

TIN-BASED MATERIALS AS ADVANCED ANODE MATERIALS FOR LITHIUM ION BATTERIES: A REVIEW

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Abstract. The lithium ion battery industry is increasingly looking for materials with a higher capacity for lithium storage than the currently used graphite anodes, for use in the next generation of more powerful rechargeable batteries. Tin is one of the best solutions available thanks to its high theoretical capacity and other technical benefits. However, tin anodes, similar to other metallic materials, suffer from high volume changes during battery cycling, leading to premature degradation of the anode. In order to overcome this problem different architectures of Sn-based composites and intermetallics have been evaluated and some of them have shown promising results. Progress towards the development of Sn-based anodes for next generation Li-ion batteries is summarized in this paper. The possibility of their usage in the battery market is also briefly discussed.

1. INTRODUCTION

Lithium ion batteries have been considered as the future source of power in emission-free vehicles, thanks to their potential to produce large amounts of power. However, in order to achieve their potential, these batteries will have to produce much higher energy densities than existing versions. On the other hand, in order to gain a considerable improvement in energy density, both the anode and cathode materials will need to be improved [1-6]. In a Li ion battery, the anode is responsible for the accommodation and release of Li ions according to the following reversible reaction:



where M is a material such as carbon [7], Si [8], Al [9], Sn [10], Ge [11], Sb [12] or In [13]. During the battery charging stage, Li ions from a lithium-containing salt such as $LiPF_6$ are electrically forced to be alloyed with M, which is connected to the nega-

tive pole of a power source. The M_xLi_y intermetallic that forms can then be decomposed after removing the power source, leading to the release of lithium ions from the anode material into the electrolyte and the simultaneous release of electrons from the anode into the external circuit. As a result, the lithium ion storage capacity of the anode is an important factor with regards increasing the current density of Li-ion batteries. Graphite, which is used as the anode material for commercial Li-ion rechargeable batteries, cannot fulfil the requirement for higher storage capacity due to its insufficient theoretical capacity of 372 mAh.g^{-1} , corresponding to the formation of LiC_6 [7]. The replacement of graphite by a metallic anode can offer benefits such as a higher specific capacity at least during the initial cycles, due to more lithium ions that can contribute to the reaction scheme (1) compared to that in graphite. The major challenge in the development of metallic anodes is the high volume change involved in the reaction scheme (1). The theoretical capacity and

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Table 1. Lithiation/delithiation characteristics of different anode materials.

Metal	Li	Si	Al	Ge	Sn	Al	graphite
Lithiated compound	Li	$\text{Li}_{22}\text{Si}_5$	Al_4Li_9	$\text{Li}_{22}\text{Ge}_5$	$\text{Li}_{22}\text{Sn}_5$	AlLi	LiC_6
Theoretical capacity (mAh.g ⁻¹)	>3800	>3000	2234	1600	994	993	372
Volume change (%)	Dendritic growth	323	-	370	300	97	9
Reference	[14]	[8]	[9]	[11]	[10]	[9]	[7]

related volume change during the lithiation/delithiation of different metallic anodes can be seen in Table 1. The excessive volume change that occurs during cycling leads to the degradation of the anode and the loss of electrical conductivity. On the other hand, lithium itself is not considered to be an appropriate anode for several reasons, including its short lifecycle, the formation of dendrites upon cycling, and its high reactivity and low melting point, which may lead to combustion and explosion [14].

While graphite has an intrinsic limitation in terms of lithiation capacity, other carbonaceous materials such as disordered carbon [7] and particularly carbon nanostructures [15-19] offer both highly reversible and irreversible capacities. Also silicon has been shown to be one of the best options for replacing existing anodes due to its high capacity. Recent achievements in production and the characterization of the above-mentioned materials have been reviewed elsewhere [20]. The current paper reports on the progress made towards the development of Sn-based materials for use as anode material in lithium ion batteries.

2. Sn-BASED ANODE MATERIALS

An equilibrium phase diagram of Li-Sn [21] shows a number of intermetallics of different compositions including $\text{Li}_{22}\text{Sn}_5$, Li_7Sn_2 , Li_3Sn , Li_5Sn , LiSn and Li_2Sn_5 . These intermetallics can be produced by the electrochemical lithiation of a tin electrode immersed in a Li ion containing an electrolyte such as LiClO_4 . According to the type of intermetallics formed, the specific charge of the electrode may change up to about 994 mAh.g⁻¹, corresponding to $\text{Li}_{22}\text{Sn}_5$ [10]. Therefore, Sn is an impressive material for anode application due to its high theoretical capacity. A special tin-based negative electrode has been under development by Sony for a commercial lithium-ion battery named Nexelion [23]. However, Li-Sn intermetallics are brittle and easily pulverized by

large Li-driven volume variation during the charge and discharge reactions, leading to the loss of electronic contact between particles and between particles and the current collector [22]. This problem, which leads to the failing of the anode, has been a major challenge in the commercialization of tin-based anodes, and efforts are being made world-wide to find solutions to overcome this limitation. The large volume change upon the lithiation of tin originates from the fact that lithium has the smallest density of 0.534 g.cm⁻³ [24] among all condensed elements, while that of tin is 7.365 g.cm⁻³ [25]. Therefore, the excessive volume change observed upon lithium insertion arises due to the sharp density difference between the host and guest materials and will increase upon production of higher content lithium intermetallics. Early suggestions on ways to reduce this volume change involved closing the potential window of cycling in order to produce lower lithium content compounds such as LiSn, which leads to the creation of less mechanical stress [22], or reducing the particle size of the anode material. It has since been proved that large absolute volume changes can be avoided when the size of the metallic host particles is kept small. The better performance of nano-Sn particles [26] compared to micron-sized particles [27] can be seen in Fig. 1. However, as can also be seen in this figure, the cycling stability remains insufficient. Furthermore, it should be recognized that the surface area of the material increases with decreasing particle size and thus the amount of Li that is irreversibly consumed for solid electrolyte interphase (SEI) formation should also increase to the same extent.

More improvement has been achieved by using a second phase in order to accommodate the excessive volume changes occurring during the charge-discharge cycles, while the matrix phase must assure electronic and ionic conductivity throughout the electrode [28]. This concept was probably triggered by understanding the observa-

tion that the coating of graphite fibres with certain metals such as amorphous Sn may improve the electrochemical performance of the material [29,30]. Further progress was made during the last decade by designing composites containing Sn and a stress-accommodating phase. Many kinds of materials have been used as the second phase, including disordered carbon [31-52], graphite [32,47,48,53,54], single-walled carbon nanotubes (SWNTs) [55,56], multi-walled carbon nanotubes (MWNTs) [57-62], semi-amorphous carbon [63], TiO₂ nanotubes [64] and semi-amorphous copper [65]. Carbon was found to be an appropriate second phase in these investigations thanks to its excellent stress-relieving properties and also its low reactivity with Sn. In fact, although many metals can easily form carbides, Sn, with the exception of compounds such as mixed titanium-tin carbide [66], has no solubility or reaction with C [67]. This characteristic makes it possible to design different architectures of tin-carbon composites without any concern over the formation of carbides, which would reduce the electrode capacity. Selected methods for the production of tin-based composites are shown in Table 2, and the electrochemical performance of the material can be seen in Fig. 1. Among the materials presented in Fig. 1, tin-filled carbon nanofibres or

nanotubes [26, 56, 62] and a Sn-microporous carbon composite [52] have shown the most promise due to their high reversible capacity and good capacity for retention. However, the multi-step processes used to produce these kinds of materials (Table 2) are typically more complicated and difficult than those used in industrial processes. A relatively more simple process was used by Lee et al. [31] for the production of carbon-encapsulated Sn-nanorods (Table 2). The authors suggested that these nanorods could be used as anode materials in rechargeable lithium-ion batteries. However, the electrochemical performance of the material was not studied. A cost-effective and industry-matched process was developed by Fray et al. [61] to produce a mixture of tin-filled carbon nanotubes and tin-core carbon sheath particles (Fig. 2) using a novel switching electrolysis method in a mixed LiCl/SnCl₂ molten salt with graphite electrodes. In this process, the continuous switching of the anode and cathode leads to the continuous reduction of tin and intercalation of lithium in both electrodes, resulting in separation of the tin-filled nanostructures into the fused salt. The resulting product is cheap, with a moderate electrochemical performance among the tin-based anode materials (Fig. 1) yet a much better performance than graphite.

Table 2. Microstructure and production process of studied tin-based anode materials.

Microstructure	Process	Reference
Carbon-encapsulated Sn-nanorods.	Reduction of tin oxide nanopowders by a gas containing N ₂ and C ₂ H ₂ at 750 °C for more than 1 h.	[31]
Sn particles embedded in the mesopores of carbon spherules coated with a layer of soft carbon.	1. Production of mesopores of carbon spherules using a catalytic pyrolyse technique. 2. Activation with H ₂ O vapour at 900 °C for 2 h. 3. Addition of product into the solution of SnCl ₄ at 140 °C for 5 h. 4. Hydrogen reduction at 900 °C for 3 h.	[33]
Sn/C composite film.	Deposition from Sn (OC (CH ₃) ₃) ₄ precursor under 1200 W microwave radiation power.	[34]
Carbon-coated Sn powders.	1. Ball milling of SnO ₂ , MgO (as Sn agglomeration inhibitor) and PVA. 2. Heating the mixture at 900 °C. 3. Removal of MgO by HCl.	[36]
Sn-carbon nanoparticles (core) encapsulated in hollow carbon nanofibres.	1. Production of core (tributyltin ((C ₄ H ₉) ₃ Sn) and mineral oil solution) - sheath (polyacrylonitrile) nanofibres by an electrospinning process.	[26]

	<ol style="list-style-type: none"> 2. Extraction of mineral oil by immersing in n-octane for more than 12 h. 3. Carbonization of the outer polyacrylonitrile to produce hollow carbon nanofibres and decomposition of tributyltin. 	
Amorphous Sn coated on MWNTs.	<ol style="list-style-type: none"> 1. Production of MWNTs by continuous ethylene decomposition process using Fe/Al₂O₃ catalyst. 2. Soaking of product into HNO₃ for 10 h. 3. Sn coating (37 wt.%) by soaking SnCl₂ solution in the presence of KBH₄ and NH₃. 	[57]
CNT-encapsulated Sn nanoparticles.	<ol style="list-style-type: none"> 1. Removing the air bubbles from the porous alumina. 2. Immersing of alumina in SnCl₂ solution. 3. Heating under N₂/C₂H₂ for 3 h at 650 °C. 4. Dissolving of alumina by NaOH. 	[56]
Tin-filled carbon nanotubes.	<ol style="list-style-type: none"> 1. Formation of SiO₂ nanowafers as substrate. 2. Growth of CNTs on the substrate. 3. Removal of substrate followed by heat treatment under H₂ at 700 °C for 10 h. 4. The oxidative opening of the carbon nanotubes. 5. Introduction of SnCl₂ into the CNTs. 6. Reduction of Sn by NaBH₄. 	[62]
Tin-filled carbon nanotubes and tin-core carbon sheath particles (Fig. 2).	Electrolysis of molten LiCl containing SnCl ₂ .	[61]
Sn-micro-porous carbon composite.	<ol style="list-style-type: none"> 1. Coating of a solution consisting of PAN and silica particles on Cu foil. 2. Dissolution of silica in NaOH. 3. Electrodepositing of Sn through micro-porous membrane. 4. Annealing at 300 °C for 4 h. 	[52]
C-Sn composite.	Co-electrodeposition of Sn and C from a hydrated bath containing SnCl ₂ and acetylene black.	[32]

3. Sn-BASED INTERMETALLIC ANODE MATERIALS

Many tin-based intermetallics and their composites have been examined as lithium storage materials and in general have shown increased long-term cycling stability compared to metallic Sn. These intermetallics include Cu₆Sn₅ [68-73], SnSb [74-79], CoSn₃ [80], CoSn [81,82], Co₃Sn₂ [82], CoSn₂ [83,84], Ni₃Sn₄ [83,85,86], Sn₂Mn [72], LaSn₃ [87], Ag₃Sn [79,88-90], SnAg₄ [90], Mo₃Sn [91], Ti_xSn_y [92], Mg₂Sn [93], SnMn₃C [94], Sn₂Fe [86,95,96], FeSn [86,97], Fe₂Sn₃ [97], Fe₃Sn₅ [97] and V₂Sn₃ [98]. Although the electrochemical performance of many of these materials is no better than that of

graphite, some of them or their composites have exhibited interesting properties. Cu₆Sn₅, as an inactive/active intermetallic has been considered widely as an alternative anode material for rechargeable lithium ion batteries. The lithiation sequence of Cu₆Sn₅ may be explained by the following phase transformations [69, 99-101]:



Li₇Sn₂ can be formed when the potential decreases to about 0.01 V, offering a considerable capacity [69]. The lithiation of the Sn/Cu₆Sn₅ thin film anode up to the formation of Li₇Sn₂ can produce a capacity of about 950 mAh.g⁻¹ in the first cycle.

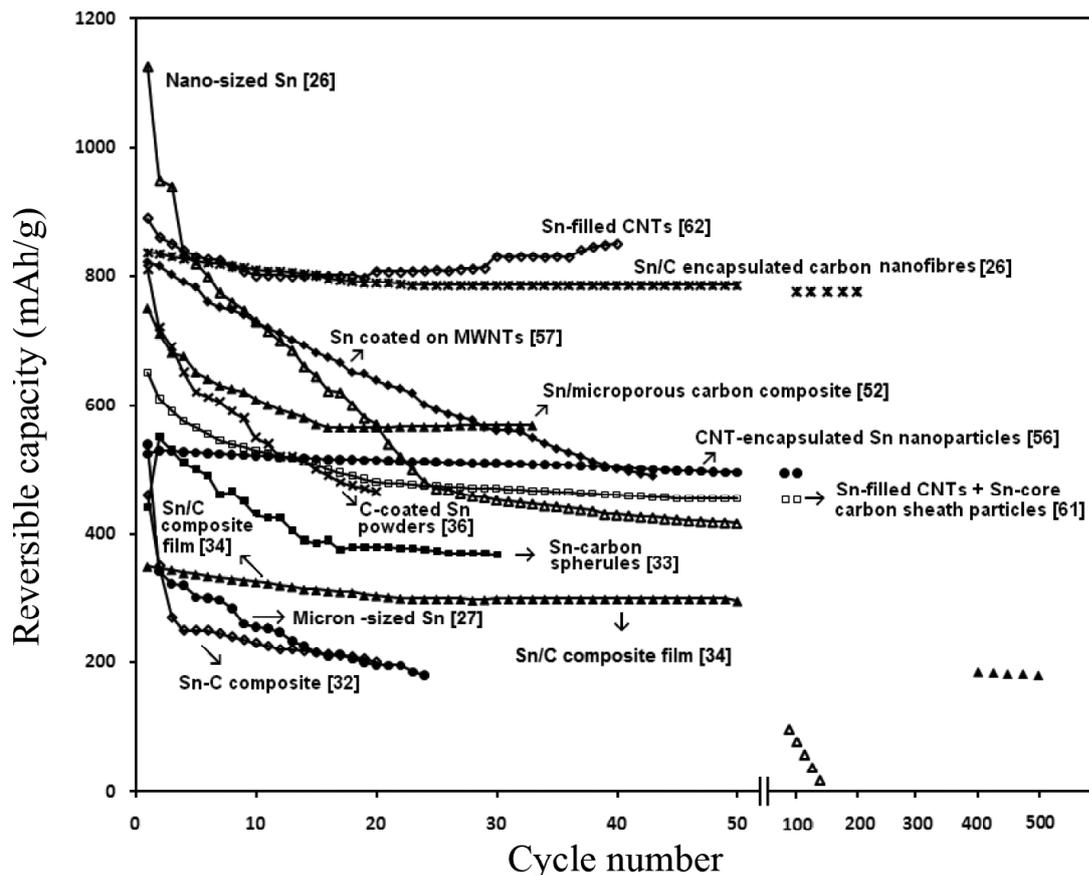


Fig. 1. Reversible capacity of different Sn-containing materials described in Table 2 versus the cycle number.

Such a high capacity (more than the theoretical capacity for Cu_6Sn_5) might be due to the fact that some of the lithium ions are stored in defective sites such as microcracks or even the grain boundary of the thin film anode in the lithiation process [69]. However, in this case, low cyclability is observed due to the intrinsic brittleness of Li_7Sn_2 and the inability of the remaining Cu to dampen the stresses upon the formation/decomposition of this phase, such that the Cu_6Sn_5 electrode provides a capacity of only about 200 mAh.g^{-1} at the 20th cycle [102]. A reversible capacity of more than 370 mAh.g^{-1} was maintained for up to 70 cycles when the lithiation of $\text{Sn}/\text{Cu}_6\text{Sn}_5$ was performed in the potential window of 0.1–1.25 V. In this situation, the phase transitions from Li_2CuSn to Li_7Sn_2 as well as from Sn to $\text{Li}_{22}\text{Sn}_5$ are partly avoided [69]. The reversible capacity of the $\text{Sn}/\text{Cu}_6\text{Sn}_5$ anode at a current density of $400 \mu\text{A.cm}^{-2}$ versus cycle numbers can be seen in Fig. 3. According to this figure, the reversible capacity increased in the first three cycles and reached the maximum (951.8 mAh.g^{-1}) at the third

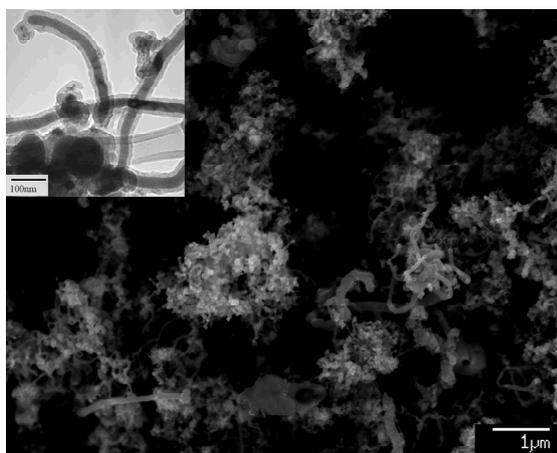


Fig. 2. SEM micrograph of tin-filled carbon nanotubes and tin-core carbon sheath particles produced by novel switching electrolysis of LiCl containing SnCl_2 -fused salt electrolyte with graphite electrodes. The inset is a TEM micrograph of the material at a higher resolution showing the detail of the tin-filled nanotubes and nanoparticles, [61].

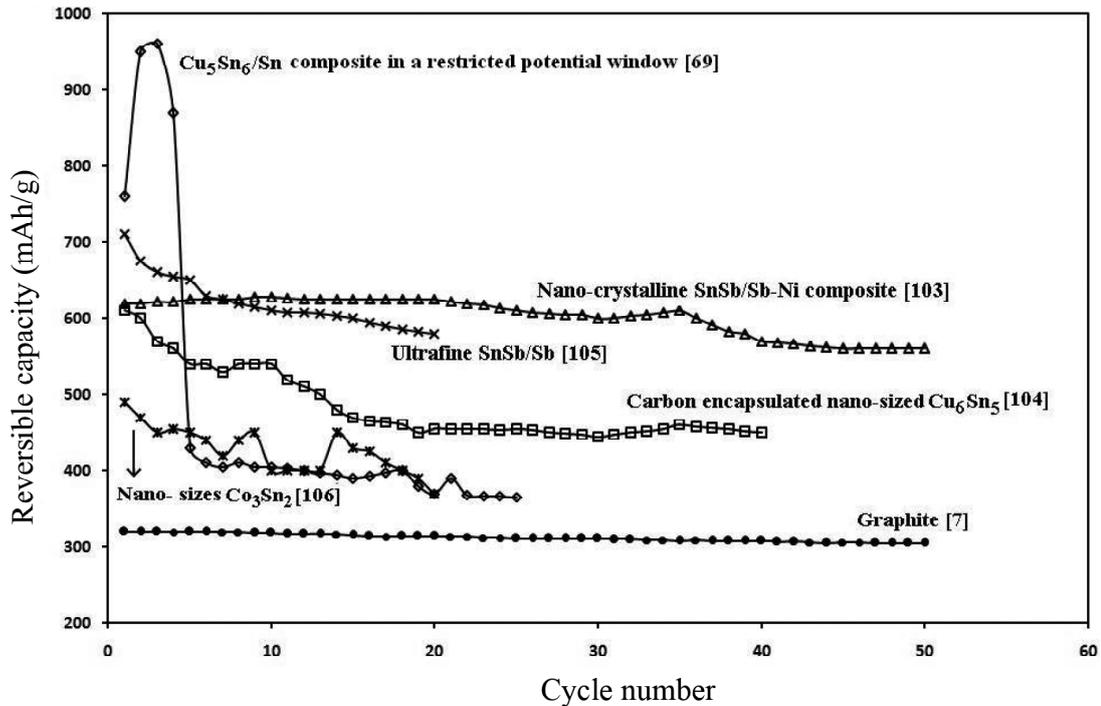


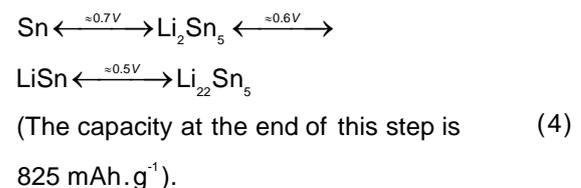
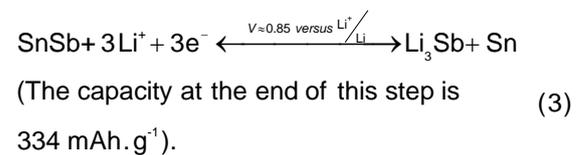
Fig. 3. Reversible capacity of some selected Sn-based intermetallic anodes versus cycle number.

cycle. This observation was attributed to the fact that most materials in the composite film were activated after the initial cycles. However, the capacity decreased rapidly in subsequent cycles, which was attributed to the formation of microcracks that were observed particularly in the more brittle Cu_6Sn_5 phase even after the first cycle in a restricted voltage window. Wachtler et al. [103] proposed a reasonable mechanism to explain the low cyclability of Li storage metals and intermetallics compared to that of carbonaceous materials. This mechanism deals with the formation of the solid-electrolyte interphase (SEI) on the electrode surfaces: in contrast to carbonaceous materials, the large volume changes in the metals and intermetallics during cycling causes cracking of the film. The electrolyte subsequently comes into contact with the new fresh surfaces of active materials and this leads to the extension of the SEI film and more loss of capacity.

Liu et al. [104] obtained a better electrochemical performance (Fig. 3) using amorphous carbon-encapsulated nano-sized Cu_6Sn_5 particles (~40 nm) containing about 30 wt.% carbon. They produced this microstructure by: (a) the production of nano-sized Cu_6Sn_5 powders via the reductive precipitation of metal chlorides with NaBH_4 from aqueous solution, (b) the encapsulation of Cu_6Sn_5 nano-particles by solution treatment of these particles, amor-

phous carbon and polyvinyl alcohol and (c) applying a high-temperature heat treatment. Lithiation of this composite in the potential window of 0.4–0.2 V led to the formation of $\text{Li}_{2.4}\text{CuSn}$ while $\text{Li}_{4.4}\text{Sn}$ was formed during further lithiation in the 0.2–0.0 V window.

Some intermetallics such as SnSb comprise two active components. Reaction of this intermetallic with lithium can lead to the formation of two lithiated phases of Li_3Sb and $\text{Li}_{22}\text{Sn}_5$ according to the following reactions [10,103]:



Therefore, when Li_3Sb is formed, the ductile phase of Sn can buffer the expansion of the first reacted phase. Wachtler et al. [103] measured a capacity of between 450–570 $\text{mAh} \cdot \text{g}^{-1}$ after 50 charge–discharge cycles for the nano-crystalline

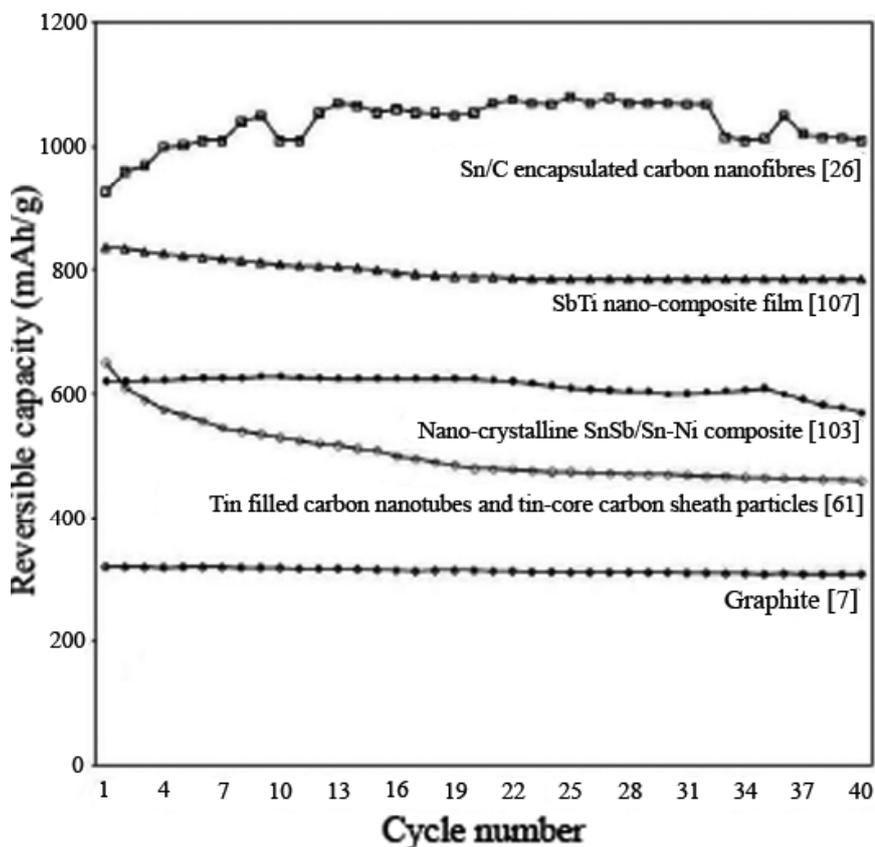


Fig. 4. A comparison between the performance of tin-based and Si-based materials and conventionally used graphite as the anode in a lithium ion battery.

Sn/SnSb–Ni composite. The capacity varied depending on the electrolyte used. Nano-crystalline Sn/SnSb and Ni powders were precipitated with NaBH_4 from aqueous solutions of the respective chloride salts. Ni was used as an electronically conductive additive. The electrochemical performance of the material is shown in Fig. 3. This study demonstrated that the electrochemical performance can be improved by adding ethylene carbonate, as a filming agent, and saturated phosphatidylcholine, as the surfactant, to the LiPF_6 electrolyte [103]. Wang et al. [105] produced an ultrafine microstructure with the chemical composition of Sn–46.5 at.% Sb comprising β -SnSb and Sn phases using an arc melting process followed by inert/reductive gas cooling. Then an electrode composed of 82 wt.% active powder, 10 wt.% acetylene black and 8 wt.% polyvinylidene fluoride dissolved in *n*-methyl pyrrolidinone was produced. The electrode exhibited considerable reversible capacity (Fig. 3) in an electrolyte of 1 M LiPF_6 in ethylene carbonate and dimethyl carbonate at a current density of 50 mA.g^{-1} [105].

It is thought that the presence of cobalt atoms assists the formation of the relatively stable amorphous Li_yCoSn_x phase during the lithiation of Co_3Sn_2 intermetallic. Alcántara et al. [106] found considerable capacity (Fig. 3) in the first cycle between 0.0 and 1.2V at a current density of 80 mA.g^{-1} for an electrode containing 77 wt.% nano- Co_3Sn_2 produced by a low temperature chemical process using SnCl_2 and $\text{Co}(\text{COOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ as the initial materials.

Naille et al. [85] found that Ni_3Sn_4 reacts electrochemically with lithium to form Li_7Sn_2 , offering a capacity of 515 mAh.g^{-1} using ^{119}Sn Mössbauer spectrometry and ab initio calculations.

Yin et al. [89] studied on the lithiation mechanism of the $\text{Sn/Ag}_3\text{Sn}$ electrode and demonstrated that the lithiation of this electrode leads to the formation of $\text{Li}_x\text{Ag}_y\text{Sn}$ and LiAg compounds.

They found that partial substitution of Ag with Fe resulted in an improvement in the cycling performance of Ag–Sn intermetallic electrodes such that the $\text{Ag}_{36.4}\text{Fe}_{15.6}\text{Sn}_{48}$ and the $\text{Ag}_{26}\text{Fe}_{26}\text{Sn}_{48}$ electrodes were capable of retaining capacities of 280 and 205

mAh.g⁻¹, respectively, over 300 cycles at a current density of 0.2 mA.cm⁻² [89].

4. FUTURE OF TIN-BASED MATERIALS AS ANODE MATERIALS IN LITHIUM ION BATTERIES

The electrochemical performance of selected materials that may be used as anode materials in the next generation of lithium ion batteries is compared along with that of conventionally used graphite in Fig. 4. These materials include Sn/C encapsulated carbon nanofibres [26], nano-crystalline SnSb/Sb-Ni composite [103], tin-filled carbon nanotubes/tin-core carbon sheath [61] and a newly developed Si/TiC nano-composite film [107] produced in the laboratory using a sol-gel/heat-treatment method. All of these new materials provide much more reversible capacity than graphite. Therefore, these emerging materials are potentially capable of fulfilling the engineering requirements at a capacity level. In particular, Si-based materials have shown the possibility of producing extremely high capacities thanks to silicon's high theoretical capacity of 4200 mAh.g⁻¹ [108]. However, future rechargeable batteries should be cheap enough to attract consumers. It should be noted that new anode material will have to be used instead of battery grade graphite materials, which typically cost from \$20 to \$40/kg. A rough cost estimation for the commercial Li-ion battery 18650 cells showed that the major materials alone make up approximately 75% of the total cell. Also, it is known that graphite accounts for about 16 wt.% of the total weight and 14 wt.% of the total material cost in a cell [109]. The replacement material cannot be much more expensive than graphite. The lower price and easier processing of tin-based materials compared to Si-based materials may affect the future of these materials in the battery industry. However, real progress in this regard cannot take place in the absence of a method that is capable of producing high performance materials in large quantities sufficiently cheaply.

5. CONCLUSION

Tin-based materials have been studied extensively as a possible replacement for current anode materials in lithium ion batteries. The major problem associated with using tin is the excessive volume change during the lithiation-delithiation process. This problem has been successfully reduced by creating microstructures such as tin-filled nanotubes

and nanofibres or using appropriate intermetallic/metal composites such as SnSb/Sb. Some products have a reversible capacity that is close to the maximum theoretical capacity of tin. These products have been produced using relatively complicated processes. On the other hand, methods such as switching electrolysis of LiCl, represent a more industrial approach. However, the future application of tin-based materials as the anode in lithium ion batteries is threatened by silicon-based materials due to the extraordinary high theoretical capacity of silicon. It seems that the production of high capacity materials by a cost-effective, industry-scalable process is the key factor for the success of tin in the lithium ion battery industry. The advantages of tin, such as its relatively high theoretical capacity, its lack of reactivity with carbon, its low melting point and its low price should be used to achieve this.

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