

Progress on Sn-based thin-film anode materials for lithium-ion batteries

HU RenZong, LIU Hui, ZENG MeiQin, LIU JiangWen & ZHU Min*

School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China

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Thin-film lithium-ion batteries are the most competitive power sources for various kinds of micro-electro-mechanical systems and have been extensively researched. The present paper reviews the recent progress on Sn-based thin-film anode materials, with particular emphasis on the preparation and performances of pure Sn, Sn-based alloy, and Sn-based oxide thin films. From this survey, several conclusions can be drawn concerning the properties of Sn-based thin-film anodes. Pure Sn thin films deliver high reversible capacity but very poor cyclability due to the huge volume changes that accompany lithium insertion/extraction. The cycle performance of Sn-based intermetallic thin films can be enhanced at the expense of their capacities by alloying with inactive transition metals. In contrast to anodes in which Sn is alloyed with inactive transition metals, Sn-based nanocomposite films deliver high capacity with enhanced cycle performance through the incorporation of active elements. In comparison with pure Sn anodes, Sn-based oxide thin films show greatly enhanced cyclability due to the *in situ* formation of Sn nanodispersoids in an Li_2O matrix, although there is quite a large initial irreversible capacity loss. For all of these anodes, substantial improvements have been achieved by micro-nanostructure tuning of the active materials. Based on the progress that has already been made on the relationship between the properties and microstructures of Sn-based thin-film anodes, it is believed that manipulating the multi-phase and multi-scale structures offers an important means of further improving the capacity and cyclability of Sn-based alloy thin-film anodes.

lithium-ion batteries, thin film, negative electrode, Sn-based alloys, Sn-based oxides

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Lithium-ion batteries are widely used nowadays as important power sources for portable electronic devices and electric or hybrid vehicle (EV/HEV) applications due to their high energy density, high voltage, and long lifespan. At present, large-scale and miniaturization are the two most important development directions for high-performance lithium-ion batteries. With respect to miniaturization, the major task is developing thin-film/micro-batteries that might be applied in micro-electro-mechanical systems (MEMS), smart cards, implantable medical devices, and so on. As for conventional batteries, high specific capacity of electrode materials is an essential requirement for thin-film batteries [1]. Moreover, ultra-thin form, good flexibility, and high energy density are the most important properties of thin-

film Li-ion batteries, which depend on the cathodes, anodes, electrolyte, and current collectors that comprise the thin-film structure [2].

In early work, lithium metal films were widely studied as anodes for thin-film Li-ion batteries. However, lithium metal is very flammable and air- and water-sensitive. Moreover, minute lithium dendrites could form on the anodes when such lithium batteries were rapidly charged, and these in turn could induce short circuits, causing the battery to rapidly overheat and catch fire. This hazard limited the application of lithium-film anodes in batteries. On the other hand, graphite, which had been used as an anode material for commercial Li-ion batteries, could not satisfy the requirements of higher storage capacity/energy density for thin-film Li-ion batteries due to its insufficient theoretical capacity of 372 mAh g^{-1} [3]. Thus, there was a strong demand

*Corresponding author (email: memzhu@scut.edu.cn)

for the development of new metallic based thin-film anode materials with higher energy density to replace graphite anodes.

Lithium is able to form well-defined intermetallic phases (Li_xM) with numerous metals M (M=Sn, Mg, Al, Sb, Ge, Si, etc.) at room temperature, which offer much higher lithium-storage capacities than lithiated graphite (LiC_6). However, alloying of such large amounts of lithium with these metals to form intermetallic phases is associated with huge volume changes. For example, the volume expansion associated with the transformation $\text{Sn} \rightarrow \text{Li}_{22}\text{Sn}_5$ is more than 250%. The large volume changes accompanying lithium insertion and extraction often lead to pulverization of the active alloy particles and therefore result in poor cycle stability, which has been the main challenge for the implementation of alloy anodes. Nevertheless, numerous studies have shown that the structural stability of lithium alloys may be significantly improved if intermetallic and/or composite hosts are employed in place of pure metals, which have led to greatly enhanced cycling performance in metallic based anodes [4]. Moreover, microstructure design and morphology regulation has also proved to be an effective way to overcome the volume change issue of such electrodes [5]. Thus, recent studies on thin-film anodes for Li-ion batteries have been largely concerned with the quest for new types of high-capacity materials, modification of the currently available materials, and microstructure design for thin films. Among the studied materials, Sn-based alloys and their oxides have attracted considerable interest because of their high theoretical specific capacities. In particular, in recent years, the fabrication of various Sn-based alloy and oxide thin-film anodes, by different methods, as well as studies of their applications in micro-batteries, has become a hot topic and great progress has been achieved. In this

paper, we review the research advances concerning Sn-based alloy and Sn-based oxide composite thin-film anodes made in the last decade.

1 Properties of Li-Sn alloys

Sn-based materials have been among the most important alternative anode materials for Li-ion batteries, and have been widely studied because of the high specific capacity of Sn. β -Sn has a tetragonal structure (space group: $I4_1/amd$, no. 141), with lattice constants of $a=0.5831$ nm and $c=0.3182$ nm. It has been proved both by *ab initio* calculations and experimentally that, at operating potentials in the range 1.0–0.3 V vs. Li/Li^+ , Sn reacts electrochemically with lithium to form different Li-rich alloy phases, such as Li_7Sn_2 , Li_7Sn_3 , $\text{Li}_{13}\text{Sn}_5$, and $\text{Li}_{22}\text{Sn}_5$ [6]. Figure 1 shows the theoretical formation potentials, specific capacities, and volume changes of Li_xSn phases ($0 \leq x \leq 4.4$). It can be seen that lithium storage in Sn by the formation of various Li_xSn phases is accompanied by large volume changes. This is very different from the intercalation compounds of graphite, which show small volume changes of less than 10%. The theoretical specific capacity of Sn is 994 mAh g^{-1} (vs. $\text{Li}_{22}\text{Sn}_5$), and its packing density is 75.46 mol/L , which is close to that of lithium metal (76.36 mol/L). Thus, the specific volume capacity of an Sn anode amounts to 7262 mAh cm^{-3} , which is almost nine times higher than that of graphite. Taking into account both the specific capacity and the volume capacity, Sn-based materials can meet the requirements for high-capacity anode materials for lithium-ion batteries, which is very important in relation to thin-film electrodes of limited thickness.

With respect to the high capacity of Sn-based materials, there are two other striking features. Firstly, the lithiation

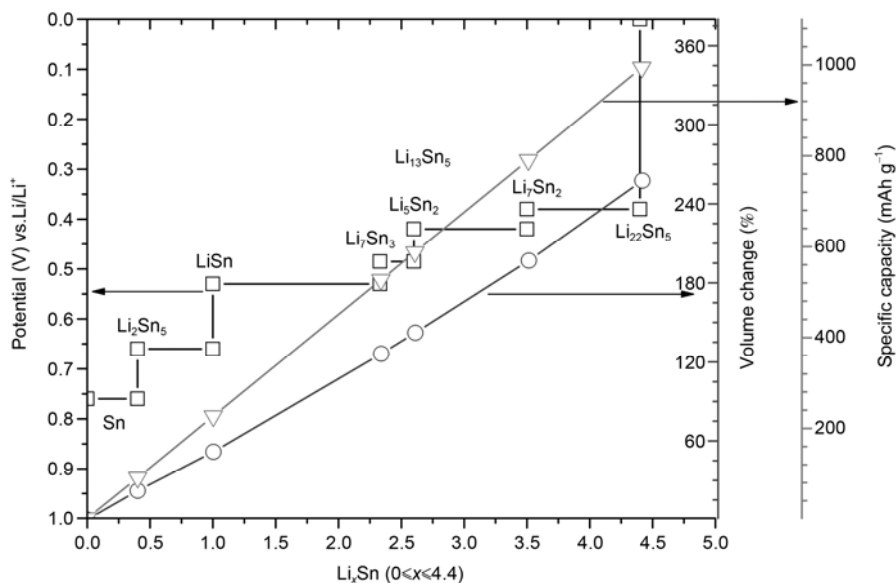


Figure 1 The theoretical formation potentials, specific capacities, and volume changes of Li_xSn phases.

potential of Sn in the range 0.8–0.3 V vs. Li/Li⁺, which is much higher than the deposition potential of lithium. Consequently, dendrite issues due to lithium deposition on the surface of electrodes, which often arise on carbon materials during rapid charging, will be absent. Secondly, there is no co-intercalation of solvents in Sn-based anode materials, allowing a wide choice of solvents for electrolytes. These advantages have prompted many extensive studies of Sn-based thin-film anodes.

2 Pure Sn thin-film anodes and their interface properties

In the following sections, we first summarize the research progress that has been made on the preparation and electrochemical performances of pure Sn thin-film anodes. Morimoto et al. [7] prepared an Sn thin-film anode with a rough surface on a Cu foil substrate by an electroplating technique. This Sn thin-film anode had a high initial discharge capacity of 860 mAh g⁻¹ but a poor cyclability, as indicated by a reversible capacity of only 200 mAh g⁻¹ after 20 cycles. Moreover, a relatively large initial irreversible capacity loss, amounting to about 23% of the total capacity, was incurred in pure Sn thin-film anodes prepared by electroplating. In order to understand the origin of this large irreversible capacity on the electroplated Sn-film anodes, the morphology changes of the Sn-film surface during lithiation and delithiation were investigated by *in situ* AFM [8]. It was revealed that surface roughening by lithium insertion and extraction occurred to a significant extent in the first and second cycles. This surface roughening destroyed the existing surface film and exposed a large area of active surface, and therefore was the reason for the appearance of large irreversible capacities in the initial discharge-charge cycles. Also with the aid of *in situ* AFM observations, Beaulieu et al. [9] confirmed that, for sputtered crystalline Sn thin-film anodes, decomposition of the surface film and consumption of the electrolyte resulted from pulverization of the electrode due to inhomogeneous volume expansion of Sn, and that this was a key factor for the poor cycle performance of the electrodes. The above results indicated that the interface properties of electrodes have a great impact on the capacity loss of Sn thin-film anodes.

The interface properties of electrodes in Li-ion batteries are associated with the formation processes and features of solid electrolyte interphase (SEI) films at the electrode/electrolyte interfaces. The formation of SEI films is mainly dependent on the properties and surface morphology of the electrode materials, the components of the electrolyte, and the operating conditions of the battery. The salient properties of SEI films include their stability, impedance, Li⁺-diffusion kinetics, and ability to prevent decomposition of the electrolyte. These features determine the lithiation/delithiation dynamics, the stability of the electrode/electrolyte interfaces,

and the cyclability and self-discharge of a battery. It was initially assumed that SEI films were only formed on graphite materials. However, it was subsequently found that SEI films are common in Sn-based anode materials, and that they have a great influence on the performances of electrodes. By means of impedance spectroscopy, Hassoun et al. [10] investigated the characteristics of an SEI film formed on the surface of an electrodeposited Sn film anode when cycled in a lithium cell. It was shown that the SEI film was formed by electrolyte decomposition catalyzed by the Sn surface, and that its characteristics depended upon the cycling rate. When the cycling rate was high, there was limited SEI film formation on the surface of the Sn film, which resulted in a high reversible capacity. For complete Li-ion batteries employing Sn-film anodes coupled with LiNi_{0.5}Mn_{1.5}O₄ cathodes, it was confirmed that the formation and decomposition of SEI layers on the Sn-film anodes did indeed influence the responses of the batteries, including their cyclability and rate capability. In order to further investigate the characteristics and functions of SEI films on Sn-film anodes, Chiu et al. [11] prepared an amorphous Sn thin-film anode, composed of nano-sized Sn particles (5–10 nm), by radio frequency (r. f.) magnetron sputtering. It was found that a relatively thick SEI film formed on the surface of the electrode upon cycling in the range 2.5–0.05 V vs. Li/Li⁺, which was effective in suppressing the pulverization of Sn particles. However, formation of the SEI film was prevented when the surface of the Sn film anode was covered by a smooth SnO₂ layer, which also enhanced the cycle performance of the amorphous Sn thin-film anode. These results suggested that the two cases, that is, with a thick SEI film and without SEI formation, would help to improve the cycle performance of Sn-film anodes. Ui et al. [12] found that an Sn-film anode prepared by pulse electrodeposition, with an average crystal size of ca. 1 μm, displayed a good initial cycling performance. Its initial coulombic efficiency reached 93.0%, indicating that the irreversible capacity attributable to SEI formation and/or the decomposition of oxides on the surface was limited. This was because the Sn crystals in this film were relatively large and thus reduced the electrode/electrolyte contact interfaces. Nevertheless, the capacity of this Sn-film anode decayed significantly after 10 discharge-charge cycles.

Pure Sn thin-film anodes have generally been prepared by electrodeposition [7,8,10,12–18], magnetron sputtering [9,11,19–21], electron-beam deposition (EBD) [22], or vacuum evaporation [23]. Figure 2 shows the initial discharge capacities of pure Sn thin-film anodes prepared by different methods. It can be seen that these initial discharge capacities are higher than the capacity limit of the graphite anode, but lower than the theoretical capacity of Sn. This may be ascribed to the microstructure and Li⁺-diffusion kinetics in the pure Sn-film anodes. Moreover, it can be seen from Figure 1 that the volume change of Sn during Li insertion is very large. Thus, even though pure Sn thin-film anodes

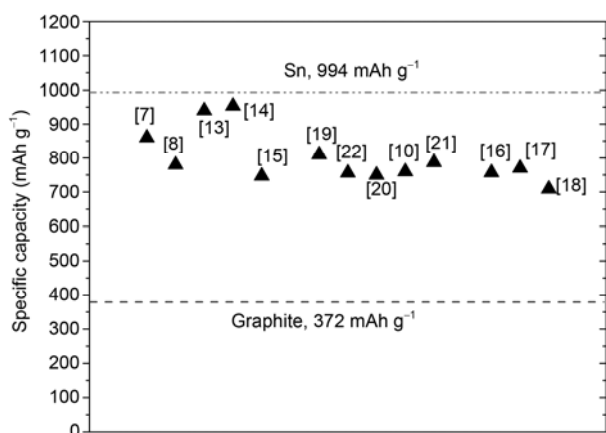


Figure 2 The initial discharge capacities of pure Sn thin-film anodes prepared by different methods.

obtained by different fabrication methods possess different microstructures, such as micro-sized crystal, nano-sized crystal, amorphous, porous, and multi-layered structure, none of these could effectively relieve the volume expansion of the pure Sn-film anodes. Thus, pulverization of the active Sn materials was unavoidable during discharge-charge cycling, which resulted in pulverized Sn fragments becoming electrically isolated from the current collectors and consequent capacity loss.

3 Sn-based alloy film anodes and their enhanced cycle performances

In order to overcome the above-described problems of capacity decay of pure Sn-film anodes, researchers turned their attention to Sn-M intermetallic compounds and/or composites, where M is an active or inactive (unreactive towards Li) component/phase. M may be a metal, alloy, oxide, and/or ceramic, which serves as a matrix buffering the volume change of the active Sn phase during lithium insertion/extraction, leading to less cracking in the Sn-M anodes and hence enhanced cyclability. Guided by this basic idea, various kinds of Sn-M alloy film anodes, composed of Sn and other active/inactive elements, have been widely researched and great progress has been achieved.

3.1 Sn-Cu thin-film anodes

Among Sn-based alloy film anodes, Sn-Cu alloy films prepared by electrodeposition have been the most frequently reported anodes. This is because Sn-Cu alloys had been previously studied and were widely regarded as alternative anode materials to graphite in Li-ion batteries. Beattie et al. [24] prepared Sn-Cu alloy films with varying Cu-Sn stoichiometries by single-bath, pulsed electrodeposition. It was found that, as the Cu content in the film was increased, specific capacity was sacrificed in favor of capacity retention.

For example, a film with a Cu-Sn atomic ratio of 3.83 yielded a specific capacity near 200 mAh g⁻¹ between 0 and 1.6 V, and retained 80% capacity after 40 cycles. Pu et al. [15] prepared a Cu/Sn/Cu multilayer film anode by initial pulsed electrochemical deposition of Sn on a Cu foil substrate, and then plating the surface of the deposited Sn with a protective Cu layer. The Cu and Sn in the multilayer film were partially alloyed to form Cu₆Sn₅ and Cu₃Sn after annealing. In this case, the annealed Cu/Sn/Cu multilayer film anode was not cracked after 50 cycles, and it displayed an initial coulomb efficiency reaching 95% and good cyclability. These results were similar to those reported by Morimoto et al. [7] and Tamura et al. [13].

The authors' research group prepared an Sn/Cu thin film of thickness about 1 μm by means of EBD. The as-prepared Sn/Cu thin-film anode showed a high initial discharge capacity and a high coulombic efficiency but poor cyclability [22]. Annealing of this Sn/Cu thin film at 200°C in vacuo yielded a Cu₃Sn/Cu₆Sn₅ composite structure, which exhibited an obvious enhancement in its cycle performance. However, due to a large irreversible capacity loss associated with increased surface roughness of the annealed electrode, the Cu₃Sn/Cu₆Sn₅ thin-film anode displayed a small reversible capacity. Therefore, an Sn/Cu₆Sn₅ composite thin film was directly prepared on a Cu foil substrate by EBD [25], which had a structure, as shown in the SEM image in Figure 3(a), of polyhedral microsized Sn particles (labeled as 1) uniformly dispersed in the Cu₆Sn₅ matrix (labeled as 2). As indicated by TEM observation, the microsized Sn particles (2–5 μm) were single crystals, while the Cu₆Sn₅ matrix was nanocrystalline, as confirmed by their corresponding SAED patterns in Figure 3(b). Further, an HRTEM image (Figure 3(c)), which was taken from the area encircled by a solid line in zone A in Figure 3(b), revealed that there was a nanocrystalline Cu₆Sn₅ layer of thickness 30 nm covering the surface of these microsized Sn particles. This unique Sn/Cu₆Sn₅ composite thin-film anode showed a higher Li⁺-diffusion rate and discharge capacity, as well as better cyclability, than those of the above Cu₃Sn/Cu₆Sn₅ thin-film anode. A reversible capacity of more than 370 mAh g⁻¹ was maintained for up to 70 cycles when the lithiation of this Sn/Cu₆Sn₅ composite film anode was performed in the potential window 0.1–1.25 V, which may be attributed to the nanostructure of the Cu₆Sn₅ matrix and the different lithiation potentials of the Sn and Cu₆Sn₅ phases. This demonstrated that a multi-phase composite structure could improve the electrochemical performance of Sn-Cu alloy film anodes.

In order to further enhance the rapid transport of lithium ions in Cu₆Sn₅ alloy thin-film anodes, a Cu₆Sn₅ alloy film with a three-dimensional (3D) foam structure was fabricated by an electrochemical deposition process [26]. This 3D Cu₆Sn₅ film anode delivered a reversible capacity of about 400 mAh g⁻¹ for up to 30 cycles between 0 and 1.5 V at a current rate of 0.5 mA cm⁻² (1 C). Furthermore, this anode

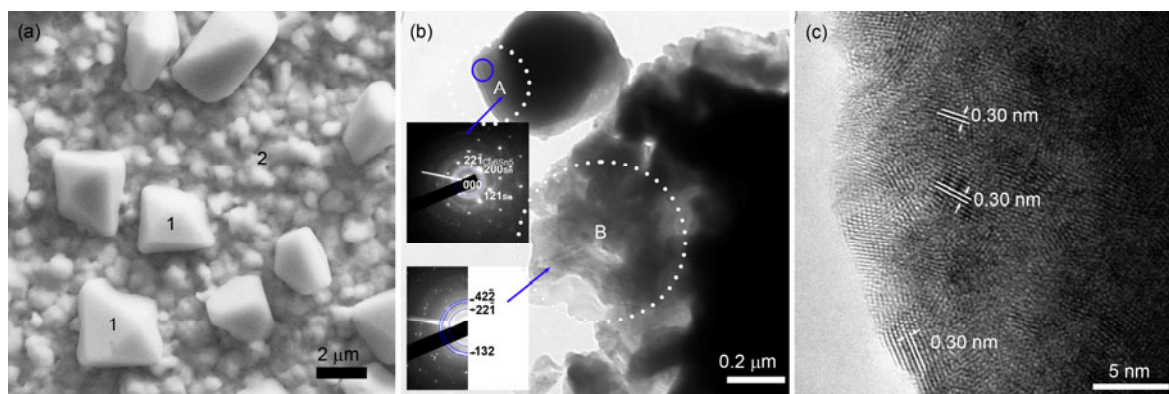


Figure 3 (a) SEM image of an Sn/Cu₆Sn₅ composite thin film; (b) TEM image; (c) HRTEM image of the area encircled by the solid line in zone A shown in (b).

exhibited superior rate capability, which may be attributed primarily to its unique porous structure and the large surface area for rapid mass transport and rapid surface reactions. For instance, the obtainable capacity (220 mAh g^{-1}) at 20 C rate was more than 50% of the capacity at 1 C rate. Using the electrodeposition process in conjunction with porous Cu foam or porous composite membrane templates, Zhang [27,28], He [29], and Huang et al. [30] prepared various 3D porous Sn-Cu alloy film anodes, which also displayed greatly enhanced cycle performances and high-rate capabilities.

Figure 4 shows a comparison of the discharge capacities and cyclabilities of Sn-Cu alloy thin-film anodes with different microstructures prepared by different methods, which indicates that the cycle performances of these Sn-Cu alloy thin-film anodes were much better than that of a pure Sn thin-film anode. This may be attributed to the good reversibility and cycling stability of the lithiation/delithiation reactions of the Cu₆Sn₅ phase in electrodes. However, their sta-

ble reversible capacities were much lower than the theoretical capacity of Sn and Cu₆Sn₅ phases, which obviously indicates that the specific capacities were sacrificed for the enhanced capacity retention.

In addition to the Sn-Cu alloy system, other binary alloy film anodes, composed of Sn and other inactive transition metals, such as Ni, Co, and Mo, have also been widely studied and are reviewed in the following subsections.

3.2 Sn-Ni thin-film anodes

Lee et al. [32] reported that crystalline Ni₃Sn₄ showed a low affinity for lithium. However, in the case of nanocrystalline Ni₃Sn₄, lithium atoms reversibly reacted with Sn atoms at the grain boundaries, and no capacity fading was observed after prolonged cycling. Moreover, Han et al. [33] found that micro-nanostructured Ni was also electrochemically active with lithium, forming Li-Ni alloy phases. The resulting

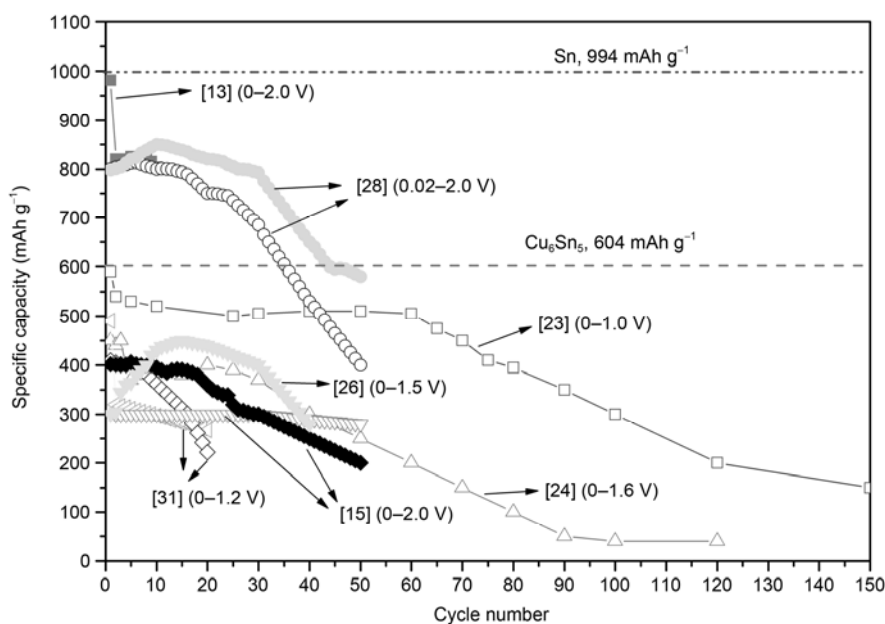


Figure 4 Reversible capacities of some selected Sn-Cu alloy film anodes versus cycle number.

nanostructured Sn-Ni alloy thin films also possessed acceptable capacities and excellent cyclability and have therefore attracted the attention of researchers. Lee et al. [34] prepared nanostructured Ni_3Sn_2 thin films on a Cu foil substrate by EBD at room temperature. These Ni_3Sn_2 film anodes exhibited excellent cycle performance over 500 cycles, and did not undergo any crystallographic phase change during cycling. Osaka et al. [35] prepared Sn-Ni alloy films with different compositions by electrodeposition. It was found that an $\text{Sn}_{62}\text{Ni}_{38}$ thin film was mainly composed of an Ni_3Sn_4 nanophase, which was identified as the key phase for high capacity and long cycle life. Thus, an $\text{Sn}_{62}\text{Ni}_{38}$ thin-film anode maintained a capacity of 650 mAh g^{-1} after 70 cycles between 0.01 and 1.2 V. In contrast, $\text{Sn}_{54}\text{Ni}_{46}$, in which only an SnNi metastable phase was identified, showed only low capacity [36]. Crosnier et al. [37] also prepared Sn-Ni thin-film anodes by electrodeposition at different current densities. In a thin film deposited at a high current density (20 A cm^{-2}), the active materials had a multi-phase composition with a small particle size (less than $1 \mu\text{m}$) and high porosity, giving rise to a high reversible capacity and favorable cycle performance. In contrast, however, a thin film deposited at a low current density (0.1 A cm^{-2}) was composed only of an Ni_3Sn_2 phase with a large particle size (about $5 \mu\text{m}$) and high density, and showed low reversible capacity. On this basis, it was surmised that the enhanced cycle performance of the Sn-Ni thin film deposited at high current density may be attributed to the smaller particle size, greater porosity, and multi-phase characteristics of the active materials in the film. Zhang et al. [38] found that there were different morphologies in Sn-Ni films electrodeposited at different temperatures, but that all of the thin films were composed of an Sn_3Ni_4 phase and an Ni_xSn_y metastable phase. However, their electrochemical performances were distinctly different. For instance, an Ni-Sn thin-film anode deposited at room temperature had a compact, cauliflower-like morphology consisting of pillars formed by aggregates of small grains, and its reversible capacity was more than 650 mA h g^{-1} during initial cycles, although significant fading occurred after 30 cycles. After the Ni-Sn was heated at 200°C , the film anodes displayed a much better cycle performance, with a specific capacity of 314 mAh g^{-1} after 100 cycles, which was obviously superior to those of the electrodeposited Ni_xSn_y thin-film anodes prepared by Hassoun et al. [39]. This high capacity retention may have been due to the formation of a smooth and compact surface during the heat-treatment process.

3.3 Sn-Co thin-film anodes

Sn-Co alloy films have also attracted widespread interest. By electro-co-deposition, Tamura et al. [40,41] fabricated several Sn-Co thin-film anodes with different microstructures, such as micro-column, micro-island, nano-crystalline, and amorphous, and studied their structures and electro-

chemical properties. It was found that different cycle performances were obtained due to the different microstructures in the Sn-Co thin films, and in particular the nano-crystalline thin film displayed the best anode performance.

For the Sn-Co alloy system, in addition to the composition and microstructure of thin films, the mechanical properties of the active materials has also been identified as a key factor affecting the cycle performance of thin-film electrodes. A macroporous Sn-Co alloy film anode could deliver a reversible capacity as high as 610 mAh g^{-1} up to the 75th cycle [42]. This was because the macroporous structure of the film imparted favorable mechanical stability that could overcome the volume expansion during lithium-insertion reactions. It was also found that an Sn-Co alloy film anode electrodeposited on a porous Cu substrate possessed a relatively large capacity and a superior cyclability to that of an Sn-Co alloy anode on a smooth Cu foil [43]. These results indicated that a 3D porous structure could adequately buffer the volume change of the active materials in films during charge-discharge cycling processes, preventing cracking and pulverization of the active materials, which therefore improved the cycle performance of the Sn-Co film anodes [44].

Bonakdarpour et al. [45] firstly investigated the viability of employing $\text{Mo}_{1-x}\text{Sn}_x$ thin films as lithium-ion anodes, which were prepared by combinatorial sputter-deposition. *In situ* X-ray diffraction analysis of $\text{Li}/\text{Mo}_{1-x}\text{Sn}_x$ cells with $x < 0.36$ showed no evidence for the formation of new phases during charge-discharge over 75 cycles. However, in films with a higher Sn content of $x > 0.4$, aggregation of Sn clusters and the formation of an Li-Sn phase were apparent after the first cycle. Surprisingly, it was found that the inclusion of a small amount of oxygen in the nanostructured Mo-Sn films seemed to prevent Sn aggregation and improved the cycling performance markedly.

Sn can easily react with transition metals (Cu, Ni, Co, etc.) to form various Sn_xM_y intermetallic compounds. However, in some of these intermetallic phases, such as Cu_3Sn , Ni_3Sn_4 , and Co_3Sn_2 , the binding energy of Sn-M is higher than that of Li-Sn, and as a consequence some of these Sn_xM_y intermetallic phases have a relatively low affinity for lithium, or are even inactive towards lithium. Hence, the reversible capacity will decrease if the amounts of these inactive intermetallic phases in film anodes are increased. Many studies have demonstrated that the phase composition of the Sn-Ni and Sn-Co alloy films is highly dependent on the components and preparation conditions of the film, and that these in turn influence the capacities and cycle performances. Based on a comprehensive literature survey, we conclude that Sn-Cu alloy films possess high reversible capacity but poor capacity retention, while Sn-Ni alloy films have relatively good cycle performance but low specific capacity. Sn-Co films show a good balance between cycling stability and capacity, and are thus expected to offer a promising alternative for high-performance anodes.

3.4 Sn-M (active element) thin-film anodes

The above-mentioned Sn-based alloy films all contained inactive metallic elements and/or intermetallic phases, which inevitably lowered the specific capacities of electrodes. However, by combining Sn with other active elements, such as Si, C, or Al, to form active compounds and/or composites in film anodes, this specific capacity loss could be reduced and/or avoided. Consequently, film anodes consisting of Sn and an active element have been intensively investigated recently.

(1) Sn-Si thin-film anodes. Beaulieu et al. [46] prepared amorphous $\text{Si}_{1-x}\text{Sn}_x$ ($0 < x < 0.5$) alloy thin films by magnetron sputtering. Among them, an $\text{Si}_{0.66}\text{Sn}_{0.34}$ thin film, which possessed a short-range ordered diamond structure, showed better conductivity, higher capacity, and superior cyclability than pure Sn or pure Si thin-film anodes. The enhanced cycle performance of this thin film could be mainly attributed to the absence of the two-phase reaction and therefore a uniform volume expansion of the amorphous Sn-Si thin film [47]. However, there was obvious charge-discharge hysteresis in the voltage-capacity profile, which was caused by the energy dissipated during the changes in the local atomic environment around the host atoms [48]. Hatchard et al. [49] examined the cycle performances and capacities of $\text{Si}_{1-x-y}\text{Al}_x\text{Sn}_y$ thin-film anodes with different compositions and structures, which were also prepared by combinatorial sputter-deposition as described by Bonakdarpour et al. [45]. It was found that, in comparison with a crystalline thin film, the amorphous Si-Al-Sn thin film had much better cycle stability and relatively lower initial irreversible capacity loss, which was less than 20% of the initial discharge capacity. Furthermore, a change in the Al content in the amorphous thin film did not have any influence on the cyclability, specific capacity, or irreversible capacity loss of the anodes. However, the amorphous-to-crystalline structure

transformation in the film resulted in obvious capacity fading during charge-discharge cycling.

The impact of the addition of rare earth elements (cerium and lanthanum-rich *misch* metal, MM) to $\text{Si}_{1-x}\text{Sn}_x$ thin-film anodes was also reported by Dahn et al. [50], and the results indicated that amorphous thin films containing 20 at%–40 at% Sn and 15 at%–20 at% MM exhibited excellent capacity retention and reversible specific capacities of about 800 mAh g^{-1} .

(2) Sn-C thin-film anodes. Li et al. [51] prepared Sn-C composite thin films (C: 0, 3.2, 6.0, 11.8 wt%) by magnetron sputtering. It was found that the capacity loss of tin could be significantly reduced by the incorporation of graphite, but its discharge capacity decreased with increasing graphite content. An Sn-6.0 wt% C thin film had a high initial discharge capacity of 750 mAh g^{-1} ; however, more than 15% of the total capacity was lost after 10 discharge-charge cycles. In contrast, an Sn/C nanocomposite thin film prepared by microwave plasma chemical vapor deposition displayed much better anode performance [52]. TEM observation confirmed that this Sn/C thin film had a unique structure of thin layers of graphitic carbon decorated with uniformly distributed Sn nanoparticles, which produced reversible capacities of 423 and 297 mAh g^{-1} at C/25 (ca. 17 mA g^{-1}) and 5°C rates between 0 and 1.1 V, respectively. During long-term cycling of the anodes, 60% of the total capacity was retained after 500 cycles at 1 C rate, which could be mainly attributed to the high porosity of the film and the fine dispersion of Sn nanoparticles embedded in the three-dimensional graphitic matrix.

An Sn-C-Ni composite thin-film anode was prepared by EBD using TiNi alloy as a reaction medium [53]. As indicated by the TEM image and schematic shown in Figure 5, this thin film had a multi-scale structure composed of many micro-sized core/shell particles, in which the cores were Sn

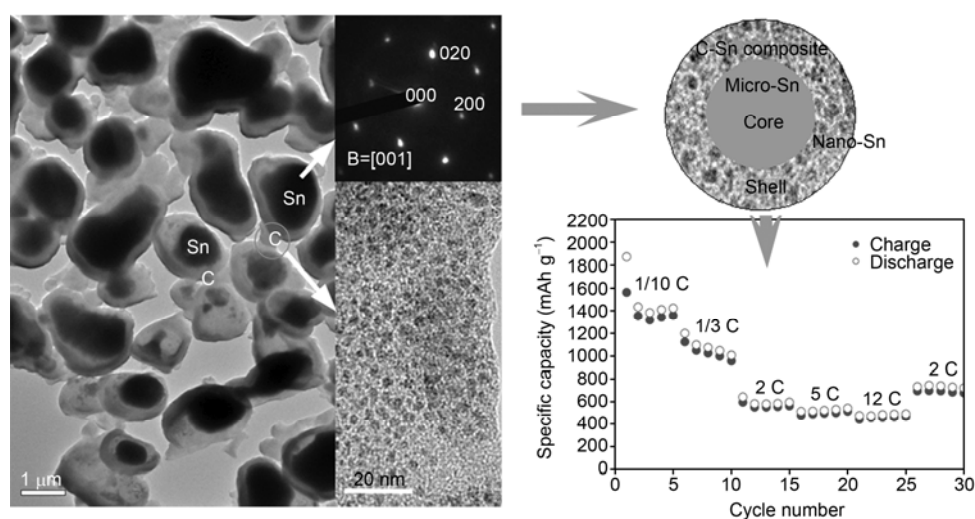


Figure 5 Multi-scale core/shell structure and C-rate performance of an Sn-C-Ni composite thin film prepared by electron beam deposition [53]. Reproduced by permission of The Royal Society of Chemistry (RSC).

single crystals and the shells were amorphous sp^2 carbon containing dispersed nano-sized Sn and Ni particles. Both the Sn and the amorphous carbonaceous shells reacted with lithium and made substantial contributions to the high total initial capacities of 1872 mAh g^{-1} at $1/10 \text{ C}$ (ca. $10 \mu\text{A cm}^{-2}$) and 472 mAh g^{-1} at 12 C between 0.01 and 1.5 V. The stable discharge capacity at 1 C was more than 600 mAh g^{-1} after 40 cycles. These good performances could be attributed to the enhanced Li^+ -diffusion kinetics and structural stability of the active materials, which resulted from the multi-scale structure of the Sn phases and the good coating of the nanocomposite carbonaceous shells on the Sn cores as well as the dispersion of nanosized Sn and Ni particles in the amorphous carbon matrix.

(3) Sn-Al thin-film anodes. In order to overcome the shortcomings of Sn-based intermetallic anode materials, immiscible Sn-Al alloys, in which the Al can also deliver a theoretical capacity of 990 mAh g^{-1} , have also been explored as lithium-ion anode materials [54]. Sn-Al thin films prepared by EBD have complex structures of Sn phases homogeneously dispersed in the Al matrix, in which the Sn phases act as diffusion channels to enhance the Li^+ -diffusion kinetics. Thus, the cycle performance of Sn-Al thin-film anodes is much better than those of pure Sn or pure Al thin-film anodes [55]. It has been found that the composition of Sn-Al thin-film anodes obviously influences their capacities and cycle performances (Figure 6). Thus, Al- x wt% Sn ($40 \leq x \leq 60$) thin-film electrodes showed a good balance between cycling ability, fast Li^+ diffusion, and acceptable capacity. In particular, an Al-40 wt% Sn thin-film anode had a unique multi-scale composite structure with faceted large single-crystalline Sn particles and Sn nanocrystallites dispersed in the Al matrix (Figure 7), and its stable reversible capacity was about 600 mAh g^{-1} [56]. However, it was found that the capacity and cycle performance of these Sn-Al thin-film anodes was difficult to improve further due to the slow diffusion of lithium ions in the Al matrix. Thus, the microstructures of the Sn-Al thin-film anodes need more optimal design to greatly facilitate the transport of lithium within them.

Based on the above-mentioned research, it is evident that Sn-based alloy thin-film anodes with crystalline structure, especially a nanocrystalline multi-phase composite structure, can attain good cycle performance. This may be attributed to effective reduction of the absolute volume change, and hence less induced stress, when utilizing nanocrystalline particles, which therefore helps maintain the structural integrity of the thin-film electrode during cycling. Moreover, nanostructured materials can provide short path lengths for both lithium ion and electron transport. Thus, Sn-based alloy thin-film anodes with various nanostructures, prepared with the assistance of nano-template membranes, have received much attention recently [57,58]. However, these processes often involve several time-consuming steps to pre-fabricate the nano-template on the Cu current collector and produce only limited amounts of materials. In contrast, nanostructured Sn-based oxide thin films are more readily obtainable, allowing for greater diversification of the nanostructures of the active materials in the oxide thin films.

4 Sn-based oxide thin-film anodes

Since the 1990s, lithium-ion battery anodes derived from

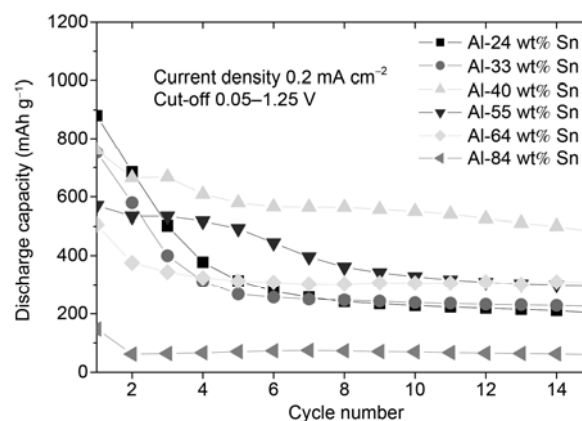


Figure 6 The cycle performances of Al-Sn thin films with different compositions.

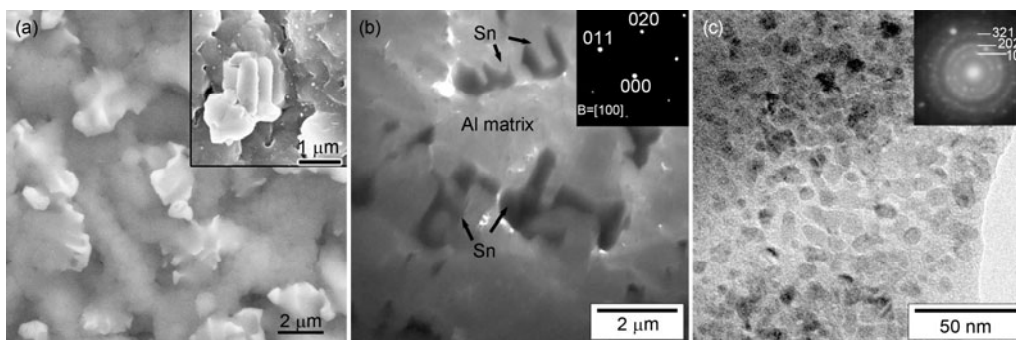


Figure 7 (a) SEM image of an Al-40 wt.% Sn thin film; (b) TEM image; (c) high-resolution TEM image of the Sn nanoparticles in the Al matrix. Reprinted with permission from [56]. Copyright 2009 American Chemical Society.

Sn-based oxides have been of considerable interest because they could, in principle, store more than twice the amount of lithium as graphite. Studies of the basic reaction mechanisms of SnO₂ with lithium have revealed that, on the first discharge, lithium bonds to the oxygen in SnO₂, forming a nanosized tin and Li₂O framework [59]. During subsequent cycling, the inactive Li₂O phase serves as a good supporting matrix to buffer the volume expansion induced by Li-Sn alloying. Accordingly, Sn-based oxide anodes display greatly enhanced cycle performance in comparison with pure Sn anodes of the same grain size. However, a critical problem concerning the application of an SnO₂ anode is that its irreversible capacity is very large due to the irreversible formation of Li₂O in the first cycle. The theoretical specific capacity of pure SnO₂ is 782 mAh g⁻¹, which is 210 mAh g⁻¹ lower than that of pure Sn. Nevertheless, SnO₂ thin film would be a favorable alternative anode material if it could deliver a stable capacity.

4.1 SnO₂ thin-film anodes

Brousse et al. [60] investigated the electrochemical performances of sol-gel-prepared SnO₂ and Sb-doped SnO₂ thin-film anodes. It was found that the capacity decayed significantly after several cycles in the case of the pure SnO₂ anode, but that a 5% Sb-doped SnO₂ film anode displayed a capacity of 250 mAh g⁻¹ after 75 cycles between 0.05 and 1.2 V. This was attributed to the Sb dopant reducing the crystal size of the SnO₂ and suppressing the growth of crystals in the film during the cycling process. Moreover, the Sb dopant enhanced the electron conductivity and improved the electrochemical activity of materials in the film anode during the initial cycles. In comparison, although without a doping element, a crystalline pure SnO₂ thin film prepared by chemical vapor deposition also displayed greatly enhanced cycle performance, as indicated by a high reversible capacity of 500 mAh g⁻¹ after 100 cycles in the range 0.15–1.15 V [61]. This suggested that the preparation method has a key influence on the anode performance of crystalline SnO₂ thin films.

Mohamedi et al. [62] prepared amorphous SnO₂ films by electrostatic spray deposition at 400°C followed by annealing at 500°C in air. These SnO₂ film anodes exhibited reversible capacities greater than 1300 mAh g⁻¹ and fast capacity fading when cycled between 0.05 and 2.5 V at 0.2 mA cm⁻². However, if the electrode was cycled between 0 and 1.0 V, a reversible capacity of 600 mAh g⁻¹ could be maintained for more than 100 cycles. It was found that a cut-off potential higher than 1.5 V could cause destruction of the Li₂O matrix physically holding the reduced Sn particles. Jiang et al. [63] were the first to prepare an SnO₂ thin film by using an ink-jet printing technique. The thickness of the monolayer thin-film electrode was about 770–780 nm, while the thickness of the SnO₂ thin film could be increased by repeating the printing procedure on the Cu foil substrate.

At a current density of 33 μA cm⁻² between 0.05 and 1.2 V, a 2.3 μm thick 10-layer SnO₂ anode delivered a high initial discharge capacity of about 812 mAh g⁻¹, which is higher than the theoretical capacity of pure SnO₂. However, the capacity decayed rapidly and decreased to just 230 mAh g⁻¹ after 50 cycles. In comparison, a nanostructured SnO₂ thin film of thickness 550 nm, prepared by immersing a Pt foil current collector in a solution consisting of tin oxide precursor material and then burning in air, displayed much better capacity retention. Thus, an initial discharge capacity of 570 mAh g⁻¹ followed by maintenance at a level of 440 mAh g⁻¹ after 50 cycles was observed at a current density of 0.32 mA cm⁻² between 0.05 and 1.2 V [64].

In addition to those prepared using sol-gel, printing, and chemical vapor deposition methods, Sn-based oxide thin films prepared by various physical vapor deposition methods have also been widely studied. Nam et al. [65] sputtered a 300 nm SnO₂ thin film into which metallic lithium was incorporated by reaction. The charge-discharge performances of this film exhibited capacities in excess of 400 mAh g⁻¹ over 75 cycles between 0 and 1.2 V. It was also found that the reacted thin films showed reduced micro-cracks created by density fluctuations, since they consisted of metallic tin, lithium oxide, and reduced tin oxide. In order to further enhance the anode performance of the lithium-reacted tin oxide anode, a multi-layer film was assembled by the evaporation of lithium metal onto an SnO₂ thin film to intentionally cause an irreversible side reaction, generating metallic tin before film fabrication [66]. The lithium-reacted tin oxide thin film did not show any irreversible side reactions of forming Li₂O and metallic Sn near 0.8 V vs. Li/Li⁺, allowing an initial charge retention of 62%, which was much higher than those of an Sn/Li₂O layered structure or an Sn/Li₂O co-sputtered thin film. However, the two Sn/Li₂O thin films showed better cycling behavior over 500 cycles than the Li-reacted tin oxide thin film between 1.2 and 0 V vs. Li/Li⁺. Li et al. [67] fabricated nanocrystalline SnO_x films by vacuum thermal evaporation of metallic tin and subsequent thermal oxidation in air at different temperatures. The composition and electrochemical properties of SnO_x (1 < x < 2) films were found to be highly dependent on the oxidation temperature. It was found that an SnO_x film fabricated at 600°C exhibited better electrochemical performance than SnO and SnO₂ thin-film anodes, yielding reversible capacities of 825 and 760 mAh g⁻¹, respectively, at a current density of 10 μA cm⁻² between 0.10 and 1.30 V.

4.2 SnO₂-MO_x thin-film anodes

In SnO₂ film anode materials, the inactive Li₂O matrix formed during the first discharge can to some extent protect and preserve the structural integrity of the Sn phase during Li insertion–extraction cycling. However, the cyclability of SnO₂ anodes is quite poor as the grain size of the active phase in the films is large. In order to further enhance the

cycle performance of the Sn-based oxide thin-film anodes, doping and coating treatments for the SnO₂ materials have been proposed.

Kim et al. [68] deposited SnO₂ and Si-doped SnO₂ thin-film anodes on an Mo/Si substrate by EBD at room temperature. Both of these SnO₂ films consisted of short-range ordered small grains (nanoscale) and exhibited good abilities to insert and extract lithium ions. However, the cycle performance of these film anodes was dependent on the cut-off voltage. In the voltage range 0.1–0.8 V, the Si-doped SnO₂ film anode delivered a reversible capacity of 320 $\mu\text{A h cm}^{-2} \mu\text{m}$ after 200 cycles, while that of the bare SnO₂ film was 200 $\mu\text{A h cm}^{-2} \mu\text{m}$. This suggested that the Si dopant played an important role as a glass-forming element in the Li-Si-O network by suppressing the growth of Sn grains, reducing the surface roughness, and enhancing film adhesion. This is similar to the mode of action of the aforementioned Sb dopant in an SnO₂ thin film [60]. Zhang et al. [70] directly fabricated an amorphous SnO₂-SiO₂ thin film with reticular porous morphology by electrostatic spray deposition. It was found that the initial discharge capacity of such an SnO₂-15% SiO₂ anode was about 1271 mAh g⁻¹, and the reversible capacity stayed at 501 mAh g⁻¹ after 100 cycles. This improved cycle performance could be ascribed to the reticular porous structure, which accommodated the volume change of the active materials during cycling. The high capacity was attributed to the addition of SiO₂, which facilitated formation of the Li-Sn alloy. Similarly, Ahn et al. [71] found that the application of a Ta₂O₅ thin film (54 nm thick) onto an SnO₂ thin-film anode served to slow the capacity decay, which was attributed to the dual role of the Ta₂O₅ film as a protective layer and in facilitating the passage of lithium ions during cycling.

In general, Sn-based oxide film anodes possess relatively high discharge capacities. However, due to unavoidable side reactions and the irreversible formation of Li₂O frameworks during the first discharge, large initial irreversible capacity losses are common among tin oxide thin-film anodes. Moreover, amorphous Li₂O frameworks in tin oxide anodes may be crumbled if the charging cut-off potential is too high, which results in aggregation of the nanosized Sn and Li_xSn and therefore leads to poor cycle performance in thin-film anodes.

5 Other Sn-based composite thin-film anodes

Thin-film materials possess somewhat different physical/chemical properties in comparison with the same materials in bulk form. Hence, the electrochemical lithiation behaviors of some functional Sn-based composite thin films, for instance other Sn-A (A=S, Se, etc.) compounds, have also been the subject of exploratory studies by researchers. Li et al. [72] prepared a net-like SnS/C nanocomposite thin-film anode by spin-coating on a copper foil, which showed fa-

vorable initial coulombic efficiency and excellent cycling stability. This could be mainly ascribed to the ultra-fine particles and the effects of the 3D net-like carbon structure, which acted as a buffer matrix to alleviate the volume expansion of the Li-Sn alloy and provided enough paths for the electrolyte to reach the active SnS materials during the discharge-charge process. Xie et al. [73] successfully fabricated a crystallized SnSe thin film by pulsed laser ablation of a mixed target of Sn and Se, the reversible discharge capacities of which were between 260 and 498 mAh g⁻¹ in the range 0.01–2.5 V. Reversible formation and decomposition of Li₂Se was found during the reaction of SnSe with lithium, which was completely different from the situation with SnO_x and SnS_x, whereby Li₂O and Li₂S were inactive.

Park et al. [74] reported the anode behaviors of Sn₄N₃ thin films, which were deposited by reactive r. f. magnetron sputtering at various deposition temperatures. It was found that the rechargeability of the Sn₄N₃ thin films was improved as the irreversible capacity fraction was increased. In this tin nitride anode, the origin of the irreversible capacity loss could be understood in terms of Li₃N formation, and after the first cycle only metallic tin took part in the electrochemical reaction, similar to the situation in tin oxide anodes.

In addition to the above-mentioned materials, multi-component thin-film anodes composed of Sn and other oxides, such as Sn-Ag-O [75] and Sn-Co-O [76], have also been reported. However, these are not discussed in detail here.

6 Concluding remarks and future work

According to the above analysis, it has been found that great progress has been made in studies of high-performance Sn-based thin-film anodes for lithium-ion batteries. Many such thin-film materials display quite favorable electrochemical properties, which to a certain extent meet the property requirements of anodes for use in thin-film lithium-ion batteries. However, the performances of these thin-film anodes are still far from a practical level.

As anode materials for thin-film Li-ion microbatteries, performances combining high energy density and long cycle life are needed. However, large initial irreversible capacity losses, i.e. low initial coulombic efficiency, and fast capacity fading, i.e. poor cyclability, are a common feature of many of the reported Sn-based thin-film materials. The reasons for the irreversible capacity loss and capacity fading are manifold. However, the main factor is that during lithiation/delithiation cycling processes the structures of active film layers are destroyed due to the huge volume change of the active materials, as well as the morphology change of the thin-film surface induced by the interaction of electrolyte with the thin films. Thus, researchers have explored the use of additives to create organic liquid electrolytes, polymer electrolytes, room temperature ionic electrolytes, inorganic

solid-state electrolytes, aqueous electrolytes, and so on, to improve the compatibility of the electrolyte with the active materials in thin-film anodes. However, it should be pointed out that thin-film microbatteries tend to be solid state, and thus the interface between active materials and electrolyte is solidified. This presents new challenges for practical application of the currently available thin-film anodes.

Considering future studies of thin-film anodes, attention should not only be focussed on the exploration of new high-capacity materials and the modification of currently available materials, but emphasis should also be placed on the microstructure design of the inner active layers of the thin-film electrodes, with a view to reducing the volume changes of electrodes and maintaining their integrity during discharge-charge cycling. We believe that manipulating the multi-phase and multi-scale structures represents an important strategy for further improving the capacity and cyclability of Sn-based alloy thin-film anodes. This is because multi-scale structures are beneficial for retarding the volume change and stress relaxation of the active materials, while multi-phase composites can increase the reversible capacities of Sn-M alloy anodes and also enhance the structural stability of electrodes. Moreover, the rapid development of thin-film technologies and microfabrication techniques, especially the breakthrough on the study of nano-materials, which continues to expand our knowledge on the chemical/electrochemical reactions of inorganic materials, should ultimately lead to the fabrication of practical thin-film anodes with favorable performances.

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