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Nano-sized Tin Oxide-Modified Graphite Composite as Efficient Anode Material for Lithium Ion Batteries

Chia-Chin Chang^{1,4,*}, *Li-Chia Chen*¹, *Tai-Ying Hung*², *Yuh-Fan Su*¹, *Huang-Kai Su*¹, *Jarrn-Horng Lin*², *Chih-Wei Hu*³, *Lakshmanan Saravanan*⁴, *Tsan-Yao Chen*³

¹ Department of Greenergy, National University of Tainan, Tainan 70005, Taiwan

² Department of Material Science, National University of Tainan, Tainan 70005, Taiwan

³ Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30013, Taiwan

⁴ R & D Center for Li-ion Battery, National University of Tainan, Tainan 70005, Taiwan *E-mail: <u>ccchang@mail.nutn.edu.tw</u>

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Nano-sized tin based compounds dispersed graphite composites, synthesized by the electroless plating process and pyrolysis method, act as efficient anode materials for lithium ion batteries (LIBs). The nano-sized tin complexes on the graphite surface can be obtained through a simple chemical reaction between $Sn(BF4)_2$ and $Na_2S_2O_4$ in aqueous solution and completely converted to SnO_2 after pyrolysis. The synthesized tin-modified graphite composites were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and high-resolution transmission electron microscopy (HRTEM). The electrochemical performance of the composites for application as anode materials in lithium-ion batteries was investigated. The average particle size of nano-SnO₂ is ~14.7 nm, as determined by HRTEM. Results of infrared spectra and electrochemical properties indicate that such an optimized nano Sn-based compound on graphite influences the formation of the thin solid electrolyte interface (SEI) in the electrode and thus improves the cycling performance, with high efficiency of 97.3% in LIBs. Nyquist plots show that during Li⁺ intercalation, the thin SEI film and the low charge transfer resistance of SnO₂-modified graphite composite anode plays important roles in improving the electrochemical properties of LIBs.

Keywords: Graphite; SnO₂; Anode; Electroless method; Lithium ion battery

1. INTRODUCTION

Lithium ion batteries (LIBs) have attracted tremendous attention from the academic and industrial sectors due to their substantially high energy and power density as compared to existing energy storage devices [1-3]. In general, graphite or carbon-based materials are widely used as the

anode in commercial LIBs owing to their lower potential plateau, acceptable capacity, and low cost [4]. However, their insufficient electrochemical performance (e.g. energy density, capacity) hinders the application of carbon materials in public transportation markets.

Sn-based composite oxides and alloys have an impressive specific capacity that overcomes the long-standing issues of the carbon anode in a LIB [5]. However, Sn-based composite anode materials exhibit rapid capacity fading owing to the pulverization and structural destruction of electrode materials caused by large changes in volume and severe particle aggregation during cycling. Recently, it has been found that Sn-based composites in combination with ductile carbon materials could effectively alleviate the multi-cycle capacity fading [6]. In such a configuration, carbon materials provide sufficient local space for facile accommodation of volume expansion, thereby preventing aggregation of Li_xSn during lithiation/delithiation processes. Furthermore, SnO₂ particles are not only a high capacity Li-intercalation material but also enhance the lithiation/delithiation behaviors of SEI between the electrolyte and the graphite surface [7]. For Sn composites/carbon anodes, nano-sized and uniformly distributed tin compounds can achieve better electrochemical performance [8-10].

There are many ways to prepare Sn compounds on graphite anode materials, such as highenergy ball-milling [11], the hydrothermal process [12], the hydrolysis method [13], microemulsion techniques [14], the pyrolysis technique [15], electroplating [16], and electroless plating [17]. Electroless plating is an efficient method to deposit Sn-based compounds on graphite for LIB application. Various Sn-based compounds, including Sn nanoparticles [18] on nanoporous Au, Sn thin film [19] for Sn-Cu alloy, a Sn-Ni alloy layer [20], Sn-P-O compounds [17], a SnO₂/Cu layer [21], Sn-Zn film [22], and Ni-Sn-P compounds [23] prepared by electroless plating have been reported. In this study, we focused mainly on synthesizing a SnO₂-modified graphite composite anode with an optimized small quantity (~5%) of nano-sized SnO₂ (14.7 nm) dispersed homogeneously on graphite surface. This article describes mainly the formation of a highly stable SEI that preserves the high ionic conductivity to increase the diffusion of Li⁺, and the presence of Sn/SnO₂ nanoparticles increases the electron transport and protects the graphite surface from electrolyte decomposition.

In this study, we developed a composite anode of graphite deposited with nano-size tin based compounds (tin sulfide and/or tin oxide) by combining electroless plating and pyrolysis methods. The effects of electroless plating conditions on the composition, morphology, crystal structure and particle size of the Sn-based composites on graphite, and their electrochemical performance when applied as the anode in LIBs, were investigated.

2. EXPERIMENTAL

2.1 Preparation of Sn-graphite composite anode

Natural graphite powders (China Steel Chemical Co., Taiwan) with an average particle size of 19.89 nm and a Brunauer-Emmett-Teller (BET) surface area of 5.0 m² g⁻¹ was used in the process. The electroless plating process and pyrolysis methods were employed to modify Sn-based complexes on the graphite anode surface by the following process. First, a metal-precursor solution was prepared by

dissolving 50 ml of Sn(BF₄)₂ (50% aqueous solution, Acros Organics) and 41.5 ml of HBF₄ (35% aqueous solution, Panreac) in 408.5 mL of de-ionized water under stirring at various controlled (bath) temperatures, and natural graphite (NG) powder was then added into the solution. Subsequently, an appropriate amount of Na₂S₂O₄.5H₂O (99.5%, Hsing Chia Chemical Industrial Co.) solution with 50 ml of HBF₄ was immediately added into the metal solution and strongly stirred at the same temperature for 30 min.

The Sn-based modified graphite powder was filtered from the solution and then rinsed with deionized water and alcohol to remove the residual sulfur until the pH value of the rinsing water reached 7. After the rinsing, the resultant powder was dried in a conventional vacuum oven, at room temperature for 3 h and then increases to 90 °C in 30 min in vacuum before being dried for another 12 h. Finally, the powder was sieved with 200 μ m mesh and defined as Sn-modified graphite. The Snmodified graphite powder was further annealed in a furnace at 450 °C under N₂ atmosphere for 2 h, and the obtained powder was defined as annealed Sn-graphite.

2.2 Material analysis

A scanning electron microscope (SEM, JEOL JSM35 operating at 20 kV) and energy dispersive spectroscopy (EDS) were used to evaluate the surface morphology and perform surface semiquantitative analysis of the various graphite anodes, respectively. The crystal structure was determined primarily by means of powder X-ray diffraction (XRD) using a RIGAKU D/MAX2500 diffractometer, Cu K α radiation, and a scan range of 20–80 degrees.

After three charge-discharge processes, the anodes were rinsed with DEC to remove the electrolyte and dried out under vacuum at 90 °C for 2 h before further material analysis. The morphology and particle size of the Sn-based nanoparticles dispersed on graphite were observed by using a transmission electron microscope (Philips/FEI Tecnai 20 G2 S-Twin transmission electron microscope including a CCD camera with the Diffpack program for diffraction pattern analysis and FEI E.O Tecnai F20 G2 MAT S-TWIN field emission gun transmission electron microscope) with digital micrograph software. Particles selected from random regions were analyzed for structural characterization by high resolution transmission electron microscopy (HRTEM). The particle size distribution was measured by image analyzer (Optimas and Quiantikov). Infrared absorption spectra were recorded *ex-situ*, with a Perkin-Elmer Spectrum 100 FTIR system. All spectra were recorded at room temperature using an attenuated total reflectance (ATR) mode with a resolution of 2 cm⁻¹ and a total of 128 scans.

2.3 Electrochemical measurements

An electrolyte of 1 mol dm⁻³ LiPF₆ in a 50:50 w/w mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was used in all tests. The electrochemical behaviors of pristine, Sn-modified graphite, and annealed Sn-graphite anodes were measured in the potential range of 0-2 V with an Autolab electrochemical analyzer (Autolab PGSTAT30, Eco Chemie) with a scanning rate of 0.1 mVs⁻

¹. Half-cells were fabricated with standard CR2032 coin cell hardware. In a constant current mode, the charge/discharge cycle behavior was evaluated galvanostatically at 0.325 mA cm⁻² over the range of 0.003–2.0 V. All the above experiments were performed in a glove box filled with argon. The electrochemical impedance spectroscopy (EIS) test of all the graphite electrodes was measured after 3 cycles to further investigate the mechanism of the enhanced electrochemical performance of the SnO₂-graphite composites. EIS measurement was performed on the coin cell by coupling the potentiostat with an Autolab frequency response analyzer locked in an amplifier and an impedance phase analyzer. A sinusoidal amplitude modulation of \pm 10 mV was used over a frequency range of 0.01 Hz to 1 MHz.

3. RESULTS AND DISCUSSION

3.1 The effects of Na₂S₂O₄ concentration on Sn-modified graphite anodes



Figure 1. Cycling performance of pristine graphite (1, black) and the graphite anodes modified by 0.25 (2, red), 0.5 (3, blue), and 1 (4, green) mol dm⁻³ Na₂S₂O₄. The modified reactions were all in Sn(BF₄)₂ solution with the same concentration at 60 °C.

The cycling performances of the various concentrations of $Na_2S_2O_4$ reductant on Sn-modified graphite anodes are shown in Figure 1. As indicated, the capacity of the pristine graphite remained steady in the first 10 cycles and then progressively decreased by 0.6% per cycle (vs. *C*₀) until the 50th cycle. Such a fading rate could be attributed to passivation-induced irreversibility caused by the formation of Li⁺-O-C complexes at defect sites on the graphite surface. In treated with a solution of 0.25 mol dm⁻³ Na₂S₂O₄, the irreversibility of the Sn-modified graphite was completely eliminated at the 50th cycle (curve 2). Further increasing the Na₂S₂O₄ concentrations to 0.5 (curve 3) and 1.0 (curve 4)

graphite anodes were also examined.

mol dm⁻³ resulted in dramatic fading of the capacity of the Sn-modified graphite anode. The significantly different behaviors of the anode modified by 1 mol dm⁻³ Na₂S₂O₄ could be ascribed to a high sulfur content. Such an impurity induces a large irreversible reaction in subsequent charge-discharge processes, leading to the formation of a thick solid electrolyte interface (SEI) on the graphite surface [24]. Based on the above results, 0.25 mol dm⁻³ Na₂S₂O₄ was chosen for reaction with a metal precursor, Sn(BF₄)₂, to form the Sn-based composites on a graphite surface. To obtain the composite

with optimum performance, the effects of the plating temperature on the capacity of Sn-modified

3.2 The effects of plating bath temperature on Sn-modified graphite anodes

Figure 2. SEM images of (a) pristine graphite and the Sn-modified graphite reacting with 0.25 mol dm⁻³ Na₂S₂O₄ at (b) 40, (c) 60 and (d) 80 °C. Inset in (d) shows the annealed Sn-graphite sample (SnO₂ nanoparticles on graphite).

Table 1. EDS results of the Sn-modified graphite powder expressed as weight percentage.

Element (wt.%)					
Plating bath	С	0	S	Sn	
Temp.					
40 °C	91.98	1.67	1.68	4.67	
60 °C	94.47	2.09	0.80	2.64	
80 °C	90.51	5.17	0.34	3.98	

SEM images of Sn-modified graphite anodes prepared at different bath temperatures are shown in Figure 2. Accordingly, nanoparticles of the Sn-based compound were distributed on the graphite surface, and their density and size increased with increases in the preparation temperature. Constituents with the corresponding compositions of experimental samples were determined by EDS analysis. As shown in Table 1, the weight ratio of O atoms increased along with the reaction temperature, whereas that of S atoms followed the opposite trend. Such a phenomenon can be explained by the reaction kinetics of the reduction agent (Na₂S₂O₄) with Sn. at defect sites on the graphite surface. Given that identical reaction times were used for the reduction of complexes $(S_2O_4^{2-})$ to Sn cations in all samples, uncompleted Sn decoration defects on the graphite surface could be expected. In this condition, an amorphous Sn(S₂O₄)₂ complex layer formed on the graphite surface. Increasing the plating bath temperature higher than 80 °C, substantially increased the O content to 5 wt%, implying the formation of tin oxide (SnO₂) on the graphite surface. At such a high temperature (~80 °C), the rates of the formation of Sn-S complexes and their subsequent condensation and dissociation into Sn dramatically increased. Therefore, the formation of multi-phase SnO₂ was facilitated on the heterogeneous graphite surface. This finding was further confirmed by XRD analysis. As shown in Figure 3, SnS and SnS₂ phase appeared in the Sn-modified graphite anode after plating at 60 °C [24-26], while SnO₂ appeared after pyrolysis, as will be discussed below. In agreement with the results of EDS analysis, amounts of pure Sn and S gradually decreased with increasing temperature in the electroless plating solution. Those results indicated the simultaneous formation of tin oxides and sulfides on the graphite surface in an electroless plating treatment. Furthermore, the deposited tin compounds could be well-controlled to be either nano-sized or amorphous.



Figure 3. XRD of pristine graphite (1, black), the Sn-modified graphite reacting with 0.25 mol dm⁻³ Na₂S₂O₄ at 40 (2, green), 60 (3, red) and 80 °C (4, blue), and the annealed Sn-graphite (5, purple).

Cyclic voltammetry measurement was employed to determine the redox reversibility and kinetics of pristine and Sn-modified graphite with lithium ions. Cyclic voltammograms (CVs) of the first scan of graphite electrodes are shown in Figure 4(a). For the anode with pristine graphite (curve (1)), the broad peak starting at 0.90 V and centered around 0.70 V, presumably revealed the formation of a passivation film [13, 36, 27]. The potential for lithium insertion is ~0.0–0.2 V, whereas the potential for lithium extraction is ~0.5 V [28].



Figure 4. (a) CVs of the first cycle for pristine graphite (black, 1) and the Sn-modified graphite reacting with 0.25 mol dm⁻³ Na₂S₂O₄ at 40 (green, 2), 60 (red, 3) and 80 °C (blue, 4). (b) CVs of the first cycle for pristine graphite (black, 1), the Sn-modified graphite (60 °C, blue, 3), and the annealed Sn-graphite (red, 5)

Compared to that of pristine graphite (curve (1)), various peaks appeared in the CVs of Snmodified graphite anodes (curves (2), (3), and (4)). The cathodic peaks at ~1.75 and ~1.25 V were ascribed to reactions, including the formation of Sn metal, Li₂S, the intercalation of Li ions into SnS or SnS_2 [26, 29-32], and the formation of the solid electrolyte interface (SEI) [26]. In the lithiation process in the first scanning cycle, a small hump in the potential range of 0.2–0.6 V appeared in the CVs of pristine graphite and was attributed to the formation of Sn_xLi_y alloys [27]. As compared to the CVs of pristine graphite, the further enhanced peak intensity at 0.2–0.4V indicated a reduced formation energy (facilitated crystal growth) of the Sn_xLi_y alloy in the Sn-modified graphite, and an anodic peak at 0.60 V was assigned to lithium de-alloying [33]. The magnitudes of lithiation and de-lithiation peaks for the Sn_xLi_y alloys were significantly decreased, indicating a reduction of the reversible capacity with increasing CV cycles.

As shown in Figure 4(a), the reversibility of lithium insertion/de-insertion between 0 and 0.4 V was obviously enhanced by depositing the proper amount of tin on the graphite surface by electroless plating at 60 °C (curve (3)). The structural evolutions between SnS and SnO (or SnO₂) with respect to plating temperature of the Sn complex were complementarily elucidated by cross-referencing the results of XRD (Fig. 3) and EDS (Table 1). These results showed that the Li intercalation/deintercalation behavior at graphite electrodes corresponded to the amount of tin compounds decorating the surface. The amount of Sn complex / Sn oxide was defined by the density of sulfuric complexes on the graphite surface and was possibly controlled by the plating temperature (i.e., the reaction kinetics of $Sn-S_2O_4$ complexes followed by oxidation) [32]. For the composite prepared in the electroless plating condition at 40 °C, the presence of large amounts of tin, sulfur, and multiple phases of tin oxide on the graphite surface were responsible for its irreversible capacity loss, which was the largest among all the samples. Also, the size of the tin oxide nanoparticles on the graphite surface was larger than that of low-temperature samples (Fig. 2(d)). The lithium insertion/de-insertion currents between 0 and 0.4 V may have been hindered by the larger particle size and the presence of impurities on the graphite surface. These cathodic peaks at around 0.6, 1.25, and 1.75 V almost disappeared after scanning for 4 cycles due to the irreversible reduction of SnS and SnS₂, and the oxidation of Li₂S at 1.9 V [26, 32].

The electrochemical behavior of the annealed Sn-graphite anode is illustrated in Figure 4 (b), along with the curves of Sn-modified and pristine graphite anodes for comparison. It should be noted that the signals indicating the reaction between Li-ion and SnS₂ at 1.75 and 1.25 V disappeared, while on the other hand, the cathodic peak related to the formation of Sn metal and Li₂O was present at around 1.0 V [34-37]. The impurities such as tin, sulfur, and tin sulfide on the graphite surface were transferred to tin oxide (SnO₂) by thermal treatments, which was confirmed by the significant SnO₂ peaks in the XRD (Fig. 3, curve 5). Based on the literature [38], it was also considered that the SnO₂ nanoparticles would protect the surface of the carbon substrate (graphite) from SEI formation. The reversible properties and the lithium insertion/de-insertion currents between 0 and 0.4 V were obviously enhanced by annealing at 450 °C. From Fig. 4 (a) and 4 (b), it is clear that the reversibility of Li-graphite intercalation/de-intercalation was enhanced in the Sn-modified graphite anode prepared at 60 °C electroless plating and at 450 °C annealed Sn-graphite anodes, with SnO₂ nanoparticles (NPs) dispersed on the graphite surface (Inset in Figure 2 (d)). It was initially assumed that SEI films formed only in graphite materials. However, it was subsequently found that SEI films are also common in Snbased anode materials, and that they have a great influence on the performance of electrodes. Our result is also in agreement with this concept and suggests that Sn-based composites may be highly involved in the formation of an SEI film on the graphite surface to improve the lithiation/delithiation process.

The cycling performances of the Sn-modified graphite anodes prepared at different temperatures are compared with that of pristine graphite in Figure 5. It can be clearly seen that the Sn-modified graphite anodes prepared at 60 and 80 °C had better cycling performance than those of anode prepared at 40 °C and pristine graphite, exhibiting an initial capacity value of 360 mAh g⁻¹. The formation of tin oxides and tin sulfides on the graphite surface was expected to derive inactive tin species as buffers to prevent particle aggregation of the tin during the cycling process. It has previously been reported [14] that the active sites on the graphite surface help to bind and stabilize the SnO₂ particles and thereby reduce the mobility of the particles on the graphite surface, suppressing particle agglomeration. They also buffer the volume changes during cycling (Li-ion intercalation and de-intercalation reactions) and enhances Li-ion storage, resulting in higher capacity retention and good cyclic performance.



Figure 5. Cycling performances of pristine (●), and Sn-modified graphite anodes reacting with 0.25 mol dm⁻³ Na₂S₂O₄ at 40 (Δ), 60 (■) and 80 °C (*).

To eliminate the effect of residual sulfur (S) on the cycling performance, the Sn-modified graphite anode obtained at 60 °C was annealed at 450 °C for 2 h (Note that the evaporation point of S is 444.7 °C). The formation of SnO₂ after this pyrolysis was clearly observed by XRD, as shown in Figure 3 [35], while no significant differences in surface morphology between the Sn-modified graphite and annealed Sn-graphite anodes were found. TEM images of the annealed Sn-graphite anode are shown in Figure 6. It can be clearly observed that the SnO₂ nanoparticles preferred to deposit on the edge plane of graphite rather than on the basal plane. This preference may have been due to the

effect of the functional groups on the edge of graphite, such as –OH or –COOH [39]. The high resolution TEM image in Figure 6 revealed that the SnO₂ particles were crystalline in structure. The inter-planar spacing was 0.34 nm, which corresponds to the (110) plane of a rutile SnO₂ lattice. The average size of these SnO₂ nanoparticles on the graphite surface, determined by TEM particle size distribution analysis (Figure 6), was 14.7 ± 2.1 nm. The nanoscale dimension shortens the diffusion length of SnO₂ and graphite for both Li⁺ and e⁻, significantly improving the rate and efficiency of lithiation/delithiation and electron transport, as governed by Fick's first law (Eqn. 1), where τ is characteristic diffusion time constant, *L* is diffusion length and *D* is material-dependent diffusion coefficient [40].

$$\tau = \frac{L^2}{D} \tag{1}$$

Infrared spectra of pristine, Sn-modified graphite, and annealed Sn-graphite anodes after the cycling test are presented in Figure 7. Verma et al. specified that EC is a highly reactive solvent that forms a mixture of Li₂CO₃ and ROCO₂Li to dominate the lithiated graphite surface chemistry (SEI structure) [41].



Figure 6. TEM and high resolution TEM images of the annealed Sn-graphite anode and histogram of the size distribution of SnO₂ on the graphite surface.

In this study, the v(CH) peaks at 2826 and 2988 cm⁻¹ indicated the formation of alkoxy species, including CH₃OLi and ROCO₂Li in pristine graphite, via reaction of (CH₂OCO₂Li)₂ with HF [42, 43]. After modification of the graphite with Sn-based complex, the IR peaks at 2826 and 2988 cm⁻¹ shifted to 2855 and 2935 cm⁻¹. This chemical shift could be attributed to the vibration responses of v(CH₂) in (CH₂OCO₂Li)₂ [42, 43]. The IR spectrum results strongly indicated the presence of Sn-based

compounds on the graphite surface. Those species inhibited the reaction of (CH₂OCO₂Li)₂ with HF and protected the carbon surface from electrolyte decomposition. Careful examination of the IR peaks of the annealed Sn-graphite anode showed behavior more symmetrical than that of the Sn-modified anode. This difference implied that the satiability of SEI film was higher in the anode with annealed Sn-graphite than the anodes with other experimental samples. EIS is a well-established technique for studying the electrode kinetics of electrode materials. Figure 8 presents the Nyquist plots of the pristine, Sn-modified graphite, and annealed Sn-graphite anode cells after 3 cycles at room temperature. The plots consist of a semicircle in the high and medium frequency ranges and a 45° inclined line in the low frequency range.



Figure 7. Infrared spectra of (1) pristine, (2) the Sn-modified graphite, and (3) the annealed Sn-graphite anodes after the cycling tests.



Figure 8. Nyquist plots of the pristine (\bullet , black), the Sn-modified graphite (\blacksquare , blue), and the annealed Sn-graphite (Δ , red) anode cells after 3 cycles at room temperature.

The semicircle was assigned to the charge transfer resistance, which is related to the charge transfer through the electrode/electrolyte interface (SEI). The inclined line corresponded to the diffusion properties (migration) of lithium ions within the electrode.

Synthesis method	Anode materials	Initial Cap./Cycle life Columbic Eff.% (cycle No.)	Ref. No.
High energy ball milling (20 h)	Graphite platelets coated 80% SnO ₂	1738 mAh g ⁻¹ @0.2 A g ⁻¹ , 60% (100)	7
Microemulsion method	16.5% SnO ₂ -(synthetic KS6) graphite	428 mAh g ⁻¹ @0.4 mA cm ⁻² , 72.4% (50)	14
Pyrolysis method	9% SnO/Sn modified graphite	272 mAh g ⁻¹ @0.325 mA cm ⁻²), 95% (50)	15
Embedding method	61% Sn/Expanded graphite composite	650 mAh g ⁻¹ @0.13 A g ⁻¹ , 80% (100),	44
In-situ coating and embedding method	64.5% SnO ₂ @C /Expanded graphite	590 mAh g ⁻¹ @1 A g ⁻¹ , 96% (600)	45
Precipitation method	50% SnO ₂ /graphite composite	550 mAh g ⁻¹ , < 77% (20)	46
Sol gel method	Tin oxide-graphite composite	748 mAh g ⁻¹ @0.5 mA g ⁻¹ , 90% (5)	47
Mechanical mixing	20% Carbon coated Sn/graphite flakes	510 mAh g ⁻¹ @50 mA g ⁻¹ , 78% (15)	48
Electroless plating and pyrolysis method	< 5% SnO ₂ decorated natural graphite particles	340 mAh g ⁻¹ @50 mA g ⁻¹ , 97.3% (50)	This work

Table 2. Performance comparison of similar Sn/SnO₂-gaphite anode materials reported previously.

The diameter of the semicircle for the annealed Sn-graphite anode was much smaller than those of the pristine and Sn-modified graphite anodes, suggesting that the charge-transfer resistance of the annealed Sn-graphite (SnO₂ NPs deposited graphite anode) was lower than that of the others. These results confirmed that the thin SEI film could preserve the high ionic conductivity of the annealed Sn-graphite composite electrode and thus that the combination of SnO₂ nanoparticles and graphite greatly enhances the rapid lithium insertion/extraction, resulting in significant improvement of the electrochemical performance over those of pristine and Sn-modified graphite electrodes. The electrochemical performances of Sn/SnO₂-graphite composite anodes from the literature, prepared under different synthesis conditions with various graphite materials, are listed in Table 2 for comparison.



Figure 9. Cycling performance of the pristine (\bullet), the Sn-modified graphite (\blacksquare), and the annealed Sn-graphite (Δ) anodes.

We anticipated that the improvement from the enhanced conductive and buffering matrix of graphite would keep the entire composite stable. As shown in Figure 9, although the pyrolysis process decreased the initial discharge capacity, the anode with annealed Sn-graphite demonstrated higher stability (capacity efficiency = 97.3%) than that of the anode with Sn-modified graphite (capacity efficiency = 83.3%) in a long-term performance test after 50 cycles. As a result, the cyclic performance of the composite materials was enhanced notably, with a reversible capacity as high as 330 mAh g⁻¹ after 50 cycles.

4. CONCLUSION

Graphite decorated with nano-tin oxides of about 14.7 nm in size, has been synthesized by combining the electroless plating process and pyrolysis method. This composite material acts as an efficient composite anode in LIBs. Due to the pyrolysis treatment, the tin sulfide (SnS and/or SnS₂) present in the composite can be completely converted to SnO₂, which obviously retards the capacity fading of the LIB anode in cycling tests. As revealed by infrared spectroscopic analysis, the structural ordering of the SEI layer is improved in the presence of Sn-based compounds on the graphite surface. These features may also protect the graphite surface from electrolyte decomposition, thereby improving the ionic conductivity and electronic mobility, and therefore substantially enhance the cyclability of the graphite anode in LIBs. This investigation of SnO₂-graphite composite as an efficient anode material for LIBs has shown that the SnO₂-graphite composite can deliver high stability and a high discharge capacity of 330 mAh g⁻¹ after 50 cycles at 0.05 A g⁻¹.

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References

- 1. D. Larcher and J.M. Tarascon, Nat. Chem., 7 (2015) 19.
- 2. J.W. Choi and D. Aurbach, Nat. Rev. Mater., 1 (2016) 16.
- 3. W. Liu, M.S. Song, B. Kong and Y. Cui, Adv. Mater., 29 (2017) 34.
- 4. S. Goriparti, E. Miele, F. De Angelis, E. Di Fabrizio, R.P. Zaccaria and C. Capiglia, *J. Power Sources*, 257 (2014) 421.
- 5. M. Zhang, T. Wang and G. Cao, Int. Mater. Rev., 60 (2015) 330.
- 6. Y.F. Deng, C.C. Fang and G.H. Chen, J. Power Sources, 304 (2016) 81.
- M.H.N. Vincent, S. Wu, P. Liu, B. Zhu, L. Yu, C. Wang, H. Huang, Z.J. Xu, Z. Yao, J. Zhou, W. Que and L.B. Konga, *Electrochim. Acta*, 248 (2017) 440.
- 8. J.S. Chen and X.W. Lou, Small, 9 (2013) 1877.
- 9. Y. Zhao, X.F. Li, B. Yan, D.J. Li, S. Lawes and X.L. Sun, J. Power Sources, 274 (2015) 869.
- 10. L.H. Liu, F. Xie, J. Lyu, T.K. Zhao, T.H. Li and B.G. Choi, J. Power Sources, 321 (2016) 11.
- 11. F. Ye, B. Zhao, R. Ran and Z. Shao, Chem. Eur. J., 20 (2014) 4055.
- 12. S. Chen, Y. Wang, H. Ahn and G. Wang, J. Power Sources, 216 (2012) 22.
- 13. J.Y. Lee, R.F. Zhang and Z.L. Liu, *Electrochem. Solid State Lett.*, 3 (2000) 167.
- 14. Y. Wang, J.Y. Lee and B.H. Chen, J. Electrochem. Soc., 151 (2004) A563.
- 15. C.C. Chang, S.J. Liu, J.J. Wu and C.H. Yang, J. Phys. Chem. C, 111 (2007) 16423.
- 16. A. Ulus, Y. Rosenberg, L. Burstein and E. Peled, J. Electrochem. Soc., 149 (2002) A635.
- 17. T. Fang, L.Y. Hsiao, J.G. Duh and S.R. Sheen, J. Power Sources, 160 (2006) 536.
- 18. Y. Yu, L. Gu, X.Y. Lang, C.B. Zhu, T. Fujita, M.W. Chen and J. Maier, *Adv. Mater.*, 23 (2011) 2443.
- 19. L.G. Xue, Z.H. Fu, Y. Yao, T. Huang and A.S. Yu, *Electrochim. Acta*, 55 (2010) 7310.
- 20. Y. Kong, J.Q. Shao, W.C. Wang, Q.F. Liu and Z.D. Chen, J. Alloy Compd., 477 (2009) 328.
- 21. C.L. Hsieh, D.S. Tsai, W.W. Chiang and Y.H. Liu, Electrochim. Acta, 209 (2016) 332.
- 22. Q.A. Ru, W. Peng, Z.W. Zhang, S.J. Hu and Y.L. Li, Rare Metals, 30 (2011) 160.
- 23. L.Y. Hsiao, T. Fang and J.G. Duh, *Electrochem. Solid State Lett.*, 9 (2006) A232.
- 24. H. Mukaibo, A. Yoshizawa, T. Momma and T. Osaka, J. Power Sources, 119 (2003) 60.
- 25. J.T. Zai, K.X. Wang, Y.Z. Su, X.F. Qian and J.S. Chen, J. Power Sources, 196 (2011) 3650.
- 26. Q.Q. Zhang, R. Li, M.M. Zhang, B.L. Zhang and X.L. Gou, *Electrochim. Acta*, 115 (2014) 425.
- 27. G.X. Wang, J. Yao, H.K. Liu, S.X. Dou and J.H. Ahn, Electrochim. Acta, 50 (2004) 517.
- 28. C.C. Chang, L.J. Her, L.C. Chen, Y.Y. Lee, S.J. Liu and H.J. Tien, *J. Power Sources*, 163 (2007) 1059.
- T. Brousse, S.M. Lee, L. Pasquereau, D. Defives and D.M. Schleich, *Solid State Ion.*, 113 (1998) 51.
- 30. T. Momma, N. Shiraishi, A. Yoshizawa, T. Osaka, A. Gedanken, J.J. Zhu and L. Sominski, J. *Power Sources*, 97-8 (2001) 198.
- 31. M. Sathish, S. Mitani, T. Tomai and I. Honma, J. Phys. Chem. C, 116 (2012) 12475.
- 32. X. Jiang, X.L. Yang, Y.H. Zhu, J.H. Shen, K.C. Fan and C.Z. Li, J. Power Sources, 237 (2013) 178.
- 33. M. Inaba, T. Uno and A. Tasaka, J. Power Sources, 146 (2005) 473.

- 34. M.V. Reddy, L.Y.T. Andreea, A.Y. Ling, J.N.C. Hwee, C.A. Lin, S. Admas, K.P. Loh, M.K. Mathe, K.I. Ozoemena and B.V.R. Chowdari, *Electrochim. Acta*, 106 (2013) 143.
- 35. K. Chang, W.X. Chen, H. Li and H. Li, Electrochim. Acta, 56 (2011) 2856.
- 36. J.G. Ren, J.B. Yang, A. Abouimrane, D.P. Wang and K. Amine, J. Power Sources, 196 (2011) 8701.
- 37. C.C. Hou, S. Brahma, S.C. Weng, C.C. Chang and J.L. Huang, Appl. Surf. Sci., 413 (2017) 160.
- K.E. Aifantis, S. Brutti, S.A. Hackney, T. Sarakonsri and B. Scrosati, *Electrochim. Acta*, 55 (2010) 5071.
- 39. G.C. Herdt, D.R. Jung and A.W. Czanderna, Prog. Surf. Sci., 50 (1995) 103.
- 40. Y. Wang, H. Li, P. He, E. Hosono and H. Zhou, Nanoscale, 2 (2010) 1294.
- 41. P. Verma, P. Maire and P. Novak, *Electrochim Acta*, 55 (2010) 6332.
- 42. D. Aurbach, Y. Gofer, M. Benzion and P. Aped, J. Electroanal. Chem., 339 (1992) 451.
- 43. D. Aurbach, B. Markovsky, I. Weissman, E. Levi and Y. Ein-Eli, *Electrochim. Acta*, 45 (1999) 67.
- 44. Y. Yan, L. Ben, Y. Zhan and X. Huang, Electrochim. Acta, 187 (2016) 186.
- 45. L. Ming, B. Zhang, J.F. Zhang, X.W. Wang, H. Li, C.H. Wang, J. Alloy Compd., 752 (2018) 93.
- 46. W.J. Jin, S.M. Park, I.P. Hong, S.Y. Lee and M.S. Kim, *Solid State Phenom.*, 124/126 (2007) 1051.
- 47. S. M. Hasanaly, AIP Conf. Proc., 1217 (2010) 187.
- 48. T. Morishita, T. Hirabayashi, T. Okuni, N. Ota and M. Inagaki, J. Power Sources, 160 (2006) 638.

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