



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

Andrzej P. Nowak¹

Received: 26 October 2017 / Revised: 26 February 2018 / Accepted: 9 March 2018
© The Author(s) 2018

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

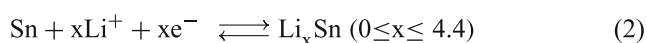
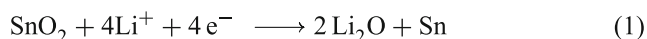
high energy/high power densities and better cycling stability and Coulombic efficiency [1].

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

✉ Andrzej P. Nowak
andnowak@pg.edu.pl

¹ Faculty of Chemistry, Department of Chemistry and Technology of Functional Materials, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland

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

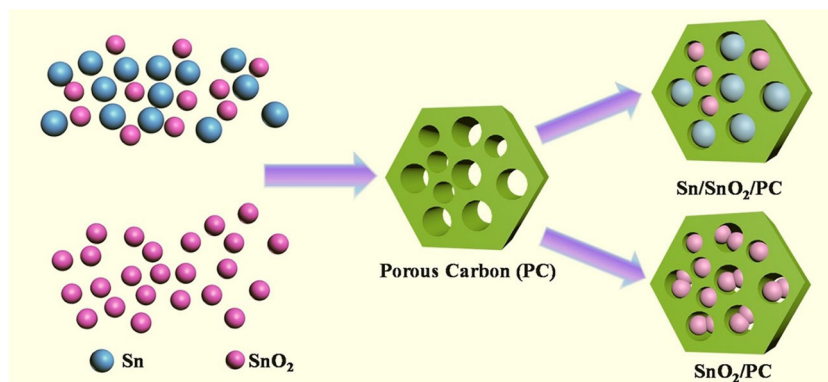


Fig. 1 Schematic illustration of the synthesis process of Sn/SnO₂/PC and SnO₂/PC reprinted from [36] with permission from Elsevier

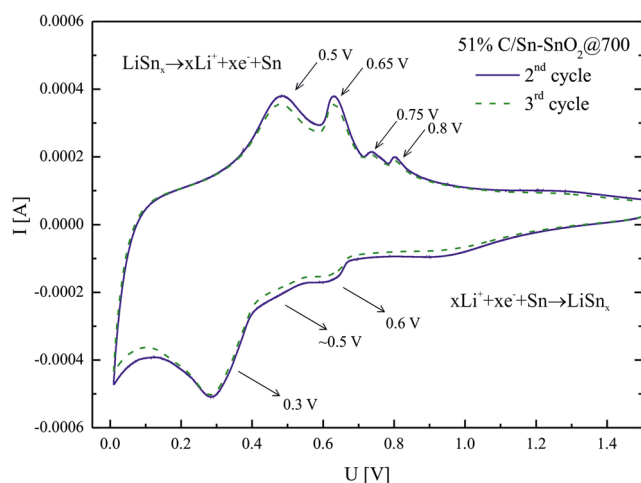
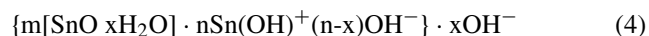


Fig. 2 CV curves of the cell containing 51% C/Sn-SnO₂@700 sample at 0.1 mV s⁻¹ scanning rate reprinted with permission from [51]. Copyright 2015, The Electrochemical Society

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

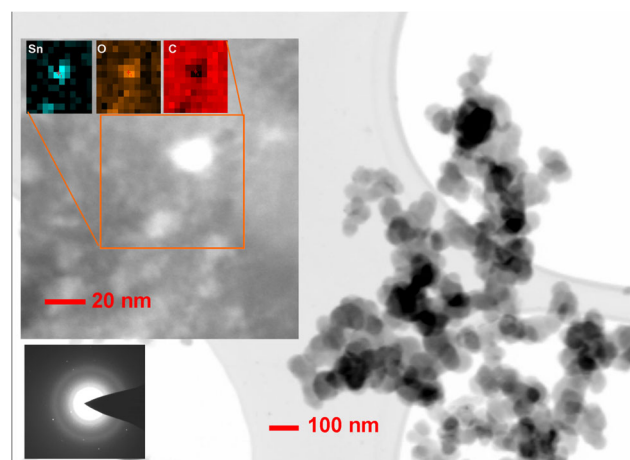


Fig. 3 TEM micrograph of the SnO@C_{gel} electrode material; inset: EDX analysis (upper left corner) and SEAD (bottom left corner) [32]. Reproduced by permission of The Royal Society of Chemistry

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

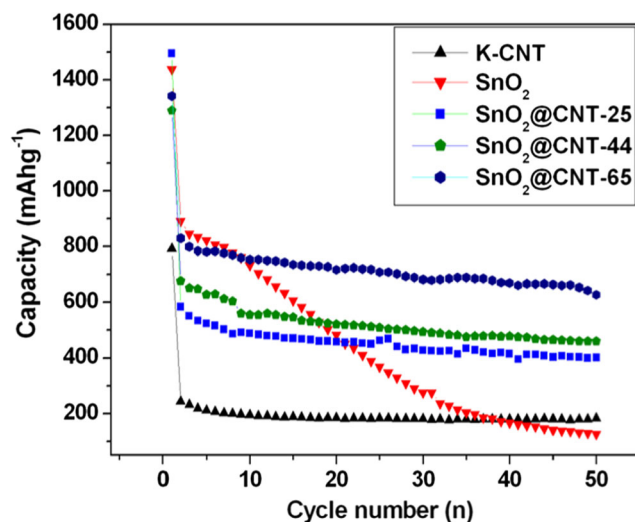
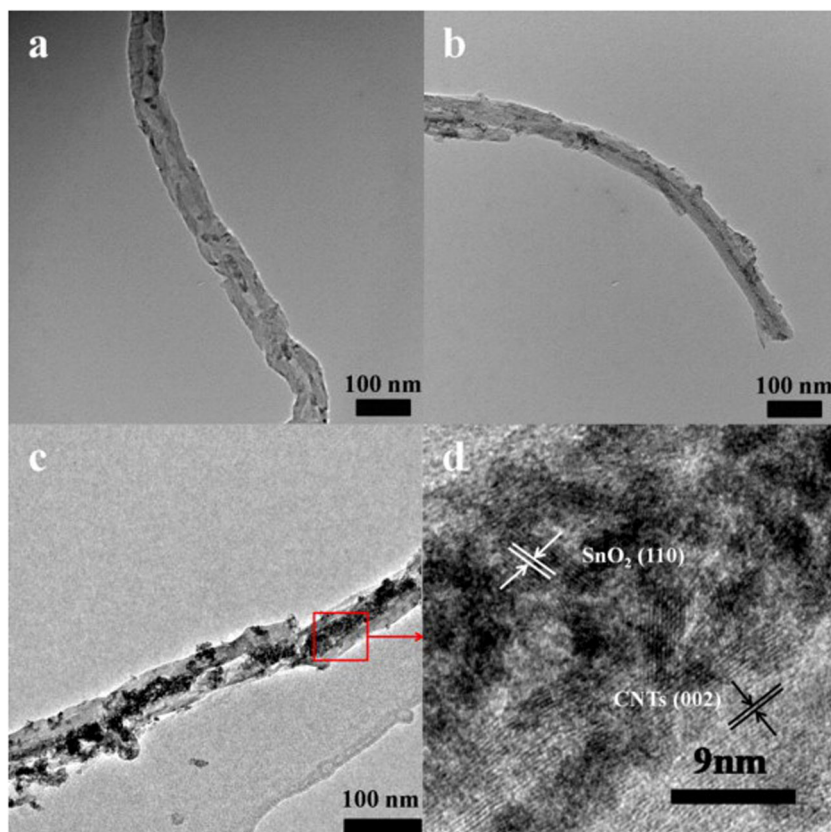


Fig. 5 Profiles of the discharge capacity vs cycle numbers at a current density of 0.2 mA cm⁻² reprinted from [71] with permission from Elsevier

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.

Funding information This work was supported by the Polish Ministry of Science and Higher Education (DS no. 032406).

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- Goodenough JB, Park K-S (2013) The Li-ion rechargeable battery: a perspective. *J Am Chem Soc* 135:1167–1176
- Tarascon J-M, Armand M (2015) Issues and challenges facing rechargeable lithium batteries. *Science* 414:359–367
- Abraham KM (2015) Prospects and limits of energy storage in batteries. *J Phys Chem Lett* 6:830–844
- Abraham KM (2012) Rechargeable batteries for the 300-mile electric vehicle and beyond. *ECS Trans* 41:27–34
- Teki R, Datta MK, Krishnan R, Parker TC, Lu T-M, Kumta PN, Koratkar N (2009) Nanostructured silicon anodes for lithium ion rechargeable batteries. *Small* 5:2236–2242
- Yu Y, Gu L, Zhu C, van Aken PA, Maier J (2009) Tin nanoparticles encapsulated in porous multichannel carbon microtubes: preparation by single-nozzle electrospinning and application as anode material for high-performance Li-based batteries. *J Am Chem Soc* 131:15984–15985
- Nitta N, Yushin G (2014) High-capacity anode materials for lithium-ion batteries: choice of elements and structures for active particles. *Part Part Syst Char* 31:317–336
- Du G, Zhong C, Zhang P, Guo Z, Chen Z, Liu H (2010) Tin dioxide/carbon nanotube composites with high uniform SnO₂ loading as anode materials for lithium ion batteries. *Electrochim Acta* 55:2582–2586
- Yan N, Wang F, Zhong H, Li Y, Wang Y, Hu L, Chen Q (2013) Hollow porous SiO₂ nanocubes towards high-performance anodes for lithium-ion batteries. *Sci Rep* 3:1568–1574
- Xie Y, Zhu F (2017) Electrochemical capacitance performance of polyaniline/tin oxide nanorod array for supercapacitor. *J Solid State Electrochem* 21:1675–1685
- Sial MAZG, Iqbal M, Siddique Z, Nadeem MA, Ishaq M, Iqbal A (2017) Synthesis and time-resolved photoluminescence of SnO₂ nanorods. *J Mol Struct* 1144:355–359
- Wei W, Du P, Liu D, Wang H, Liu P (2017) Facile mass production of nanoporous SnO₂ nanosheets as anode materials for high performance lithium-ion batteries. *J Colloid Interf Sci* 503:205–213
- Liu L, Song P, Wei Q, Zhong X, Yang Z, Wang Q (2017) Synthesis of porous SnO₂ hexagon nanosheets loaded with Au nanoparticles for high performance gas sensors. *Mater Lett* 201:211–215
- Miao C, Liu M, He Y-B, Qin X, Tang L, Huang B, Li R, Li B, Kang F (2016) Monodispersed SnO₂ nanospheres embedded in framework of graphene and porous carbon as anode for lithium ion batteries. *Energy Stor Mater* 3:98–105
- Wen W, Zou M, Feng Q, Li J, Lai H, Huang Z (2016) SnO₂ nanospheres among GO and SWNTs networks as anode for enhanced lithium storage performances. *J Energy Chem* 25:445–449
- Park JJ, Park S, Kim DH, Jeong H, Lee S (2017) SnO₂ nanowires decorated with forsythia-like TiO₂ for photoenergy conversion. *Mater Lett* 202:48–51
- Mukherjee S, Schuppert N, Bates A, Jasinski J, Hong J-E, Choi MJ, Park S (2017) An electrochemical and structural study of highly uniform tin oxide nanowires fabricated by a novel, scalable solvoplasma technique as anode material for sodium ion batteries. *J Power Sources* 347:201–209
- Li L, Yin X, Liu S, Wang Y, Chen L, Wang T (2010) Electrospun porous SnO₂ nanotubes as high capacity anode materials for lithium ion batteries. *Electrochem Commun* 12:1383–1386
- Yang M, Li X, Yan B, Fan L, Yu Z, Li D (2017) Reduced graphene oxide decorated porous SnO₂ nanotubes with enhanced sodium storage. *J Alloy Compd* 710:323–330
- Song L, Yang S, Wei W, Qu P, Xu M, Liu Y (2015) Hierarchical SnO₂ nanoflowers assembled by atomic thickness nanosheets as anode material for lithium ion battery. *Sci Bull* 60:892–895
- Demir-Cakan R, Hu YS, Antonietti M, Maier J, Titirici MM (2008) Facile one-pot synthesis of mesoporous SnO₂

- microspheres via nanoparticles assembly and lithium storage properties. *Chem Mater* 20:1227–1229
22. Chen JS, Cheah YL, Chen YT, Jayaprakash N, Madhavi S, Yang YH, Lou XW (2009) SnO₂ nanoparticles with controlled carbon nanocoating as high capacity anode materials for lithium-ion batteries. *J Phys Chem C* 113:20504–20508
 23. Ding S, Luan D, Boey FYC, Chen JS, Lou XW (2011) SnO₂ nanosheets grown on graphene sheets with enhanced lithium storage properties. *Chem Commun* 47:7155–7157
 24. Wen Z, Cui, Kim H, Mao S, Yu K, Lu G, Pu H, Mao O, Chen J (2012) Binding Sn based nanoparticles on graphene as the anode of rechargeable lithium-ion batteries. *J Mater Chem* 22:3300–3306
 25. Wang D, Yang J, Li X, Geng D, Li R, Cai M, Sham TK, Sun X (2013) Layer by layer assembly of sandwiched graphene/SnO₂ nanorod/carbon nanostructures with ultrahigh lithium ion storage properties. *Energy Environ Sci* 6:2900–2906
 26. Wang J, Song W-L, Wang Z, Fan L-Z, Zhang Y (2015) Facile fabrication of binder free metallic tin nanoparticle/carbon nanofiber hybrid electrodes for lithium-ion batteries. *Electrochim Acta* 153:468–475
 27. Akhir M-A-M, Mohamed K, Lee HL, Rezan SA (2016) Synthesis of tin oxide nanostructures using hydrothermal method and optimization of its crystal size by using statistical design of experiment. *Procedia Chem* 19:993–998
 28. Noh M, Kim Y, Kim MG, Lee H, Kim H, Kwon Y, Lee Y, Cho J (2005) Monomer-capped tin metal nanoparticles for anode materials in lithium secondary batteries. *Chem Mater* 17:3320–3324
 29. Song H, Li X, Cui Y, Xiong D, Wang Y, Zeng J, Dong L, Li D, Sun X (2015) Controllable lithium storage performance of tin oxide anodes with various particle sizes. *Int J Hydrogen Energ* 40:14314–14321
 30. Liu J, Liu X-W (2012) Two-dimensional nanoarchitectures for lithium storage. *Adv Mater* 24:4097–4111
 31. Hu R, Sun W, Zeng M, Zhu M (2014) Dispersing SnO₂ nanocrystals in amorphous carbon as a cyclic durable anode material for lithium ion batteries. *J Energy Chem* 23:338–345
 32. Nowak AP, Lisowska-Oleksiak A, Siuzdak K, Sawczak M, Gazda M, Karczewski J, Trykowski G (2015) Tin oxide nanoparticles from laser ablation encapsulated in a carbonaceous matrix — a negative electrode in lithium-ion battery applications. *RSC Adv* 5:84321–84327
 33. Chojnacka A, Świętosławski M, Maziarz W, Dziembaj R, Molenda M (2016) An influence of carbon matrix origin on electrochemical behaviour of carbon-tin anode nanocomposites. *Electrochim Acta* 209:7–16
 34. Yang J, Xi L, Tang J, Chen F, Wu L, Zhou X (2016) Three-dimensional porous carbon network encapsulated SnO₂ quantum dots as anode materials for high-rate lithium ion batteries. *Electrochim Acta* 217:274–282
 35. Zhou X, Xi L, Chen F, Bai T, Wang B, Yang J (2016) In situ growth of SnO₂ nanoparticles in heteroatoms doped cross-linked carbon frameworks for lithium ion batteries anodes. *Electrochim Acta* 213:633–640
 36. Li X, Li X, Fan L, Yu Z, Yan B, Xiong D, Song X, Li S, Adair KR, Li D, Sun X (2017) Rational design of Sn/SnO₂/porous carbon nanocomposites as anode materials for sodium-ion batteries. *Appl Surf Sci* 412:170–176
 37. Sher Shah MSA, Lee J, Park AR, Choi Y, Kim W-J, Park J, Chung C-H, Kim J, Lim B, Yoo PJ (2017) Ultra-fine SnO₂ nanoparticles doubly embedded in amorphous carbon and reduced graphene oxide (rGO) for superior lithium storage. *Electrochim Acta* 224:201–210
 38. Ao X, Jiang J, Ya Ruan, Li Z, Zhang Y, Sun J, Wang C (2017) Honeycomb-inspired design of ultrafine SnO₂@C nanospheres embedded in carbon film as anode materials for high performance lithium- and sodium-ion battery. *J Power Sources* 359:340–348
 39. Gupta A, Dhakate SR, Gurunathan P, Ramesha K (2017) High rate capability and cyclic stability of hierarchically porous Tin oxide (IV)-carbon nanofibers as anode in lithium ion batteries. *Appl Nanosci* 7:449–462
 40. Liang J, Yu X-Y, Zhou H, Wu HB, Ding S, Lou XW (2014) Bowl-like SnO₂@Carbon hollow particles as an advanced anode material for lithium-ion batteries. *Angew Chem Int Ed* 53:12803–12807
 41. Du G, Zhong C, Zhang P, Guo Z, Chen Z, Liu H (2010) Tin dioxide/carbon nanotube composites with high uniform SnO₂ loading as anode materials for lithium ion batteries. *Electrochim Acta* 55:2582–2586
 42. Xie J, Varadan VK (2005) Synthesis and characterization of high surface area tin oxide/functionalized carbon nanotubes composite as anode materials. *Mater Chem Phys* 91:274–280
 43. Lou XW, Deng D, Lee JY, Archer LA (2008) Preparation of SnO₂/carbon composite hollow spheres and their lithium storage properties. *Chem Mater* 20:6562–6566
 44. Lian P, Wang J, Cai D, Ding L, Jia Q, Wang H (2014) Porous SnO₂@C/graphene nanocomposite with 3D carbon conductive network as a superior anode material for lithium-ion batteries. *Electrochim Acta* 116:103–110
 45. Lian P, Zhu X, Liang S, Li Z, Yang W, Wang H (2011) High reversible capacity of SnO₂/graphene nanocomposite as an anode material for lithium-ion batteries. *Electrochim Acta* 56:4532–4539
 46. Zhang Z, Peng X, Guo Z, Cai C, Chen Z, Wexler D, Li S, Liu H (2012) Carbon-coated SnO₂/graphene nanosheets as highly reversible anode materials for lithium ion batteries. *Carbon* 50:1897–1903
 47. Fan J, Wang T, Yu C, Tu B, Jiang Z, Zhao D (2004) Oxides/Carbon composite as the negative-electrode material for lithium-ion batteries. *Adv Mater* 16:1432–1436
 48. Han W-Q, Zettl A. (2003) Coating single-walled carbon nanotubes with tin oxide. *Nano Lett* 5:681–683
 49. Bonino CA, Ji L, Lin Z, Toprakci O, Zhang X, Khan SA (2011) Electrospun carbon-tin oxide composite nanofibers for use as lithium ion battery anodes. *ASC Appl Mater Inter* 3:2534–2542
 50. Sun Y, Zhao C, Shen M, Pan Z, Liu X (2016) SnO₂ nanoparticles encapsulated by curved graphite layers as anode materials for Li-ion batteries with high performances. *J Alloy Compd* 683:191–197
 51. Chojnacka A, Molenda M, Bakierska M, Dziembaj R (2015) Electrochemical performance of Sn/SnO₂ nanoparticles encapsulated in carbon matrix derived from plant polysaccharides. *ECS Trans* 64:165–171
 52. Deng Y, Fang C, Chen G (2016) The developments of SnO₂/graphene nanocomposites as anode materials for high performance lithium ion batteries: a review. *J Power Sources* 304:81–101
 53. Li Y, Lu X, Wang H, Xie C, Yang G, Niu C (2015) Growth of ultrafine SnO₂ nanoparticles within multiwall carbon nanotube networks: non-solution synthesis and excellent electrochemical properties as anodes for lithium ion batteries. *Electrochim Acta* 178:778–785
 54. Kamali AR, Fray DJ (2011) Tin-based materials as advanced anode materials for lithium ion batteries: a review. *Rev Adv Mater Sci* 27:14–24
 55. Li X, Zhong Y, Cai M, Balogh MP, Wang D, Zhang Y, Li R, Sun X (2013) Tin-alloy heterostructures encapsulated in amorphous carbon nanotubes as hybrid anodes in rechargeable lithium ion batteries. *Electrochim Acta* 89:387–393
 56. Goriparti S, Miele E, De Angelis F, Di Fabrizio E, Zaccaria PR, Capiglia C (2014) Review on recent progress of nanostructured anode materials for Li-ion batteries 257:421–443

57. Lee JY, Zhang R, Liu Z (2000) Lithium intercalation and deintercalation reactions in synthetic graphite containing a high dispersion of SnO. *Electrochem Solid State Lett* 3:167–170
58. Read J, Foster D, Wolfenstine J, Behl W (2001) SnO₂-carbon composites for lithium-ion battery anodes. *J Power Sources* 98:277–281
59. Chojnacka A, Molenda M, Bakierska M, Dziembaj R (2014) Novel method of preparation of C/Sn-SnO₂ nanocomposite Li-ion anode material derived from plant polysaccharides. *Procedia Eng* 98:2–7
60. Li W, Chen M, Wang C (2011) Spherical hard carbon prepared from potato starch using as anode material for Li-ion batteries. *Mater Lett* 65:3368–3370
61. Wilamowska M, Graczyk-Zajac M, Riedel R (2013) Composite materials based on polymer-derived SiCN ceramic and disordered hard carbons as anodes for lithium-ion batteries. *J Power Sources* 244:80–86
62. Chen Y, Song B, Chen RM, Lu L, Xue J (2014) A study of the superior electrochemical performance of 3 nm SnO₂ nanoparticles supported by graphene. *J Mater Chem. A* 2:5688–5695
63. Zhang X, Wang B, Sunarso J, Liu S, Zhi L (2012) Graphene nanostructures toward clean energy technology applications. *Wiley Interdiscip Rev Energy Environ* 1(3):317–336
64. Yang S, Yue W, Zhu J, Ren Y, Yang X (2013) Graphene-based mesoporous SnO₂ with enhanced electrochemical performance for lithium-ion batteries. *Adv Funct Mater* 23(28):3570–3576
65. Zhu X, Zhu Y, Murali S, Stoller MD, Ruoff RS (2011) Reduced graphene oxide/tin oxide composite as an enhanced anode material for lithium ion batteries prepared by homogenous coprecipitation. *J Power Sources* 196:6473–6477
66. Lu M, Cheng H, Yang Y (2008) A comparison of solid electrolyte interphase (SEI) on the artificial graphite anode of the aged and cycled commercial lithium ion cells. *Electrochim Acta* 53:3539–3546
67. Jin S, Li J, Daniel C, Mohanty D, Nagpure S, Wood DL (2016) The state of understanding of the lithium-ion-battery graphite solid electrolyte interphase (SE) and its relationship to formation cycling 105:52–76
68. Chen G, Wang Z, Xia D (2008) One-pot synthesis of carbon nanotube@ SnO₂-Au coaxial nanocable for lithium-ion batteries with high rate capacity. *Chem Mater* 20:6951–6956
69. Zhang HX, Feng C, Zhai YC, Jiang KL, Li QQ, Fan SS (2009) Cross-stacked carbon nanotube sheets uniformly loaded with SnO₂ nanoparticles: a novel binder-free and high-capacity anode material for lithium-ion batteries. *Adv Mater* 21:2299–2304
70. Zhao N, Wang G, Huang Y, Wang B, Yao B, Wu Y (2008) Preparation of nanowire arrays of amorphous carbon nanotube-coated single crystal SnO₂. *Chem Mater* 20:2612–2614
71. Zhang H, Song H, Chen X, Zhou J, Zhang H (2012) Preparation and electrochemical performance of SnO₂@carbon nanotube core-shell structure composites as anode material for lithium-ion batteries. *Electrochim Acta* 59:160–167
72. Li Y, Lu X, Wang H, Xie C, Yang G, Niu C (2015) Growth of ultrafine SnO₂ nanoparticles within multiwall carbon nanotube networks: non-solution synthesis and excellent electrochemical properties as anodes for lithium ion batteries. *Electrochim Acta* 178:778–785
73. Jin Y-H, Min K-M, Seo S-D, Shim H-W, Kim D-W (2011) Enhanced Li storage capacity in 3 nm diameter SnO₂ nanocrystals firmly anchored on multiwalled carbon nanotubes. *J Phys Chem C* 115:22062–22067
74. Xu C, Sun J, Gao L (2011) Synthesis of multiwalled carbon nanotubes that are both filled and coated by SnO₂ nanoparticles and their high performance in lithium-ion batteries. *J Phys Chem C* 113:20509–20513
75. Huang B, Yang J, Zhou X (2014) Hierarchical SnO₂ with double carbon coating composites as anode materials for lithium ion batteries. *J Solid State Electrochem* 18:2443–2449
76. Guo Q, Qin X (2014) Flower-like SnO₂ nanoparticles grown on graphene as anode materials for lithium-ion batteries. *J Solid State Electrochem* 18:1031–1039