



## Review article

# Tin-based anode materials with well-designed architectures for next-generation lithium-ion batteries



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## H I G H L I G H T S

- Recent progress in tin-based anode materials by focusing on structural designs.
- Preparations, structures, morphologies and cycle performance of tin-based anodes.
- Merits and disadvantages of tin-based anodes for lithium-ion battery applications.
- Future proposals and perspectives of tin-based lithium-ion battery development.

## A R T I C L E I N F O

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## A B S T R A C T

Tin (Sn) has long been considered to be a promising replacement anode material for graphite in next-generation lithium-ion batteries (LIBs), because of its attractive comprehensive advantages of high gravimetric/volumetric capacities, environmental benignity, low cost, high safety, etc. However, Sn-based anodes suffer from severe capacity fading resulting mainly from their large volume expansions/contractions during lithiation/delithiation and subsequent pulverization, coalescence, delamination from current collectors, and poor Li<sup>+</sup>/electron transport. To circumvent these issues, a number of extraordinary architectures from nanostructures to anchored, layered/sandwich, core-shell, porous and even integrated structures have been exquisitely constructed to enhance the cycling performance. To cater for the rapid development of Sn-based anodes, we summarize the advances made in structural design principles, fabrication methods, morphological features and battery performance with focus on material structures. In addition, we identify the associated challenges and problems presented by recently-developed anodes and offer suggestions and perspectives for facilitating their practical implementations in next-generation LIBs.

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## 1. Introduction

Lithium-ion batteries (LIBs) have been widely used in portable electronic devices, such as mobile phones, laptops and medical microelectronic devices, owing to their obvious advantages of superior energy densities (120–180 W h kg<sup>-1</sup>), low memory effects, long life cycle, low environmental impacts [1–5]. Electrode

materials are responsible for the transport of charges and storage of energy in LIBs, and thus are one of the most important components [6,7]. Accordingly, these materials are key to achieving high energy/power densities, high rate capacity, high Coulombic efficiency and cycling stability [8–13].

Graphite has been widely used in commercial LIBs since 1990. However, it is an unsuitable anode material for the next-generation LIBs required for electrical vehicles, smart electrical grid systems and wearable electronic devices [14–17], because of the safety concerns caused by its potential very close to that of Li metal, and its low gravimetric capacity of 372 mA h g<sup>-1</sup> and volumetric capacity of 850 mA h cm<sup>-3</sup> corresponding to a lithiation reaction to form LiC<sub>6</sub> [18–22].

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Novel anode materials of higher Li-storage capability and operational safety than graphite are therefore required for next-generation LIBs [23]. Li-alloy based materials, such as silicon (Si), tin (Sn) and germanium (Ge), have long been considered as alternatives, due to their higher specific capacities and lower operating potentials than graphite and the resulting higher energy/power densities [24–26]. Although Sn shows a lower gravimetric capacity of  $991 \text{ mA h g}^{-1}$  calculated from the formation of  $\text{Li}_{4.4}\text{Sn}$  ( $\text{Sn} + 4.4\text{Li}^+ + 4.4\text{e}^- \leftrightarrow \text{Li}_{4.4}\text{Sn}$ ) than Si ( $4200 \text{ mA h g}^{-1}$ ), it has a comparable volumetric capacity of  $2020 \text{ mA h cm}^{-3}$  vs. Si ( $2400 \text{ mA h cm}^{-3}$ ), which is attractive for high-capacity LIB applications [27–30]. Sn also exhibits a slightly higher discharge voltage (0–400 mV) than metallic Li that could reduce safety concerns associated with the carbon anode during cycling [31]. Additionally, Sn has an electrical resistivity of  $1.1 \times 10^{-7} \Omega \text{ m}$  at room temperature, which is nearly an order of magnitude lower than that of graphite. However, like other Li-alloy based elements (e.g., Si), pure Sn (particularly bulk Sn) is intrinsically prone to severe capacity deterioration and limited cycle life, primarily caused by its great volume changes of  $\sim 300\%$  during lithiation/delithiation, and subsequent pulverization, formation of solid electrolyte interphase (SEI), inhibition of  $\text{Li}^+$ /electron transport, and delamination from current collectors [16,32,33].

To address the problems associated with the Sn lithiation/delithiation, a large number of Sn-based compounds, such as  $\text{Cu}_6\text{Sn}_5$  and  $\text{SnO}_2$ , have been explored to improve the cycling stability albeit at the sacrifice of capacity [34–37]. Considerable efforts are furtherly made towards reducing the sizes to micro- or even nano-scaled level to alleviate the volume change and facilitate the  $\text{Li}^+$ /electron transport by increasing the surface area-to-volume ratios and decreasing the diffusion lengths (Scheme 1) [38–43]. Though the Sn-based nanomaterials exhibit improved cycling performance compared to their bulk counterparts, their practical applications in next-generation LIBs are still impeded by the ineluctable volume change, severe aggregation, intricate preparation, much SEI formation, low tap/packing density and areal/volumetric capacities, etc. [37,44,45] To overcome most of these new issues, the Sn-based nanomaterials are usually transformed into anchored, layered/sandwich, core-shell, porous or even integrated structures. Furthermore, they are assembled into large-sized (especially micrometer-sized) anodes for increasing the tap/packing density and energy/power densities. Likewise, direct fabrication of large-sized Sn-based anodes with the abovementioned structures without the two-step transition from nano-scale to macro-/micro-scale also provides a convenient means of improving the cycling stability and increasing the tap/packing density and gravimetric/areal/volumetric capacities. In short, whether preparing the nano-sized or macro-/micro-sized Sn-based materials, they must be endowed with the aforementioned structural/morphological

characteristics, which allow the relief of the volume expansion/contraction upon lithiation/delithiation, transfer of  $\text{Li}^+$ /electron and suppression of the SEI formation, thereby resulting in the enhanced cycling performance for potential LIB applications.

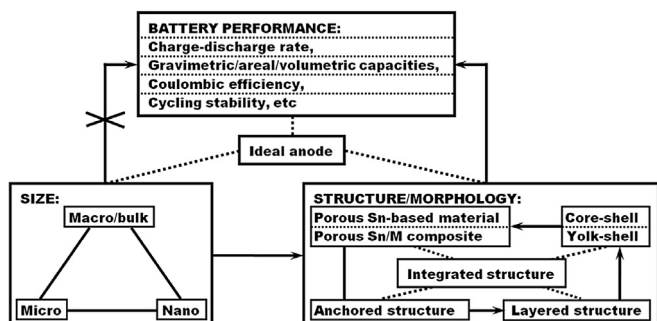
It would also be interesting to briefly review the developing history of Sn-based electrode materials in LIBs. Ever since the first commercialization of LIBs by Sony Corporation in 1991, a lot of efforts have been devoted to developing Sn-based electrodes with novel structures to replace the low-capacity graphite anodes for their practical implementations in commercial batteries. Fuji Film introduced a Sn composite oxide as carbon alternative in 1997, however, it was not successful because of the poor cycling performance [46]. In 2005, Sony Corporation announced a new-generation 14430-sized LIB (14 mm in diameter by 43 mm tall) with the trade name of Nexelion for use as a four-cell battery pack in Handycam camcorder products [47–49]. The anode material of the Nexelion LIBs is composed of a Sn–Co–C composite, which is mainly amorphous or microcrystalline aggregates [50]. According to Sony, the 14430 Nexelion cell has several advantages over the conventional 14430 cells: (1) 30% increase in capacity (910 mA h vs. 700 mA h), (2) 20% increase in power (3.15 W h vs. 2.60 W h) at 0.2 C rate, (3) 20% increase in volumetric energy density ( $478 \text{ W h L}^{-1}$  vs.  $395 \text{ W h L}^{-1}$ ), (4) 10% increase in gravimetric energy density ( $158 \text{ W h kg}^{-1}$  vs.  $144 \text{ W h kg}^{-1}$ ), (5) 20% increase in charge efficiency at room temperature, and (6) 40% increase in discharge capacity at  $-20^\circ \text{C}$  [51]. In 2011, Sony Corporation realized the Nexelion LIBs with the 18650 size for use in notebook computers by optimizing the structure of the amorphous Sn–Co–C anodes to prevent the deformation caused by the Sn volume change during lithiation/delithiation [52–54]. The capacity of the 18650 Nexelion cell was enhanced to 3.5 A h by increasing charging final voltage to 4.3 V and discharging final voltage to 2.0 V. The battery with a total weight of 53.5 g exhibited high gravimetric and volumetric energy densities of  $226 \text{ W h kg}^{-1}$  and  $723 \text{ W h L}^{-1}$ , respectively. These inspiring progress has further rekindled another wave of interest in Sn-based anode materials for LIB applications [50].

Based on the abovementioned discussions, we would like to highlight the critical importance of controlling material structure when designing state-of-the-art Sn-based anodes, and outline the up-to-date progress in Sn-based electrode materials for their promising implementations in next-generation LIBs. This review article stands in sharp contrast to previous review papers on the similar topic, in which Sn-based anode materials are simply classified into nanomaterials and their composites with other components without articulately manifesting the essential anode construction principles [36,37,41,42,55]. It is hoped the readers will clearly understand how to develop Sn-based electrode materials from the new perspective. The structural design principles, fabrication methods, morphological features, and cycling performance of a few typical Sn-based anode materials are also reviewed to enable better maturing of the practical applications of Sn-based anodes in next-generation LIBs.

## 2. Tin-based compounds

### 2.1. Intermetallic compounds

Many Sn-based two-component and multi-component intermetallics, such as Sn–Cu, Sn–Ni, Sn–Fe, Sn–Zn, Sn–Co, Sn–Mn, Sn–Sb, Sn–Bi, Sn–Ti, Sn–Se, Sn–Ge, Sn–Sb–Ag, Sn–Fe–Ag, Sn–Ti–Sb and Sn–Sb–Co, have been examined as potential anode materials [35,54,56–68]. Most display better long-term cycling stabilities than metallic Sn, but poorer Li storage capability [35,56–65].



**Scheme 1.** Schematic presentation of a structural/morphological evolution of Sn-based anode materials for next-generation LIBs.

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