is very low taking into account that in most cases, the number of cycles did not exceed the value of 100. Nowadays, the end of battery life is the point at which 80% of the initial capacity is reached. Thus, in a practically applied battery, a much lower capacity fade is required. Hence, the application of high capacity and high cyclability tin oxide-carbonaceous-based materials manufactured by a cost-effective, industrial-scalable process is the key parameter for usage of such materials in next-generation lithium-ion batteries.

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