Challenges and Development of Tin-Based Anode with High Volumetric Capacity for Li-Ion Batteries

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Abstract

The ever-increasing energy density needs for the mass deployment of electric vehicles bring challenges to batteries. Graphitic carbon must be replaced with a higher-capacity material for any significant advancement in the energy storage capability. Sn-based materials are strong candidates as the anode for the next-generation lithium-ion batteries due to their higher volumetric capacity and relatively low working potential. However, the volume change of Sn upon the Li insertion and extraction process results in a rapid deterioration in the capacity on cycling. Substantial effort has been made in the development of Sn-based materials. A SnCo alloy has been used, but is not economically viable. To minimize the use of Co, a series of Sn–Fe–C, Sn₃Fe, Sn–C composites with excellent capacity retention and rate capability has been investigated. They show the proof of principle that alloys can achieve Coulombic efficiency of over 99.95% after the first few cycles. However, the initial Coulombic efficiency needs improvement. The development and application of tin-based materials in LIBs also provide useful guidelines for sodium-ion batteries, potassium-ion batteries, magnesium-ion batteries and calcium-ion batteries.

Keywords Li-ion batteries · Tin-based anode · Sn–Fe–(C) · High volumetric capacity

1 Introduction

Lithium-ion batteries, over the last 40 years, have successfully taken over in turn portable electronics, then electric vehicles (BEVs), plug-in hybrid electric vehicles (PHEVs) and hybrid electric vehicles (HEVs) and now large-scale grid storage due to their high energy density and long cycle life [1–5]. In awarding the 2019 Nobel Prize, the Nobel committee claimed “They (John B. Goodenough, M. Stanley Whittingham, Akira Yoshino) created a rechargeable world.” In the global electric vehicle market, it is expected to exceed more than USD 151.6 billion by 2024 at a compound annual growth rate (CAGR) of 11.0% [6]. Unit sales are anticipated to reach 97 million vehicles worldwide by 2025 [7]. A major factor behind

the growth of electric vehicles is that various governmental agencies are encouraging the sale of these vehicles, which could solve the negative effect of climate change along with alarming pollution. The ever-increasing energy density needs for mass deployment of EVs to replace the majority of gasoline powered transportation bring challenges to batteries.

Oxides are the predominant cathode material in Li-ion batteries used for vehicular propulsion in 2020. BMW is using lithium–nickel–manganese–cobalt oxide (NMC) in their electric cars, and Tesla’s electric vehicle battery cathodes are lithium–nickel–cobalt–aluminum oxide (NCA). Nissan Leaf adopts their positive materials from lithium–manganese oxide (LMO) to NMC, which largely increased energy density. Chevrolet Bolt EV and Ford Focus also use oxide cathodes. LiFePO₄ is the preferred cathode material in China. In all these cases, the dominant anode is a carbonaceous material, which has a very low theoretical volumetric capacity, 747 Ah L^{−1}, taking up essentially half the volume of the cell. Thus, for any significant advancement in the energy storage capability, the carbon must be replaced with some other higher-capacity material. Ideally, lithium metal could be used with a capacity of 3860 Ah kg^{−1} and 2062 Ah L^{−1} [8, 9], but the

The author, Prof. Stanley Whittingham, was awarded the Nobel Prize in Chemistry in 2019. His perspective article is very important to promote EER.

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use of Li metal has been limited by the formation and growth of Li dendrites as well as loss due to side reactions with the electrolyte. No safe solution has been found in the past 50 years. There have been various attempts to suppress the Li dendrites, including electrolyte modification (electrolyte additives, solid state electrolytes, etc.), membrane modification and lithium metal modification (the artificial SEI, the lithiophilic matrix, the conductive matrix, etc.). An alternative lithium container host to carbon must be found before a solution is found. Silicon and tin are the favorite candidates, and both are being extensively studied, as each of these can react with over four Li ions per Si or Sn, achieving capacities essentially the same as that of pure lithium, 2000 Ah L⁻¹. As shown in Fig. 1, the volumetric capacity of just 2 Li/Sn is more than double that of carbon [10]. However, both Sn and Si expand around 300% on reaction with Li, damaging the electrode structure resulting in capacity fading. Some commercial battery carbon anodes have small amounts of silicon, boosting their performance slightly. In this review, we will focus on Sn-based materials as anodes in lithium-ion batteries.

2 Tin Lithiation Mechanism and Volume Expansion

Li₂Sn₅, LiSn, Li₇Sn₃, Li₅Sn₂, Li₁₃Sn₅, Li₇Sn₂ and Li₂₂Sn₅ (or Li₁₇Sn₄) phases at 415 and 25 °C were determined by coulometric titrations in Huggins' group [11, 12]. These results were consistent with the Li–Sn phase diagram. The calculated and experimental voltage profile from a tin negative electrode material in Dahn's work [13] shows that the theoretical electrochemical voltage profile compared well with experiment for $x < 2.5$ in Li_{*y*}Sn, which matched well with formation of the bulk Li–Sn alloy phases Li₂Sn₅ and LiSn [14]. For $y > 2.5$, the equilibrium structures predicted by the phase diagram were not easily formed in an electrochemical cell at room temperature, which may be due to low atom mobility at room temperature originating from the high melting point of the Li-rich phase [15]. Zhang et al. [16] introduced elastic strain energy into the calculated electrochemical voltage, suggesting that in selective equilibrium ($y > 2.33$), the thermodynamic driving force was not enough to promote nucleation of the new equilibrium phase due to the elastically constrained conditions.

The volume change from tin to fully lithiated tin (Li_{4.4}Sn) approaches 260% based on the densities of bulk tin and Li₂₂Sn₅ [17, 18]. During the lithiation and delithiation process, one Li–Sn phase grows at the expense of another, and the difference in lattice parameters and structure between the two neighboring Li–Sn alloys will cause accumulation and release of stress [19], which may cause particles to crack and

Fig. 1 Capacity of tin relative to carbon. Reproduced with permission from Ref. [10]. Copyright 2011, IOP Publishing Ltd.

SEI reformation, potentially losing the connection with the current collector, then failure of the electrode, resulting in a rapid deterioration in the cycling [20]. Substantial effort has been made to overcome these problems, including the design and exploration of different Sn-based compounds with variable morphology (sizes, shapes, textures, porosity, etc.).

3 Tin-Based Anode Materials

3.1 Sn Oxide Glass and Other Sn-Based Oxide

In 1997, Fujifilm Celltec Co., Ltd., announced its Stalion battery using tin-based amorphous oxide containing Sn–O as the active center for lithium insertion and other glass-forming elements [21], which could provide a gravimetric capacity of > 600 mAh g⁻¹, corresponding to more than 2200 Ah L⁻¹. This finding caused many researchers, who had been focused on improved carbonaceous anodes since Sony Company commercialized carbon in 1990, to switch to alternative materials. Idota et al. [22] obtained around 200 patents surrounding the Fuji cell, describing the preparation process and electrochemical performance on tin, other group IV elements, oxides and oxide composite glasses. Dahn et al. [14, 23] studied the electrochemical performance and structure change of the reaction of lithium with different tin oxide glasses, which demonstrated significant irreversible capacity loss ranging from 200 to 700 mAh g⁻¹ in the first cycle. The original materials do not reform after lithium removal, and amorphous inactive lithium oxide is formed. The rate of Sn aggregation in the glass heavily depends on the cycling voltage range and the spectator/the Sn ratio and the temperature at which the cells were cycled. Over the years, various Sn-based oxides or Sn-based oxide glasses were reported with high capacities, good cycling and rate performance. However,

they failed to be commercialized because of the high irreversible capacity loss in the first cycle, particularly in the case of tin oxides, where electrochemically inactive Li_2O is formed.

3.2 Sony's Sn–Co–C Alloy

In European patent application, Kawakami and Asao had an extensive body of work on Sn–Co–metal [24]. They showed that the Sn–Co alloy with the most disordered structures had the longest life. In 2005, Sony released their new Nexelion 14430-sized battery containing a nanostructured Sn–Co–C-based negative electrode and claimed that the lithium-ion storage volumetric capacity was increased more than 30% over conventional lithium-ion batteries. Fan et al. [25] showed that Sony's amorphous tin electrode comprised 5-nm primary particles with a 1:1 tin-to-cobalt ratio and about 5% titanium; these were aggregated into 1- μm secondary particles (Fig. 2). The pair distribution function (PDF) method, which directly probes a local atomic-scale structure by examining atomic correlations, gave the answer that the local ordering of Sony's SnCo was similar to that of crystalline SnCo. This material could be described as a nanocrystalline Sn–Co stabilized by C and Ti. The discharge and charge curves of Sony's SnCo anodes are characteristic of single-phase behavior. A discharge capacity of 550 mAh g^{-1} was obtained in the first cycle, corresponding to an irreversible capacity loss of 150 mAh g^{-1} , which reached

about 25% of the whole capacity. The electrode stabilized at 400 mAh g^{-1} for 30 cycles at 0.5 mA cm^{-2} , which was much superior than crystalline SnCo and Sn. Dahn et al. also tested the cycling performance of a commercial 14430 Nexelion cell from a Sony battery pack [26]. They used a $\sim 1\text{C}$ charge/discharge rate for the first 30 cycles, and the battery was charged at $\sim C/3$ and discharged at $\sim 1\text{C}$ for the 30 to the 375th cycles and at a $\sim C/3$ rate for the rest 225 cycles. After 600 cycles, the capacity was still above 600 mAh . However, the high price and toxicity of Co did not allow market penetration beyond the initial camcorder application.

3.3 Sn–Fe–(C) System

Encouraged by the success of Sony's Sn–Co–C anode, research focused on Sn–M (M is the inactive metal) materials, such as Sn–Cu alloy, Sn–Ni alloy, Sn–Fe alloy and Sn–Co alloy. The introduction of the electrochemically inactive metal M serves as a sink to hold the tin so that it is less reactive with the electrolyte than free tin metal. A carbon coating further protects the Sn–M compounds from side reactions. The reaction equation for Sn–M (M is the inactive metal) alloy during the lithiation and delithiation process can be summarized as follows:

Fig. 2 SEM (a) and TEM (b) images of the amorphous tin–cobalt anode. Reproduced with permission from Ref. [25]. Copyright 2007, IOP Publishing Ltd.

For Sn–Co, Sn–Fe, Sn–Ni and Sn–Cu systems, the practical volumetric capacities of some common intermetallic compounds, shown in Table 1, are in the following order: Sn_5Fe (2517 Ah L^{-1}) > Sn_2Co (2323 Ah L^{-1}), Sn_2Fe (2324 Ah L^{-1}) > Sn_4Ni_3 (2231 Ah L^{-1}) > Sn_5Cu_6 (2056 Ah L^{-1}). Among them, Fe is non-toxic (environmentally friendly) and the least expensive (abundant), so is the obvious choice. Mao et al. [27] prepared intermetallic phases and mixtures in the Sn–Fe–C Gibbs' triangle by mechanical alloying methods or by direct melting of elemental powders. The experimental capacity for Sn_2Fe was 800 mAh g^{-1} . During the first charge of such cells, about 650 mAh g^{-1} of Li can be extracted up to 1.5 V. Sn_2Fe reacts in Li/ Sn_2Fe cells to form lithium-tin alloys and very small metallic iron grains [28]. Nwokeke et al. [29] detected superparamagnetic iron (and/or tin-doped iron) nanoparticles during discharge by both electron paramagnetic resonance (EPR) and Mössbauer spectroscopy. Magnetic measurement by Dong et al. [30] showed that the particle size of Fe was about 3 nm. Some Fe particles of a larger size (5–10 nm) could remain after the first charge. Unreacted Fe accumulation continues upon the second delithiation process, approaching those of metallic Fe. Such coarsening contributed to the capacity loss upon cycling [28, 30].

Similar to FeSn_2 , CoSn_2 alloy could deliver an initial discharge capacity of 602 mAh g^{-1} with Coulombic efficiency of 85% [31]. The high capacity in CoSn_2 and FeSn_2 might be explained by the crystal structure. The open channels located within CoSn_2 and FeSn_2 crystal lattices, which are parallel to the [001] direction, are surrounded by adjacent Sn atoms, promoting the penetration and alloying of Li^+ with the Sn host [31–33]. For other Sn–Fe or Sn–Co alloy, such as Fe_5Sn_3 , Fe_3Sn_2 , FeSn , Co_3Sn_2 and CoSn , the channels are smaller, distorted and/or mixed with Sn atoms and transition metal atoms, which limited Li^+ transport. Wang et al. [34]

synthesized monodisperse nanospheres of the intermetallic FeSn_5 phase via a nanocrystal conversion protocol using pre-formed Sn nanoparticles as templates and resolved the new phase structure, shown in Fig. 3a. FeSn_5 belongs to the tetragonal phase in the $P4/mcc$ space group, along with the defect structure $\text{Fe}_{0.74}\text{Sn}_5$. The lattice parameters of $\text{Fe}_{0.74}\text{Sn}_5$ were refined as $a=b=6.91369 \text{ \AA}$, $c=5.88967 \text{ \AA}$. It has a lot of similarities with that of FeSn_2 (Fig. 3a, b). It has proved that FeSn_5 is one intermediate phase between Sn and FeSn_2 [34–36]. $\text{Fe}_{0.74}\text{Sn}_5$ has a high capacity of 750 mAh g^{-1} (Fig. 3c), but a poor cycle life. Xin et al. synthesized MSn_5 ($M=\text{Fe}$, Co and FeCo) nanoparticles with the same crystal structure, identical particle surface morphology and a similar particle size distribution (30–50 nm) (Fig. 3d–f), which are ideal for a comparison of the electrochemical performance, reaction mechanisms, thermodynamics and kinetics. FeSn_5 , $\text{Fe}_{0.5}\text{Co}_{0.5}\text{Sn}_5$ and CoSn_5 phases belong to tetragonal structure in the $P4/mcc$ space group. They all had a core–shell structure consisting of a ~30-nm single-crystalline intermetallic core and a ~4-nm amorphous oxide shell. During the charge/discharge process, some cracking of the FeSn_5 nanoparticles could be clearly observed after the first cycle, while $\text{Fe}_{0.5}\text{Co}_{0.5}\text{Sn}_5$ and CoSn_5 almost kept their original morphology. After 100 cycles, only the Fe signal could be detected in the region of TEM image, indicating the separation of Fe from Sn and aggregation of Sn particles may result in a quick capacity decline of FeSn_5 [37].

This issue of capacity decay needs to be addressed. In general, the method of ball milling is favored by industry. Dahn reported earlier on the Sn–Fe system including Sn_2Fe –C and $\text{Sn}_2\text{Fe}/\text{SnFe}_3\text{C}$ active/inactive composites [27, 38]. A microscopic mixture of 25% Sn_2Fe (active) and 75% SnFe_3C (inactive) shows 200 mAh g^{-1} with good capacity retention for 50 cycles. Using the mechanochemical method, which is low cost, facile and easily scaled up, a Sn–Fe–C composite was prepared [10]. Ti, Al and Mg were used as the reducing agents with different grinding media. The result showed that these nanosized Sn–Fe–C-based alloys produced by titanium reduction have much better capacity retention. Similar to Ti in Sony's amorphous SnCoC anode, the role of titanium was probably to stabilize the compound. For grinding media (soft iron, hard iron and zirconia), the material of Ti-reducing agents with soft iron balls displayed higher capacity than graphitic carbon even after 280 cycles. Figure 4a–f shows the comparison between nanosized Sn–Fe–C alloy with Ti as a reducing agent prepared by using a soft steel grinding medium and Sony's SnCoC material. The discharge and charge rate capabilities of Sn–Fe–C composites were superior to that of commercial SnCoC anodes without the need of expensive cobalt.

Further, Dong et al. [39] optimized the total grinding time, the graphite content, the carbon type and the Ti

Table 1 Lithiated density, gravimetric and volumetric capacity of Sn, Sn_5Fe , Sn_2Fe , Sn_2Co , Ni_3Sn_4 and Cu_6Sn_5 for the formation of $\text{Li}_{4.4}\text{Sn} + M$ compared with Li metal and graphite

Alloy	Lithiated density	Gravimetric capacity (mAh g^{-1})	Volumetric capacity (Ah L^{-1})	Volume expansion (%)
Li	0.534	3860	2062	Infinite
Graphite	2.16	372	804	10%
Sn	2.58	993	2562	258%
Sn_5Fe	2.71	929	2517	242%
Sn_2Fe	2.89	804	2324	250%
Sn_2Co	2.92	796	2323	265%
Sn_4Ni_3	3.08	724	2231	234%
Sn_5Cu_6	3.40	604	2056	174%

Fig. 3 **a, b** FeSn₅ and FeSn₂ crystal structures from the [001] view direction; **c** reversible capacities of FeSn₅ and FeSn₂ nanospheres as anodes in Li-ion batteries. Reproduced with permission from Ref. [34]. Copyright 2011, American Chemical Society. **d–f** SEM; **g–i**

HRTEM; and **j–l** STEM–EDS elemental mapping images of FeSn₅, Fe_{0.5}Co_{0.5}Sn₅ and CoSn₅ nanospheres. Reproduced with permission from Ref. [37]. Copyright 2015, The Royal Society of Chemistry

content. They showed that the optimum mechanochemical synthetic conditions are mixing SnO, Ti and graphite with a molar ratio of 1:0.25:10 and total grinding time of 8 h by using hard balls. Such optimized Sn–Fe–C composite could deliver 2.4 Ah mL⁻¹ for the first charge and maintain 60% of its original capacity for 170 cycles at a C/10 rate. The Sn–Fe–C composite also displayed excellent rate capability with 1.6 Ah mL⁻¹ over 140 cycles at a 1C rate, corresponding to about double that of graphite displayed in Fig. 4g, h. Interestingly, the capacity after the first cycle was larger than that of the formation of Li_{4.4}Sn and LiC₆, and some highly saturated LiC₂ could be invoked.

3.4 The Design of Sn–Fe–(C) and Sn–C Nanostructure Materials

Design and exploration of nanostructure materials are effective methods to improve the electrochemical performance of Sn-based alloy, which could reduce the absolute

volume change, shorten ion and electron transport lengths, and benefit permeation of electrolytes, thus enhancing the reaction kinetics during the lithium insertion/extraction process. Dispersing Sn–(Fe) alloy nanoparticles in a carbon matrix with some void space can alleviate the volume expansion, which could largely improve the electrochemically cycling and rate performance, such as Fe_{0.74}Sn₅@ reduced graphene oxide nanocomposites [40]. Among them, pyrolysis of carbon matrix precursors with Sn–(Fe) sources toward preparation of nanostructured materials has received researchers' much attention. Table 2 summarizes electrochemical performance including the voltage range, the mass loading, the ratio among active materials, the binder and carbon, initial Coulombic efficiency and cycling stability of some typical Sn–(Fe)–C alloys with different structures [41–54]. Although the introduction of a carbon source (graphene, amorphous porous carbon, ordered mesoporous carbon and carbon nanotubes/nanofibers) and void space can bring good electrochemical

Fig. 4 Lithium removal and insertion rate capability of Sn–Fe–C alloy in the voltage range of 0.01–1.2 V (a, b), 0.01–1.5 V (c, d) and the corresponding capacity retention (e, f) with Sony's amorphous SnCo anode. Reproduced with permission from Ref. [10]. Copyright 2011, IOP Publishing Ltd. **g, h** Volumetric capacity of optimized Sn–Fe–C composites cycled under C/10 and 1C. Reproduced with permission from Ref. [39]. Copyright 2016, Wiley

performance, more than 1000 cycles with high gravimetric capacity, the volumetric energy density may be greatly reduced. Moreover, the structure of porous, or void, or large surface areas will need a large amount of electrolytes.

Xin et al. [36] designed a series of nanosized Sn₅Fe alloys, which was derived from the chemical transformation of pre-formed Sn nanoparticles as templates. Their results show that Sn₅Fe alloy is the main phase at lower temperature and that Sn₂Fe always exists in higher temperature, even with a high Sn ratio. The stability of Sn₅Fe alloy decreases with increasing temperature. Both the composition and the morphology of Sn–Fe alloy can be controlled by adjusting temperature and reagent molar ratios. Figure 5a–h shows the primary particle sizes of the four Sn–Fe alloys are tens of nanometers, and the morphology changes with the

increasing Fe reactant content from spherical to cubic and to ultrasmall/irregular particles. The composition is Sn₅Fe for Sn–Fe-1 and Sn–Fe-2, Sn₅Fe@Sn₂Fe for Sn–Fe-3 and Sn₂Fe for Sn–Fe-4, shown in Fig. 5i–p. Furthermore, the Sn–Fe-3 sample with Sn₅Fe@Sn₂Fe displays core–shell structure, where the shell is Sn₂Fe with a core of Sn₅Fe. The formation mechanism was as follows: Sn₅Fe was first formed by using Sn as a template when the Fe reactant content was low; gradually, Sn₅Fe was transferred to Sn₂Fe from the surface of the particles as more and more Fe reactants were added; finally, Sn₂Fe will spread through the whole particles.

Cycling and rate performance of a series of Sn–Fe alloys was tested in the voltage range of 0.01–1.5 V, displayed in Fig. 5q–r. Sn–Fe-1 material with Fe defects had ~1.43 Ah mL⁻¹ for 25 cycles, and then, the capacity quickly decayed

Table 2 Summary of structures, voltage ranges, mass loading, ratios among active materials, binders and carbon, initial Coulombic efficiency, cycling stability of some Sn–(Fe)–C alloys as anodes in lithium-ion batteries

Sn–(Fe)–C alloy with different structures	Voltage range (V)	Mass loading (mg cm^{-2})	Active material/binder/carbon	Initial Coulombic efficiency (%)	Cycling stability				Reference
					Current density	Cycling number	Capacity (mAh g^{-1})	Capacity retention (%)	
Nanoporous Sn–Fe@C	0.01–2.0	–	70:15:15	–	0.1 A g^{-1}	100	441	57	[41]
Ultrafine Sn–Fe alloys in hierarchical carbon frameworks	0.01–2.0	–	80:10:10	55	0.1 A g^{-1}	500	516	62.5	[42]
Ultrafine Sn in hierarchically porous N-doped carbon	0.05–3.0	0.1–0.15	80:10:10	78.5	0.1 A g^{-1}	300	788	92.4	[43]
Double-shelled hollow carbon spheres confining tin	0.01–3.0	0.9–1.2	80:10:10	62	0.1 A g^{-1}	130	1100	77.8	[44]
Graphene-confined Sn nanosheets	0.05–2.0	–	80:10:10	66.5	50 mA g^{-1}	60	590	64	[45]
Graphene networks anchored with Sn@graphene	0.005–3.0	–	80:10:10	69	0.2 A g^{-1}	100	1089	87.5	[46]
Uniform nano-Sn/C composite	0–3.0	1.0	70:15:15	69	0.25C	130	710	100	[47]
Ultra-small Sn nanoparticles embedded in nitrogen-doped porous carbon	0.01–2.0	–	80:10:10	75	0.2 A g^{-1}	200	722	95.4	[48]
Encapsulated Sn nanoparticles in amorphous carbon nanotubes	0.01–2.0	1.5	70:10:20	63.2	0.2 A g^{-1}	100	749	71	[49]
Sn-based nanoparticles encapsulated in a porous 3D graphene network	0.005–3.0	1.5	80:10:10	63	2 A g^{-1}	1500	566	80	[50]

Table 2 (continued)

Sn-(Fe)-C alloy with different structures	Voltage range (V)	Mass loading (mg cm^{-2})	Active material/binder/carbon	Initial Coulombic efficiency (%)	Cycling stability				Reference
					Current density	Cycling number	Capacity (mAh g^{-1})	Capacity retention (%)	
Inserting Sn nanoparticles into the pores of TiO_{2-x} -C nanofibers	0–3.0	–	80:10:10	67	0.1 A g^{-1}	200	957	91.6	[51]
Tailored yolk-shell Sn@C nanoboxes	0.005–3.0	1.0	80:10:10	61	0.2 A g^{-1}	500	810	90	[52]
Ultrasmall Sn nanoparticles embedded in spherical hollow carbon	0.05–2.0	1.5–2.0	80:10:10	71.9	4.0 A g^{-1}	6000	423	92.1	[53]
Ultrasmall Sn nanodots embedded inside N-doped carbon microcages	0.005–2.0	0.8	80:10:10	55	1 A g^{-1}	1600	437	74.2	[54]

to $\sim 0.64 \text{ Ah mL}^{-1}$ after 100 cycles. Sn-Fe-2 material with richer Fe delivered a capacity of $\sim 1.48 \text{ Ah mL}^{-1}$ for 25 cycles and still kept 1.31 Ah mL^{-1} after 100 cycles. The Sn-Fe-3 sample with core-shell structure shows superior capacity retention, in which the capacity maintained 1.55 Ah mL^{-1} after 200 cycles at the C/2 rate, corresponding to nearly 100% of the initial capacity and $\sim 90.2\%$ of the highest charging capacity. The average capacity loss of Sn-Fe-3 anodes was only 0.049% per cycle according to 90.2% capacity retention, and Coulombic efficiency exceeded 99.5% for most of the cycles. The capacity of Sn-Fe-4 electrodes with the highest initial capacity gradually dropped. Therefore, the calculated volumetric capacity of the core-shell anode, Sn-Fe-3, is close to twice that of carbon (0.8 Ah mL^{-1}) after 200 cycles. Further, the core-shell Sn-Fe-3 electrode could deliver 94.8%, 84.3%, 72.1% and 58.2% of the 0.1C capacity at 0.2C, 0.5C, 1C and 2C and show the best maintenance of capacity after 90 cycles among the four samples.

4 Toward Commercialization

4.1 Key Requirements of Anode in Commercialization

To satisfy the high energy requirement of commercial anode, several parameters are really important.

4.1.1 Volumetric Capacity

For all alloy-based anodes, the volumetric and gravimetric capacities of the active elements are higher than that of graphite. Further, volumetric capacities are more important in practical cells, no matter in portable communication electronics, battery electric vehicles, plug-in hybrid electric vehicles or hybrid electric vehicles. For Sn-based materials, the theoretical volumetric capacity (2562 Ah L^{-1}) after lithiation is essentially the same as that of pure lithium (2062 Ah L^{-1}) and is 2.5 times larger than that of graphite. Sn-based materials are good candidates to replace graphitic carbon as the anode for the next-generation lithium-ion batteries. However, much of the research has only focused on gravimetric capacities or calculated with respect to alloy volume before lithiation. The true volumetric capacity must be calculated

Fig. 5 (a–d) SEM images, (e–h) TEM images, (i–l) SAED images and (m–p) HRTEM images zooming in local areas in corresponding TEM images of the four materials: Sn–Fe-1, Sn–Fe-2, Sn–Fe-3 and Sn–Fe-4; q–r cycling and rate performance of Sn–Fe-1, Sn–Fe-2, Sn–Fe-3 and Sn–Fe-4 samples. Reproduced with permission from Ref. [36]. Copyright 2019, American Chemical Society

in the fully charged state, as for these tin-based materials, the volume of the lithiated anode is much larger (approaching 300% larger) than that of Sn or Sn_yM. In contrast, the volume of the cathode changes by less than 10%. In addition, the introduction of a large porous/void structure or an inactive matrix will greatly reduce the volumetric energy

density; so even if the cycling performance is improved, it is not a positive approach. Using a mechanochemical method, we prepared a Sn–Fe–C alloy [39], which has superior discharge and charge rates than Sony's SnCoC anode. It also displayed a volumetric capacity of 1600 Ah L⁻¹ over 140 cycles at a 1C rate, corresponding to about double that of

graphite. For nanostructured Sn–Fe alloy [36], the volumetric capacity attained 1550 Ah L⁻¹ after 200 cycles at a current density of 0.5C, corresponding to nearly 100% of the initial capacity and ~90.2% of the highest charging capacity. The Coulombic efficiency exceeded 99% after the first cycles, showing that the performance is stabilized without the need of a large porous structure.

4.1.2 Working Voltage Range

In addition to the volumetric capacity, the working voltage range is another critical parameter for anode use. For graphite, it has an average voltage of 150 mV versus Li/Li⁺ and a flat voltage profile, rendering a high overall full cell voltage. For the Sn anode, the plateau voltage is 0.77, 0.69, 0.448, 0.446, 0.439, 0.437 and 0.426 V for Li₂Sn₅, LiSn, Li₇Sn₃, Li₅Sn₂, Li₁₃Sn₅, Li₇Sn₂ and Li₂₂Sn₅ (or Li₁₇Sn₄), respectively [55]. Although the voltage of Li–Sn alloy is a little higher than that of graphite, which will decrease the full cell voltage, it is safer than graphite as it inhibits the potential nucleation and growth of lithium dendrites. In addition, in the case of thermal runaways and fire, the energy of combustion is much less for tin- than for a carbon-based anode. The cycling stability of alloy anodes can be improved by controlling either lower or upper cutoff voltage ranges [14, 23], which controls volume expansion/contraction of particles and cracking/pulverization of electrodes. Moreover, the volumetric capacity at around 2 Li/Sn reaches more than double that of carbon, as shown in Fig. 1. However, there are a number of reports of Sn-based composites with different structures and morphology, a large range of voltage and a sloping voltage profile to get more gravimetric capacity, which will result in low working voltage in full cells. Table 2 summarizes the electrochemical performance of some Sn–(Fe)–C alloys in different voltage ranges; for example, it is too broad when the voltage range was set between 0 and 3.0 V.

4.1.3 Cycling Stability

The cycling life of a lithium-ion battery is the number of full charge–discharge cycles to reach 80% of the battery capacity. It is mainly affected by charge/discharge current density, voltage ranges and temperature [56]. For the half-cell, lithium metal was used as both counter and reference electrodes. Cyclable lithium is infinitely supplied from the lithium metal, and there is an excess electrolyte enough for its consumption. Tin-based materials in many reports can have long cycling with good capacity retention at high charge/discharge rates, as shown in Table 2 [43, 46–48, 51–53]. When a tin-based anode was combined with a cathode in a full cell, the lithium source and the electrolyte are limited. Any

consumption of cyclable lithium and electrolytes originating from the side reactions will lead to fast cycling deterioration in a full cell.

Other parameters, such as ratios among active materials, binders, carbon and mass loading of electrode, will all affect the cycling stability and energy density of anodes.

4.1.4 Choice of Electrolyte

The commercial electrolytes in lithium-ion batteries are non-aqueous solutions, in which normally the lithium hexafluorophosphate (LiPF₆) salt is dissolved in different organic carbonate solvents. These include ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC) and/or ethyl methyl carbonate (EMC). To improve the capacity retention and Coulombic efficiency of tin-based anodes, fluoroethylene carbonate (FEC) is always added into the electrolyte. Seo et al. [57] showed that cells containing either 5% or 10% FEC have the best capacity retention and the lowest electrochemical impedance. Yang et al. [58] revealed that the additive amount of 2% FEC is enough to derive the benefits in the cells when the current density is C/9. In Sony's patent, they tried different combinations of the electrolytes, showing that if the solvent contained FEC, the cycle characteristics were improved and the FEC content could be in a large range from 1 to 80 wt% [59]. A stable FEC-derived SEI layer may be the reason for improved cycling stability, while continuous electrolyte decomposition and variation in the composition and concentration of the SEI species are observed in EC-based electrolytes in Sn-based electrodes [60].

4.2 Challenge

At present, carbon-based materials cannot satisfy the ever-increasing energy density needs for mass deployment of EVs due to their low gravimetric/volumetric capacity (340 mAh g⁻¹ or 747 Ah L⁻¹). Ideally, lithium metal should be used, but it faces the challenge of formation and growth of dendrites. Tin-based materials with higher volumetric capacity and lower working voltage are scientifically one of the most promising candidates to replace graphite. Until now, various Sn-based materials have been designed and explored. However, some of them cannot meet the requirement of high energy density when volumetric capacity, working voltage ranges, mass loading, binders and carbon are considered. From Sony's SnCoC to our Sn–Fe–C or SnFe alloy, the first cycle capacity loss needs to be improved.

The irreversible capacity loss in the first cycle comes from (1) electrolyte decomposition/formation of the SEI film at the electrode/electrolyte surface. SEI films are mainly composed of Li₂CO₃ and lithium alkyl carbonates (ROCO₂Li)

in tin-based materials [61–63]. On cycling, the SEI film will become thicker and thicker, contributing to both initial Coulombic efficiency and the later capacity decay. (2) Reduction of the surface oxidized layer. The surface amorphous oxide layer always exists in Sn-based materials after exposure to air. Protesescu et al. [64] demonstrated that the surface of Sn nanoparticles was covered with shell1/shell2 structure of SnO/SnO₂ phases, using surface-enhanced nuclear magnetic resonance, Mössbauer and X-ray absorption spectroscopy. During the lithiation process, the surface-oxidized layer was reduced to Sn and Li₂O before Sn reacts with Li to form Li–Sn alloy. (3) Defective carbon. Defective carbon resulting from high energy milling is believed to be another major reason for the first cycle larger charge capacity. This is supported by Matsumura's results [65] that in addition to the graphitic layers storing lithium, the edge of graphitic layers and the surface of crystallites in disordered carbon formed from the ball mill process can also store lithium.

5 Conclusion and Future Prospects

From the beginning of 1997, tin-based materials have been considered as a possible substitute for carbon in lithium batteries due to their higher theoretical volumetric capacity than that of lithiated graphites. Encouraged by the success of Sony's 14430 battery (Sn–Co–C anodes), various Sn–Fe–C/Sn–Fe/Sn–C composites were evaluated as the anode for lithium-ion batteries. Compared with Sn–Co–C anodes, Sn–Fe–C alloy with lower price has superior discharge and charge rate capabilities. Further, the optimized Sn–Fe–C composite with a molar ratio of 1:0.25:10 and total grinding time of 8 h by using hard balls also displayed excellent rate capability with 1.6 Ah mL^{−1} over 140 cycles at a 1C rate, corresponding to about double than that of graphite. Sn_yFe nanostructured materials with core–shell structure also show superior capacity retention, in which the capacity could maintain 1.55 Ah mL^{−1} after 200 cycles at a C/2 rate, corresponding to nearly 100% of the initial capacity and ~90.2% of the highest charging capacity. In addition, for Sn–Co–C alloy, the high price and toxicity of Co will minimize its use in cost-sensitive application.

However, the first cycle capacity loss resulting from the side reaction of Sn–Fe–C or Sn–Fe alloy needs to be further reduced for commercialization. Some possible strategies include (1) thin and dense SEI films. To improve the cycling performance, fluoroethylene carbonate (FEC) as solvent was always added in the electrolyte. However, the introduction of FEC will lead to the formation of a thick SEI film. (2) The reduction of surface oxidized layers. Nanostructured materials can improve the electrochemical stability, but they will reduce the tap density, increase the consumption of SEIs and create more oxidized layers. The primary particles of

the four Sn_yFe nanostructured alloys are tens of nanometers in size and are covered with a 3–5-nm amorphous oxidized layer. It is critical for nanostructured materials to design micro-sized secondary particles consisting of nanosized primary particles. Moreover, prelithiation of Sn–Fe–C or Sn–Fe alloy anodes can directly eliminate the impact of the irreversible capacity loss. Different lithiated states can be obtained by electrochemical and chemical lithiation method.

In addition to possible use in lithium-ion batteries, tin-based materials are regarded as good candidates for sodium-ion batteries (SIBs), potassium-ion batteries (KIBs), magnesium-ion batteries (MIBs) and calcium-ion batteries (CIBs). They offer higher gravimetric and volumetric capacity in these alkali (earth)-ion batteries. Meanwhile, the reaction mechanism is likely similar in all the battery systems. The development and application of tin-based materials in LIBs provide insights for these other battery systems.

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