Graphical Abstract

Correlations between microstructure and electrochemical performance of N-doped carbon-coated Sn_xO_y ($x=1$ and $y=0$ and 2) anodes with various metal loadings, nitrogen contents, and Sn particle size.

1
2
3
4 **Nitrogen-doped Carbon-coated Sn_xO_y ($x = 1$ and $y = 0$ and 2) Nanoparticles for**
5 **Rechargeable Li-Ion Batteries**
6
7

8
9 Mahbuba Ara, Venkateswara Rao Chitturi, Steven O. Salley and K. Y. Simon Ng^{*}
10

11
12
13 Department of Chemical Engineering and Materials Science, Wayne State University, Detroit,
14 MI 48202
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50

51
52 ^{*} Corresponding author. Tel.: +1 313 577 3805; fax: +1 313 577 8171.
53

54 E-mail address: sng@wayne.edu (K. Y. Simon Ng).
55
56
57
58
59
60
61
62
63

Abstract

Polyacrylonitrile was used as a precursor to coat N-doped carbon (NC) on Sn_xO_y ($x = 1$ and $y = 0$ and 2) nanoparticles. The effect of NC coating on electrochemical performance of Sn_xO_y anodes was investigated. Fine dispersion of metal nanoparticles coated with carbon was observed from microscopic analysis. Systematic studies were performed to understand the electrochemical behavior as well as Li-ion battery performance of the prepared materials. Noticeable capacity improvements for NC- SnO_2 and NC-Sn were achieved over carbon-coated particles reported previously in the literature. Among the investigated materials, 50 wt% NC- SnO_2 nanoparticles exhibited the best reversible capacity of 621 mAhg^{-1} while 60 wt% NC-Sn exhibited the highest capacity of 450 mAhg^{-1} at 100 mA/g after 50 cycles. Electrochemical studies revealed that the carbon shell can effectively increase the stability of the active materials and improve the cycling performance for lithium-ion batteries. NC-protected Sn nanoparticles were also synthesized using poly(vinylpyrrolidone) as a precursor and this material exhibited a significantly high discharge capacity of 650 mAhg^{-1} at 100 mA/g after 50 cycles. The studies performed on the Sn-based anodes show the potential of carbon content/coating level and metal particle size for improved Li-ion battery performance.

Keywords

Lithium-ion battery; tin; tin oxide; nitrogen-doped carbon-coating; anode.

1. Introduction

Lithium-ion batteries have had remarkable success as power sources for portable electronic devices [1]. In order to make this battery technology truly competitive for hybrid and fully electric vehicles, further improvement in terms of energy and power density is still needed [2-5]. For this purpose, considerable effort has been devoted to replace the carbon (specific capacity 372 mAhg^{-1}) at the anode by Si (4200 mAhg^{-1}), Sn (992 mAhg^{-1}), SnO_2 (787 mAhg^{-1}) etc. based materials, as the theoretical capacities are much higher than that of carbon. Compared to Si-based materials, Sn-based materials have advantages of lower price and easier processing for lithium-ion battery anode [6]. However, these materials suffer from poor cyclic performance, due to large volume changes during insertion/extraction of Li^+ , involving the alloying/dealloying reactions ($\text{Sn} + 4.4\text{Li}^+ + 4.4\text{e}^- \leftrightarrow \text{Li}_{4.4}\text{Sn}$) [7-9]. In order to alleviate the volume strain accompanying the pulverization of the Sn-based electrode materials upon cycling, carbon incorporation into the anode architecture has been studied extensively, for instance, encapsulation of nanoparticles in hollow carbon spheres [10-12], core-shell structures [13, 14], carbon-coated nanoparticles [15-17] and nanostructured composites with carbon [18-21]; however all of these configurations are not without challenges.

Nano-sized Sn-based materials have higher elasticity and deformability and offer shorter distances for Li^+ ion diffusion, thereby increasing the lithium storage ability of the electrode [22]. However, nanoparticles tend to aggregate into larger particles during charge/discharge cycles and pulverize, resulting in capacity fading. Furthermore, nanoparticles provide higher surface area which increases the extent of side reactions with electrolyte and formation of SEI layers. This attribute promotes the consumption of Li^+ irreversibly and contributes to capacity fading. One strategy to address these problems is the coating of Sn or SnO_2 nanoparticles by

1
2
3
4 carbon to act as a passivation layer and to prevent the aggregation [15, 16, 23-26]. Recently,
5
6 reports have been published on N-doped carbon-coated nanoparticles with higher lithium storage
7
8 capability than plain carbon-coating [27-29]. It has been shown from first principle calculations
9
10 that N-doped carbon-coating can enhance the interfacial stability and electronic conductivity,
11
12 resulting in improved electrochemical kinetics [30]. For Sn-based anodes, no studies have yet
13
14 reported on N-doped carbon-coating. Therefore, it is desirable to investigate the electrochemical
15
16 performance of N-doped carbon-coated Sn and SnO₂ electrode materials for the Li-ion battery.
17
18
19
20
21

22 Herein, a novel N-doped carbon coating of Sn (NC-Sn) and SnO₂ (NC-SnO₂)
23
24 nanoparticles using carbonized PAN was reported. Furthermore, N-doped carbon-coated Sn
25
26 nanoparticles with 18 nm in size (NC-Sn-18) were synthesized by chemical reduction method
27
28 using PVP as a protecting agent as well as the carbon source to get highly dispersed
29
30 nanoparticles. The electrochemical performance of NC-Sn-18 was compared with the larger N-
31
32 doped carbon-coated Sn particles (NC-Sn-200) prepared using PAN as the carbon source.
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

2. Experimental

2.1. Preparation of NC-SnO₂ and NC-Sn particles

SnO₂ nanoparticles were synthesized by the sol-gel method [31] using SnCl₄·5H₂O as a precursor. Five aqueous mixtures of SnCl₄·5H₂O (i.e., 4.4 g, 233 mL) were prepared and then 0.5 g, 1.0 g, 1.5 g, 2.5 g, and 3.5 g of polyacrylonitrile (PAN, PolySciences) were dispersed vigorously for one hour with a magnetic stirrer. A 0.1 M NaOH aqueous solution was added individually into these mixtures, at a rate of 1 mL/min under vigorous stirring. The resultant white solution was sonicated (Branson 2510, 100 W) for 10 min and then centrifuged at 3000 rpm (Eppendorf International, Centrifuge 5804R) to collect the precipitate. The precipitate was washed with DI water and ethanol sequentially until the pH of the filtrate was close to 7. The solid product was dried under vacuum at 80 °C and carbonized at two different temperatures of 500 and 700 °C. The carbonization was performed similarly to the procedure of Zhu et al. [32], where the dried powder was placed in a tube furnace and then subjected to heating at a rate of 10 °C until 270 °C and held at 270 °C for 30 min to stabilize the coating. Then, after cooling down to room temperature, the coating was carbonized by heating to 500/700 °C for 2 h in a N₂ atmosphere. Five different concentrations of carbon-coated Sn-based materials at two different temperatures were prepared, denoted as S-500 and S-700.

2.2. Preparation of modified NC-Sn particles

PVP (polyvinylpyrrolidone, Sigma-Aldrich) based carbon-coating synthesis was followed by chemical reduction at room temperature. Tin salt (SnCl₂·2H₂O) solution in DI water was injected to the solution containing PVP (1 g) and NaBH₄ (2 g) in DI water (100 mL) where the

ratio of Sn^{2+} to PVP was 1:5. The reaction was performed in a three-neck round-bottomed flask immersed in an ice bath. Prior to the reaction, the system was purged with pure Ar for 20 minutes. The injection rate of Sn salt was maintained at 1 mL/min and, after adding the salt, the solution was stirred vigorously for three hours using a magnetic stirrer. After the reaction completed, the precipitates was collected by centrifugation and washed with ethanol and dried in a vacuum oven for 12 hours. Finally, nitrogen-doped carbon-coated Sn (NC-Sn) particles were obtained by carbonizing in a tube furnace under an Ar/H₂ (5% H₂) atmosphere at 500 °C for 1h.

2.3. Characterization

The as-prepared carbon-deposited Sn particles were characterized by transmission electron microscopy (TEM, JEOL-2010 at 200 kV) and field emission scanning electron microscopy (FESEM, JSM-7600F at 15 kV). Chemical composition analysis was done using the equipped Energy Dispersive X-ray Spectrometer (EDS). Powder X-ray diffraction (XRD) was performed using a Rigaku SmartLab high resolution $\theta/2\theta$ XRD system with a graphite monochromator with Cu K α radiation ($\lambda=1.5406$ Å). Scattering angles (2θ) of 10-90° at a scanning rate of 4°/min were used. Thermogravimetric analysis (TGA) was conducted with a thermal gravimetric analyzer (Perkin Elmer Pyris-1) from 25 to 1000 °C at a rate of 10 °C/min under controlled airflow. X-ray photoelectron spectroscopy (XPS) analysis was conducted with a PHI 670 Scanning Auger Nanoprobe (Physical Electronics, Chanhassen, MN) at 220 W X-ray power to further investigate the binding characteristics of the material. A survey scan was first initiated and then high resolution multiplexes on each element of interest with 23.5 eV pass energy was performed.

2.4. Electrochemical tests

To fabricate an electrode, a slurry of the active materials (80 wt%), conductive carbon (CENERGY Super C65, Timcal Graphite & Carbon) (10 wt%), and polyvinylidene fluoride (10 wt%) were dissolved in n-methyl pyrrolidinone and coated onto the Cu foil substrate. The as-prepared electrodes were dried in a vacuum oven at 100 °C for 12 h. The material was then assembled into test cells (#2032 coin cell) using lithium-metal foil as the negative electrode, a micro porous polypropylene separator (Celgard 2320), and an electrolyte of 1 M LiPF₆ in a 1:1(w/w) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Cells were assembled inside an argon filled glove box where both the moisture and oxygen content were below 1 ppm. All cells were tested at a constant current density of 100 mA/g between fixed voltage limits of 2 V to 0.05 V using a Maccor series 4200 battery tester. The current density and electrode capacities were calculated based on the total mass of the active materials. Electrochemical impedance spectroscopy (EIS) measurement was performed using a Gamry Reference 3000 from 1 MHz to 0.01 Hz at 3.5 mV rms.

3. Results and Discussion

3.1. TGA analysis

TGA was performed in air, in order to quantify the amount of Sn and SnO₂ in the composites. Figs. 1a and b show the TGA profiles of different samples as a function of temperatures. No weight loss was observed until 300 °C for S-500 materials while the S-700 Sn-C materials were stable up to 360 °C. This is attributed to the difference in oxygen content in the materials. At 500 °C, the SnO₂ mass percent was determined to be about 82, 69, 59, 50 and 45% respectively in five different samples with 0.5 g, 1.0 g, 1.5 g, 2.5 g, and 3.5 g precursor PAN,

1
2
3
4 respectively. The variations in the compositions with the PAN precursor are tabulated in Table 1.
5
6 In the case of S-700, the weight increase after 520 °C resulted from the oxidation of Sn particles
7
8 ($\text{Sn} + \text{O}_2 \rightarrow \text{SnO}_2$) while the weight loss from 360° to 520 °C is associated with the burning of
9
10 carbon to make CO_2 ($\text{C} + \text{O}_2 \rightarrow \text{CO}_2$). The composition of Sn for S-700 materials was
11
12 determined using the equation [33]: $\text{Sn (wt\%)} = 100 \times (\text{molecular weight of Sn/ molecular}$
13
14 $\text{weight of SnO}_2) \times (\text{final weight of SnO}_2/ \text{initial weight of Sn-C materials})$. The calculated
15
16 compositions are 85%, 73%, 60%, 45%, and 38% for S-700 with 0.5 g, 1.0 g, 1.5 g, 2.5 g, and
17
18 3.5 g precursor PAN, respectively. These compositions are listed in Table 2.
19
20
21
22
23
24
25
26

27 **3.2. XRD analysis**

28
29 To identify the crystalline structure, the XRD pattern of the as-prepared nanocomposite
30
31 powder was investigated (Fig. 1). In Fig. 1c , the diffraction peaks at around 27, 34, 52, and 66°
32
33 are assigned to the index numbers of SnO_2 (110), (101), (211), and (301), respectively. These
34
35 peaks are in good agreement with the tetragonal rutile structure of SnO_2 particles which present
36
37 as cassiterite following the reference pattern JCPDS 41-1445. The low intensity diffraction peaks
38
39 due to metallic Sn were present for the S-500 materials, especially for 45 wt% sample. This is
40
41 attributed to the small extent of carbothermal reduction occurring even at 500 °C with the
42
43 presence of higher carbon content. The average crystal sizes were calculated by using Scherrer's
44
45 equation [34]. SnO_2 grain sizes were obtained as 12, 10, 8, 8, 7, and 10 nm, for 82, 69, 59, 50, 45
46
47 wt% and pure SnO_2 , respectively, for the S-500 material, obtained from the strongest (101) peak
48
49 ($2\theta = 34^\circ$). Fig. 1d presents the XRD patterns of the as prepared S-700 materials carbonized at
50
51 700 °C and pure Sn powder (commercial). All diffraction peaks can be readily indexed to
52
53 tetragonal tin (JCPDS card No. 04-0673). Sn particles show a highly crystalline nature. No
54
55
56
57
58
59
60
61
62
63
64
65

intensive peak belonging to carbon is detected for any of the materials, demonstrating the amorphous carbon existence [35].

3.3. SEM/TEM observations

Microstructural changes can clearly be observed with the carbonization temperature and the precursor amount of PAN in Figs. S1 and S2 (supplementary info.). It can be seen that SnO₂ nanoparticles are predominantly encapsulated by surrounding carbon only for the 50 and 45 wt% materials (Fig. S1). On the other hand, 60 wt% Sn (Fig. S2) revealed a homogeneous distribution of Sn particles with an average size ca. 200 nm. This is attributed to the optimum ratio of C/Sn where polymerization and carbonization lead to higher homogeneity in both size and distribution of the particles.

EDS elemental mapping of the materials are presented in Figs. S3a and b. All the spectra show peaks for Sn, O, N and C, which is also evident from the elemental mapping. Sn and SnO₂ particles are covered with carbon and the presence of N in the carbon is evident. N-doping can increase the defects in the carbon structure, which leads to higher lithium storage and Li⁺ diffusion [30, 34].

Transmission electron microscopic (TEM) images recorded for the S-500 and S-700 materials are shown in Figs. 2a-e and 3a-e, respectively. Highly dispersed fine particles within the carbon matrix with 3-7 nm diameters are observed in all the prepared materials. The increase in the amorphous carbon content is apparent in the materials, where thin layers to multiple layers of carbon coating appear. In the case of 50 and 45 wt% samples, it's hard to discern the uncovered SnO₂ nanoparticles. Fig. 2d inset presents one single SnO₂ particle (5 nm) with a

carbon layer of 2 nm for the 50 wt% material. It is expected that the carbon layer can act as a barrier to avoid the aggregation of SnO₂ nanoparticles during Li⁺ insertion/extraction. Figs. 3a-e for the S-700 materials reveal the spherical Sn particles covered with the carbon layers. All the other materials present the same trend as the SEM images with varying PAN precursor, where 60 wt% shows smaller particles (~200 nm) than that of 85 and 73 wt%, while carbon layers are increased for the 45 and 38 wt% samples.

3.4. Electrochemical Performances

The discharge/charge curves of the NC-Sn (S-500) and NC-SnO₂ (S-700) nanoparticles are shown in Figs. 4a and b. The plateau above 0.9 V (vs. Li/Li⁺) in the first discharge process (Fig. 4a) corresponds to the irreversible reduction of SnO₂ to form Li₂O and Sn. The voltage region below 0.6 V (vs. Li/Li⁺) is attributed to the Li-Sn alloy reactions. The corresponding regions in the charge curves can also be observed, which are attributed to the delithiation reaction. It can be noted that first cycle discharge and charge capacity varies from high to low with reduced content of SnO₂. In Fig. 4b, a different trend can be observed with the variation of Sn content, where 60 wt% Sn in the NC-Sn electrodes shows the largest discharge/charge specific capacity. This can be attributed to the particular combination of C/Sn ratio with the carbon coating of Sn particles where significant Li⁺ can diffuse. 85 wt% NC-Sn shows one plateau at 1.3 V (vs. Li/Li⁺), which is due to the electrolyte decomposition catalyzed by Sn [36, 37]. The plateau at around 0.8 V is attributed to SEI formation on the surface, while the plateaus below 0.7 V correspond to alloying reactions to form Li_xSn (i.e. Li₂Sn₅, LiSn, Li₅Sn₂, Li₇Sn₂, and Li₂₂Sn₅) [38, 39]. Multiple oxidation (charge cycle) voltage plateaus are apparent after 0.8 V

(vs. Li/Li^+) due to the step-wise dealloying reactions occurring in phase transformations upon Li extraction from Li_xSn alloys.

The electrochemical performance of the NC- SnO_2 and NC-Sn nanoparticles in the potential range of 0.05-2.0 V were tested up to 50 cycles. Figs. 4c and d compare the electrochemical properties of the as-prepared NC- SnO_2 and NC-Sn nanostructures, respectively. The first cycle discharge/charge capacities for NC- SnO_2 vary as follows: 1714/1006, 1637/910, 1637/980, 1675/1051, 1620/1006, and 1609/496 mAhg^{-1} , with coulombic efficiencies of 58.7, 55.8, 59.8, 62.7, 62.1, and 30.8%, for 82, 69, 59, 50, and 45 wt% NC- SnO_2 and pure SnO_2 , respectively. All six samples have large irreversible capacities (Fig. 4c) in the first cycle. The irreversible capacities can be ascribed to the reduction of SnO_2 and the formation of a passivating solid electrolyte interphase (SEI) film. The capacity retentions are 33%, 21%, 41%, 62%, 48%, and 4% for 82, 69, 59, 50, 45 wt% NC- SnO_2 and pure SnO_2 , respectively. The SnO_2 nanoparticles' large initial discharge capacity declines rapidly after 10 cycles (202 mAhg^{-1}), which indicates the pulverization of the anode. In the same way, higher loading of SnO_2 induced more mechanical strain and pulverization upon cycling, whereas the increased carbon-coating layers with higher content of carbon can hinder lithium diffusion, resulting in poor capacity. In comparison to all materials, 50 wt% NC- SnO_2 nanostructures exhibit the best cyclic retention with the reversible capacity of 621 mAhg^{-1} . This capacity closely matches the theoretical capacity calculated based on the capacity of amorphous carbon as 186 mAhg^{-1} (i.e. $372 \text{ mAhg}^{-1} \times 0.5$) and SnO_2 particles as 391 mAhg^{-1} (i.e. $782 \text{ mAhg}^{-1} \times 0.5$) for 50 wt% NC- SnO_2 . A slightly higher capacity than theoretical capacity observed in the present study is ascribed to N-doping of the carbon and presence of the defect sites, which usually helps to intercalate more Li^+ ions into the carbon network [27]. This electrochemical performance is still superior to that

reported for carbon-coated SnO₂ materials [12, 15, 17, 23, 24] without nitrogen doping. For example, after 50 cycles at 100 mA/g, Chou et al. [15] and Chen et al. [12] found reversible capacity of 502 mAhg⁻¹ with 90 wt% SnO₂ loading and 495 mAhg⁻¹ with 74 wt% SnO₂ content; whereas, Wang et al. [23] achieved 390 mAhg⁻¹ at 200 mA/g after 100 cycles with core-shell SnO₂/C anodes. Therefore, N-doped carbon coating of SnO₂ benefitted from higher interface charge transfer and electrical conductivity [31, 34]. The high capacity retention of the 50 wt% NC- SnO₂ nanoparticles can be attributed to the optimum carbon-coating structure with the highest amount of N-contents with smaller particles (from Table 1). The carbon layer can act effectively as a buffer layer during cycling to alleviate the mechanical stress caused by the severe volume change during lithium insertion/extraction, to prevent the disintegration of the active materials and the aggregation of tin nanoparticles in the electrode. Optimization of the carbon-coating thickness by controlling the carbon content were also reported previously for enhanced capacity and recyclability [15, 40]. Too thick of a carbon layer can hinder the Li diffusion and entrapped the reactive species, resulting in lowering the capacity.

For the NC-Sn materials (Fig. 4d), the first cycle discharge/charge capacities vary as follows: 1022/680, 1033/773, 1140/903, 866/682, 1136/853, and 1050/760 mAhg⁻¹, with coulombic efficiencies of 66.4, 74.8, 79.2, 78.7, 75.1, and 72.4%, for 85, 73, 60, 45, and 38 wt% NC-Sn and pure Sn, respectively. The reversible capacity retentions after 50 cycles are 20%, 23%, 51%, 42%, 30%, and 0.2 % for 85, 73, 60, 45, 38 wt% NC-Sn and pure Sn, respectively. The 60 wt% NC-Sn shows the highest capacity retention among all five NC-Sn anodes of 462 mAhg⁻¹ with 99% coulombic efficiency. This result is comparable to that reported previously for carbon-incorporated Sn anodes without nitrogen-doping [20, 21, 41]. Morishita et al. [42] and Jung et al. [14] achieved 500 and 357 mAhg⁻¹ after 10 cycles at less than 50 mA/g current

density for non-N-doped carbon coated Sn particles. In contrast, Zhou et al. [43] studied Sn nanoparticles encapsulated in N-doped graphene particles and obtained 480 mAhg^{-1} at 100 mA/g after 100 cycles with decaying capacity. It is possible that although the particles are entrapped inside graphene layers, still experiencing the aggregation/pulverization during cycling for lacking the protection of the individual particle by carbon. Carbon-coating helps to maintain the electrical contact between the particles for the alleviation of severe volume change of tin. Therefore, both N-doping and carbon-coatings of the particles are necessary for stable and enhanced capacity retention.

Furthermore, the findings of this study suggest that with higher content of tin, the particles are not completely encased by carbon, resulting in aggregation and cracking, leading to deterioration of reversible capacity. However, with higher carbon (45 and 38 wt% Sn samples), thick layers of carbon around the particles might hinder the Li^+ ion diffusion to the Sn particles, resulting in poor capacity [27]. Only 60 wt% NC-Sn is showing the optimum thickness of carbon coating (Fig. 3c) which reflects to the highest capacity retention. Similar trends were observed by Morishita et al. [42], who studied metallic Sn content of 96, 80 and 75 wt% to optimize the thickness of the carbon coating and found best result for 75 wt% material.

In Figs. 4e and f, the eminent electrode reactions are more clearly shown from the cyclic voltammograms (CV) of NC-SnO₂ (50 wt%) and NC-Sn (60 wt%) based on the best cyclic reversibility from Figs. 4c and d. An apparent reduction peak at 0.8 V (vs. Li/Li^+) is observed only during the first cycle, which can be assigned to the irreversible reduction of the SnO₂ and electrolyte decomposition. A broad reduction peak near 0.2 V (vs. Li/Li^+) is attributed to the insertion of Li into metallic Sn and carbon materials. The corresponding oxidation peak around 0.6 V (versus Li/Li^+) is also found. Another oxidation peak at about 1.3 V can be tentatively

assigned to the partial oxidation of Li_2O [44]. The second and third CV curves completely merge together implying the reversibility. Fig. 4f shows the typical CV of NC-Sn (60 wt%) electrode in the initial three cycles at a scan rate of 0.1 mV s^{-1} from 0.05 to 2 V. During the first cathodic sweep, the broad reduction peak from 0.7 to 0.1 V is ascribed to both the reduction of Sn and the decomposition of the electrolyte to form SEI film, corresponding to the capacity loss during the first cycle. However, from the second cycle, three distinct peaks that are located at 0.33, 0.52, and 0.63 V can be found, being initiated from the formation of Li_xSn alloys [39]. In the anodic sweep, oxidation peaks between 0.4 and 0.9 V are assigned to the dealloying reactions of Li_xSn [38]. All peaks are not completely reproducible after the first cycle. This indicates that the carbon-coating of the Sn particles are not stable enough due to the cracking of the carbon-shell due to the mechanical stress developed during electrochemical cycling [14].

3.5. XPS analysis

XPS measurements are shown only for the 50 wt% NC- SnO_2 and 60 wt% NC-Sn materials which exhibited the best electrochemical performance in Fig. 5. The surface of NC- SnO_2 and NC-Sn are composed of 62 wt% and 74 wt% carbon. 6 wt% oxygen for NC-Sn is probably initiated by the oxidation of the sample due to the exposure to the ambient air. However, Sn contents on the surface of both 50 wt% NC- SnO_2 and 60 wt% NC-Sn are detected as only 12.8 and 13.3%, which are far less than the overall composites. This result suggests that most of the SnO_2 and Sn particles are encased inside the carbon [45]. The nitrogen species are introduced by the pyrolysis of PAN, and the as obtained nitrogen contents from XPS are tabulated in Table 3. as 10 and 6 wt% nitrogen in NC- SnO_2 and NC-Sn, respectively. The introduction of N improves the conductivity of the carbon layer and charge transfer at the

1
2
3
4 interface [34]. Detailed analysis of the high-resolution XPS spectra of the N 1s (inset pictures of
5
6 Fig. 5) revealed three configurations of nitrogen binding: pyridinic N of 72 and 49 wt%, Pyrrolic
7
8 N of 11 and 29 wt%; and graphitic N of 17 and 22 wt% for NC-SnO₂ and NC-Sn, respectively. It
9
10 has been reported that the pyridinic configuration is the most favorable for Li cycling [46-48]
11
12 which creates strong binding energies with carbon by generating defects, providing stable Li
13
14 hosting [48]. It is evident that NC-SnO₂ has higher pyridinic N than NC-Sn, with a relative
15
16 difference of 18 units, which is possibly due to the low heat treatment temperature of 500 °C
17
18 during carbonization for NC-SnO₂ [49]. Therefore, smaller particle size and higher pyridinic N
19
20 content might result in higher Li⁺ holding capability for NC-SnO₂ versus NC-Sn.
21
22
23
24
25
26

27 The only variable in the preparation of these samples for NC-SnO₂ or NC-Sn from PAN
28
29 is the carbonization temperature, indicating that temperature has significant effect on the amount
30
31 of N doping, its configuration, the nanoparticle size and types. In order to get better performance
32
33 for NC-Sn based materials, lower-temperature N-doped carbon coating technique has been
34
35 adopted for smaller Sn nanoparticles in the subsequent studies.
36
37
38
39
40
41
42

43 3.6. Sn particle size modification

44
45
46 N-doped carbon coatings of nano-sized Sn particles were synthesized by low temperature
47
48 reduction with PVP as the capping agent and carbon source. From Fig. 6a, TGA analysis reveals
49
50 the Sn composition of 64 wt% following the equation [33] : $\text{Sn (wt\%)} = 100 \times (\text{molecular weight of Sn} / \text{molecular weight of SnO}_2) \times (\text{final weight of SnO}_2 / \text{initial weight of Sn-C materials})$. Fig. 6b shows the XRD patterns of commercial Sn and C-coated Sn particles. The
51
52 average Sn crystal sizes were calculated by using Scherrer's equation [34] as 18 nm obtained
53
54
55
56
57
58
59
60
61
62
63
64
65

from the strongest (200) peak ($2\theta = 31^\circ$), whereas commercial Sn has been provided as > 100 nm. TEM (Fig. 6c) examination shows that Sn nanoparticles are fully covered individually with thin layers of carbon. The inset of Fig. 6c shows the close-up examination of one single particle, where external coating (< 5 nm thickness) is homogenously conforming to its shape. From XRD and TEM analysis, the average particle size has been confirmed as 18 nm. Hence, the material is denoted as NC-Sn-18, whereas, NC-Sn of 60 wt% as NC-Sn-200 based on the particle size. Fig. 6d demonstrates the XPS spectra of NC-Sn-18 with the high resolution N 1s spectra configuration (inset). Table 3 summarizes the computed surface composition of the particles. Carbon and nitrogen contents are found to be 70.8 and 2.8 wt%, respectively, indicating similar amounts of nitrogen incorporation as those reported previously [27-29]. High resolution XPS spectra of the N 1s peak in Fig. 6d (inset) reveal that the binding configurations with carbon are similar to those of NC-Sn-200: pyridinic N, pyrrolic N and graphitic N, and the resulting binding is mostly pyridinic in nature (73.5%).

Fig. 7a exhibits the charge/discharge voltage profiles for the first three cycles of NC-Sn-18 anodes at 100 mA/g current density. First cycle discharge and charge capacities are 1116 mAhg⁻¹ and 904 mAhg⁻¹ with coulombic efficiency of 81% which is higher than NC-Sn-200 (79%). In the voltage profiles, the characteristic plateaus show the same characteristics as carbon-coated nano-sized Sn-based anodes [16, 25]. All properties are tabulated in Table 4 for NC-Sn-18 and NC-Sn-200 materials. Fig. 7b exhibits the cyclic performance at 100 and 500 mA/g for NC-Sn-18 and NC-Sn-200 anodes. It can be seen that the capacity retention is 650 mAhg⁻¹ (at 100 mA/g) for NC-Sn-18 after 50 cycles, which is equivalent to 70% of reversible charge capacity. At 500 mA/g, the capacity retentions are 432 and 241 mAhg⁻¹ for NC-Sn-18 and NC-Sn-200, respectively. Capacity decay in the first 10 cycles for the NC-18 material can be due

to the irreversible Li^+ insertion into the disordered amorphous carbon structure [50] and some extent of electrolyte decomposition catalyzed by the presence of Sn particles [51]. On the other hand, irreversible capacity loss appears before the first 20 cycles for NC-Sn-200, which is attributed to the pulverization of the large Sn particles as the carbon-shield fractures and falls apart with cycling [14]. Overall, the electrochemical performance of NC-Sn-18 is superior to the other carbon coated materials reported previously [16, 25, 26, 42, 52]. These results suggest that smaller nanoparticles provide the advantage of forming a stable SEI passivation layer. On the other hand, larger particles experience continuous cracking and agglomeration due to the fracture of the carbon protective layers, which promotes the formation of the SEI unremittingly, which results in capacity fading [14, 51]. Cyclic voltammetry studies of NC-Sn-18 electrodes shows the characteristic features of Li-Sn alloying [53] (Fig. 7c), corresponding to the reversible formation of the different Li_xSn alloy phases [54, 55]. However, the very broad anodic peak at about 0.1 V, indicates lithium storage of carbonaceous materials [56]. Fig. 7d displays the impedance spectra of NC-Sn-18 and NC-Sn-200 before and after 50 cycles. NC-Sn-200 revealed higher charge transfer resistance (R_{ct}) than NC-Sn-18, before and after (inset of Fig.7d) 50 cycles. This is attributed to the increased polarization from the pulverized particles in the NC-Sn-200 and interface reaction with the electrolyte species upon cycling [57].

4. Conclusions

NC-SnO₂ and NC-Sn materials were synthesized by carbonization of PAN at different temperatures of 500 and 700 °C followed by carbothermal reduction in an inert atmosphere. The SnO₂ and Sn particles were successfully encapsulated within the N-doped carbon layers. The 50 wt % NC-SnO₂ and 60 wt% NC-Sn presented better capacity retention with optimum carbon

contents/coating. Modified size of Sn particles of 18 nm diameter with the N-doped conductive coating was also synthesized successfully which exhibited superior specific capacity, rate performance and excellent capacity retention ability. The results demonstrate that N-doped carbon coating with optimum thickness and smaller particles play important role in Sn-based anode materials for lithium-ion battery applications.

Acknowledgement

Financial support from the Department of Energy (Grant# DE-EE0002106) is gratefully acknowledged.

References

- [1] T. Nagaura, K. Tozawa, Lithium ion rechargeable battery, Prog. Batt. Solar Cells 9 (1990) 209.
- [2] M. Armand, J.-M. Tarascon, Building better batteries, Nature 451 (2008) 652.
- [3] J. Tollefson, Charging up the future, Nature 456 (2008) 436.
- [4] B. Scrosati, J. Garche, Lithium batteries: status, prospects and future, J. Power Sources 195 (2010) 2419.
- [5] B.G. Pollet, I. Staffell, J. L. Shang, Current status of hybrid, battery and fuel cell electric vehicles: from electrochemistry to market prospects, Electrochim. Acta 84 (2012) 235.
- [6] A. R. Kamali, D. J. Fray, Tin-based materials as advanced anode materials for lithium ion batteries: a review, Rev. Adv. Mater. Sci. 27 (2011) 14.
- [7] A. Courtney, J. R. Dahn, Key Factors Controlling the Reversibility of the Reaction of Lithium with SnO_2 and Sn_2BPO_6 Glass, J. Electrochem. Soc. 144 (1997) 2943.
- [8] O. Mao, R. A. Dunlap, J. R. Dahn, Mechanically Alloyed Sn-Fe(-C) Powders as Anode Materials for Li-Ion Batteries: I. The $\text{Sn}_2\text{Fe-C}$ System, J. Electrochem. Soc. 146 (1999) 405.
- [9] L. Y. Beaulieu, J. R. Dahn, The Reaction of Lithium with Sn-Mn-C Intermetallics Prepared by Mechanical Alloying, J. Electrochem. Soc. 147 (2000) 3237.
- [10] X. W. Lou, D. Deng, J. Y. Lee, L. A. Archer, One-pot synthesis of carbon-coated SnO_2 nanocolloids with improved reversible lithium storage properties, Chem. Mater. 20 (2008) 6562.
- [11] W.-M. Zhang, J.-S. Hu, Y.-G. Guo, S.-F. Zheng, L.-S. Zhong, W.-G. Song, L.-J. Wan, Tin-Nanoparticles Encapsulated in Elastic Hollow Carbon Spheres for High-Performance Anode Material in Lithium-Ion Batteries, Adv. Mater. 20 (2008) 1160.

- [12] Y. Chen, Q. Z. Huang, J. Wang, Q. Wang, J. M. Xue, Synthesis of monodispersed SnO₂@C composite hollow spheres for lithium ion battery anode applications, *J. Mater. Chem.* 21 (2011) 17448.
- [13] L. B. Chen, X. M. Yin, L. Mei, C. C. Li, D. N. Lei, M. Zhang, Q. H. Li, Z. Xu, C. M. Xu, T. H. Wang, Mesoporous SnO₂@carbon core-shell nanostructures with superior electrochemical performance for lithium ion batteries, *Nanotechnology* 23 (2012) 035402.
- [14] Y. S. Jung, K. T. Lee, J. H. Ryu, D. Im, S. M. Oh, Sn-carbon core-shell powder for anode in lithium secondary batteries, *J. Electrochem. Soc.* 152 (2005) A1452.
- [15] S-L. Chou, J.-Z. Wang, C. Zhong, M. M. Rahman, H.-K. Liu, S.-X. Dou, A facile route to carbon-coated SnO₂ nanoparticles combined with a new binder for enhanced cyclability of Li-ion rechargeable batteries, *Electrochim. Acta* 54 (2009) 7519.
- [16] M. Noh, Y. Kwon, H. Lee, J. Cho, Y. Kim, M. G. Kim, Amorphous Carbon-Coated Tin Anode Material for Lithium Secondary Battery, *Chem. Mater.* 17 (2005) 1926.
- [17] X. W. Lou, J. S. Chen, P. Chen, L. A. Archer, One-pot synthesis of carbon-coated SnO₂ nanocolloids with improved reversible lithium storage properties, *Chem. Mater.* 21 (2009) 2868.
- [18] F. D. Lupo, C. Gerbaldi, G. Meligrana, S. Bodoardo, N. Penazzi, Novel SnO₂/Mesoporous Carbon Spheres Composite Anode for Li-ion Batteries, *Int. J. Electrochem. Sci.* 6 (2011) 3580.
- [19] S. Nama, S. Kim, S. Wia, H. Choi, S. Byun, S.-M. Choi, K. T. Lee, S.-I. Yoo, B. Park, The role of carbon incorporation in SnO₂ nanoparticles for Li rechargeable batteries, *J. Power Sources* 211 (2012) 154.
- [20] Y. Lee, Y.-M. Kang, Sn nanocrystal/carbon composites as high-capacity anode materials for lithium rechargeable batteries, *J. Power Sources* 196 (2011) 10686.

- [21] H. Wang, Q. Li, S. Hu, F. Wang, Z. Yan, Novel Sn/C composite anode material for lithium-ion batteries, ECS Trans. 16 (2009) 19.
- [22] B. K. Guo, J. Shu, K. Tang, Y. Bai, Z. X. Wang, L. Q. Chen, Nano-Sn/hard carbon composite anode material with high-initial coulombic efficiency, J. Power Sources, 177 (2008) 205.
- [23] F. Wang, X. Song, G. Yao, M. Zhao, R. Liu, M. Xu, Z. Sun, Carbon-coated mesoporous SnO₂ nanospheres as anode material for lithium ion batteries, Scr. Mater. 66 (2012) 562.
- [24] R. Yang, W. Zhao, J. Zheng, X. Zhang, X. Li, One-Step Synthesis of Carbon-Coated Tin Dioxide Nanoparticles for High Lithium Storage, J. Phys. Chem. C 114 (2010) 20272.
- [25] D. Bresser, F. Mueller, D. Buchholz, E. Paillard, S. Passerini, Embedding tin nanoparticles in micron-sized disordered carbon for lithium- and sodium-ion anodes, Electrochim. Acta 128 (2014) 163.
- [26] J. Ren, X. He, K. Wang, W. Pu, The impact of carbon shell on a Sn–C composite anode, Ionics 16 (2010) 503.
- [27] R. C. d. Guzman, J. Yang, M. M.-C. Cheng, S. O. Salley, K.Y. S. Ng, Effects of graphene and carbon coating modifications on electrochemical performance of silicon nanoparticle/graphene composite anode, J. Power Sources 246 (2014) 335.
- [28] C. Guo, J. Mao, D. Wang, Nitrogen-doped carbon coated SiO nanoparticles Co-modified with nitrogen-doped graphene as a superior anode material for lithium-ion batteries, RSC Adv. 4 (2014) 35717.
- [29] H. Ming, J. Ming, X. Li, Q. Zhou, L. Jin, Y. Fu, J. Adkins, Z. Kang, J. Zheng, Synthesis of N-doped carbon coated metal oxide nanoparticles for enhanced Li-ion storage ability, RSC Adv. 3 (2013) 15613.

- [30] Z. J. Ding, L. Zhao, L. M. Suo, Y. Jiao, S. Meng, Y. S. Hu, Z. X. Wang, L. Q. Chen, Towards understanding the effects of carbon and nitrogen-doped carbon coating on the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in lithium ion batteries: a combined experimental and theoretical study, *Phys. Chem. Chem. Phys.* 13 (2011) 15127.
- [31] L. Korosi, K. Mogyrosi, R. Kun, J. Nemeth, I. Dekany, Preparation and photooxidation properties of metal oxide semiconductors incorporated in layer silicates, *Prog. Colloid Polym Sci.* 125 (2004) 27.
- [32] Z. Zhu, Z. Liu, Y. Gu, Y. Gu, Formation of N_2 during carbonization of polyacrylonitrile using iron catalyst, *Fuel* 76 (1997) 155.
- [33] K. Wang, X. M. He, L. Wang, J. G. Ren, C. Y. Jiang, C. R. Wan, Preparation of Cu_6Sn_5 -Encapsulated Carbon Microsphere Anode Materials for Li-ion Batteries by Carbothermal Reduction of Oxides, *J. Electrochem. Soc.* 153 (2006) A 1859.
- [34] L. Zhao, Y. S. Hu, H. Li, Z. X. Wang, L. Q. Chen, Porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Coated with N-Doped Carbon from Ionic Liquids for Li-Ion Batteries, *Adv. Mater.* 23 (2011) 1385.
- [35] D. Deng, J. Y. Lee, Reversible storage of lithium in a rambutan-like tin-carbon electrode, *Angew. Chem., Int. Ed.* 48 (2009) 1660.
- [36] B. Luo, B. Wang, X. L. Li, Y. Y. Jia, M. H. Liang, L. J. Zhi, Reduced graphene oxide-mediated growth of uniform tin-core/carbon-sheath coaxial nanocables with enhanced lithium ion storage properties, *Adv. Mater.* 24 (2012) 1405.
- [37] Y. S. Jung, K. T. Lee, J. H. Ryu, D. Im, S. M. Oh, Sn-carbon core-shell powder for anode in lithium secondary batteries, *J. Electrochem. Soc.* 152 (2005) A1452.
- [38] C. Wanga, A. J. Appleby, F. E. Little, Electrochemical study on nano-Sn, $\text{Li}_{4.4}\text{Sn}$ and $\text{AlSi}_{0.1}$ powders used as secondary lithium battery anodes, *J. Power Sources*, 93 (2001) 174.

- [39] R. A. Huggins, Lithium alloy negative electrodes, *J. Power Sources*, 81 (1999) 13.
- [40] X. W. Lou, C. M. Li, L. A. Archer, Designed Synthesis of Coaxial SnO₂@carbon Hollow Nanospheres for Highly Reversible Lithium Storage, *Adv. Mater.* 21 (2009) 2536.
- [41] B. Duan, W. Wang, H. Zhao, B. Xu, K. Yuan, Y. Yang, Nano-Sn/Mesoporous Carbon Parasitic Composite as Advanced Anode Material for Lithium-Ion Battery, *J. Electrochem. Soc.* 159 (2012) A2092.
- [42] T. Morishita, T. Hirabayashi, T. Okuni, N. Ota, M. Inagaki, Preparation of carbon-coated Sn powders and their loading onto graphite flakes for lithium ion secondary battery, *J. Power Sources* 160 (2006) 638.
- [43] X. Zhou, J. Bao, Z. Dai, Y. Guo, Tin Nanoparticles Impregnated in Nitrogen-Doped Graphene for Lithium-Ion Battery Anodes, *J. Phys. Chem. C* 117 (2013) 25367.
- [44] S. J. Han, B. C. Jang, T. Kim, S. M. Oh, T. Hyeon, Simple synthesis of hollow tin dioxide microspheres and their application to lithium-ion battery anodes, *Adv. Funct. Mater.* 15 (2005) 1845.
- [45] J. Ren, X. He, K. Wang, W. Pu, The impact of carbon shell on a Sn–C composite anode, *Ionics* 16 (2010) 503.
- [46] H. Wang, C. Zhang, Z. Liu, L. Wang, P. Han, H. Xu, K. Zhang, S. Dong, J. Yao, G. Cui, Nitrogen-doped graphene nanosheets with excellent lithium storage properties, *J. Mater. Chem.* 21 (2011) 5430.
- [47] D. Deng, X. Pan, L. Yu, Y. Cui, Y. Jiang, J. Qi, W. Li, Q. Fu, X. Ma, Q. Xue, G. Sun, X. Bao, Toward N-doped graphene via solvothermal synthesis, *Chem. Mater.* 23 (2011) 1188.

- [48] C. Ma, X. Shao, D. Cao, Nitrogen-doped graphene nanosheets as anode materials for lithium ion batteries: a first-principles study, *J. Mater. Chem.* 22 (2012) 8911.
- [49] M. S. A. Rahaman, A. F. Ismail, A. Mustafa, *Polym. Degrad. Stab.* 92 (2007) 1421.
- [50] I. Kim, G. E. Blomgren, P. N. Kumta, Sn/C Composite Anodes for Li-Ion Batteries, *Electrochem. Solid-State Lett.* 7 (2004) A44.
- [51] N. Pereira, L. C. Klein, G. G. Amatucci, Particle size and multiphase effects on cycling stability using tin-based materials, *Solid State Ionics* 167 (2004) 29.
- [52] D. Wang, X. Li, J. Yang, J. Wang, D. Geng, R. Li, M. Cai, T.-K. Sham, X. Sun, Hierarchical nanostructured core-shell Sn@C nanoparticles embedded in graphene nanosheets: spectroscopic view and their application in lithium ion batteries, *Phys. Chem. Chem. Phys.* 10 (2013) 3535.
- [53] Z. P. Guo, Z. W. Zhao, H. K. Liu, S. X. Dou, Electrochemical lithiation and de-lithiation of MWNT-Sn/SnNi nanocomposites, *Carbon*, 43 (2005) 1392.
- [54] M. Winter, J. O. Besenhard, Electrochemical lithiation of tin and tin-based inter-metallics and composites, *Electrochim. Acta*, 45 (1999) 31.
- [55] I. A. Courtney, J. S. Tse, O. Mao, J. Hafner, J. R. Dahn, Ab initio calculation of the lithium-tin voltage profile, *Phys. Rev.* 58 (1998) 15583.
- [56] W. Xing, J. S. Xue, J. R. Dahn, Optimizing pyrolysis of sugar carbons for use as anode materials in lithium-ion batteries, *J. Electrochem. Soc.* 143 (1996) 3046.
- [57] K. E. Aifantis, S. A. Hackney, J. P. Dempsey, Design criteria for nanostructured Li-ion batteries, *J. Power Sources* 165 (2007) 874.

List of Figure Captions

Fig. 1. TGA curves (a) and XRD patterns (b) of different NC-SnO₂ and NC-Sn materials.

Fig. 2. TEM images of different (a-e) NC-SnO₂ materials. Inset of (d): single SnO₂ nanoparticle with carbon-coating.

Fig. 3. TEM images of different (a-e) NC-Sn materials.

Fig. 4. Galvanostatic charge-discharge profiles for the first cycle (a) and (b), cyclic performance at a current density of 100 mA/g (c) and (d), and cyclic voltammograms (scan rate 0.1 mV/sec) (e) and (f), for different NC-SnO₂ and NC-Sn materials.

Fig. 5. XPS spectra of 50 wt% NC-SnO₂ and 60 wt% NC-Sn materials. Inset: High resolution N 1s spectra of 50 wt% NC-SnO₂ (left) and 60 wt% NC-Sn (right).

Fig. 6. TGA curve (a), XRD patterns (b), TEM images (c), and XPS spectra with inset of high resolution N 1s spectra (d) of NC-Sn-18.

Fig. 7. Galvanostatic charge-discharge profiles for first, second and third cycles @ 100 mA/g (a), cyclic performance @ 100 and 500 mA/g (b), and cyclic voltammograms (scan rate 0.1 mV/sec) (c), and impedance spectroscopy before and after 50 cycles (inset picture) (d) of NC-Sn-18 and NC-Sn-200 anodes.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table 1.

Compositions, average particle size, nitrogen contents and specific discharge capacities after 50 cycles at 100 mA/g of various NC-SnO₂ materials derived from different amount of PAN.

PAN (g)	SnO ₂ (wt.%)	C (wt.%)	Particle size (nm)	Nitrogen content (wt%)	Specific capacity (mAh/g)
0.5	82	18	12	7.3	223
1.0	69	31	10	8.2	184
1.5	59	41	8	9.1	470
2.5	50	50	8	10.3	621
3.5	45	55	7	8.4	451

Table 2.

Compositions, average particle size, nitrogen contents and specific discharge capacities after 50 cycles at 100 mA/g of various NC-Sn materials derived from different amount of PAN.

PAN (g)	Sn (wt.%)	C (wt.%)	Particle size (nm)	Nitrogen content (wt.%)	Specific capacity (mAh/g)
0.5	85	15	800	4.9	144
1.0	73	27	500	5.4	184
1.5	60	40	200	6.0	450
2.5	45	55	180	4.7	291
3.5	38	62	150	3.8	255

Table 3.

XPS elemental composition of the prepared NC-SnO₂ (50 wt%), NC-Sn-200, and NC-Sn-18 materials.

Element	NC-SnO ₂ wt%	NC- Sn-200 wt%	NC-Sn-18 wt%
C 1s	61.9	74.6	70.8
Sn 3d	12.8	13.3	20.9
N 1s	10.3	6.0	2.8
Pyridinic-N	71.6%	49.1%	73.5%
Pyrrolic-N	10.8%	28.9%	10.4%
Graphitic-N	17.5%	22.0%	16.1%

Table 4.

Compositions, average particle size, nitrogen contents and specific discharge capacities after 50 cycles at 100 mA/g of various NC-Sn materials derived from PAN and PVP.

Electrode	Sn (wt.%)	C (wt.%)	Particle size (nm)	Nitrogen content (wt.%)	Specific capacity (mAh/g)
NC-Sn-18	64	36	18	2.8	650
NC-Sn-200	60	40	200	6.0	450