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Petal-shaped SnO_2 free-standing electrodes with electrically conducting layers via a plasma-activated nitrogen doping process for high performance lithium-ion batteries



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ABSTRACT

SnO₂ Free-standing anodes are regarded as a potential negative electrode for high energy lithium ion batteries (LIBs). However, they suffer from poor rate capability and reversibility because of very low electric conductivity of SnO₂. In this study, in order to endow electrical conductivity to the surface of SnO₂ particles, a novel and facile method using a plasma are employed to dope nitrogen into the lattice of SnO₂. The SnO₂ free-standing anode was fabricated by carbonizing an electro-spun fiber sheet followed by depositing SnO₂ particles on the surface of carbon nanofibers (CNF) comprising the sheet through a hydrothermal process.

The best N-doped SnO₂ anode obtained under an optimized condition exhibits a 23 times higher specific capacity of 767 mAh g⁻¹ than that of a pristine SnO₂ anode (<32 mAh g⁻¹) at a high current density of 3.0 A g⁻¹. Furthermore, in a long-term cycle test at 0.1 A g⁻¹, this anode shows a high retention capability with a specific capacity of 909 mAh g⁻¹ and Coulombic efficiency (CE) of 99.3% after 100 cycles. Based on the extensive physical/electrochemical characterizations and performance tests, a mechanism is proposed explaining the roles of N-doped SnO₂ layer in the electrochemical reactions. Overall, the plasma-treated SnO₂ anode exhibits significantly improved capacity retention, rate capability and long-term cycle stability by forming an electrically conducting layer on the surfaces of SnO₂ particles. Therefore, this plasma technique is confirmed to be a very facile and effective way to significantly improve the performance of SnO₂ anode for LiBs.

1. Introduction

With increasing demand for rechargeable LIBs having high energyand power-densities from various applications, such as mobile electronics, electric vehicles, energy storage systems, etc., lots of efforts have been made to develop advanced anode materials that can overcome the theoretical capacity limit (372 mAh g⁻¹) of conventional graphite [1–5]. Among various candidates SnO_2 is considered as one of the most promising materials because it has a high Li ion storage capacity (1,494 mAh g⁻¹), a low operating potential (0.25 V vs. Li⁺/Li), and nontoxicity. The lithium storage mechanism into SnO_2 is explained as consisting of conversion and alloying reactions [1]:

$$SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O$$
⁽¹⁾

$$Sn + 4.4Li^+ + 4.4e^- \rightarrow Li_{4.4}Sn \tag{2}$$

However, there are some drawbacks with this material such as huge volume change and poor reversibility during charge/discharge processes, which result in a low rate capability and a fast capacity fading [6,7]. Various approaches have been tried to overcome these problems by employing nano-structured SnO₂ and carbon host materials having electrical conductivity [7–14]. One of them is to use a free-standing SnO₂ anode material consisting of a porous carbon substrate such as carbon paper, carbon cloth, and carbon sheet decorated with nano-sized SnO₂ particles. The free-standing anodes made of carbon or metal sheets have advantages of high specific capacity over conventional electrodes made of granular materials because they do not need ancillary electrode

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components such as binder and electric conducting additives which negatively contribute to the specific capacity of battery. Moreover, their porous 3D structures with a high specific surface area can enable high loading of active material as well as provide large contact area between SnO₂ and electrolyte [15–17].

Nevertheless, there remains a hurdle of low electrical conductivity of SnO₂ that deteriorates the performance of free-standing SnO₂ electrodes. As the SnO₂ particles are directly exposed to the electrolyte, their low electric conductivity can retard the electrochemical reaction between electrode and electrolyte due to slow electron transport at the surface of nonconductive SnO₂ particles [10,13,18]. Electrical conductivity of SnO₂, however, can be improved by reducing the band gap of the material through N-doping. Wang et al. [18] reported N-doped SnO2 nanoparticles fabricated via laser pyrolysis using SnCl₄·5H₂O and C₂H₄/ NH₃ as precursors to endow the anode materials with high cyclability and rate capability. Guan et al. [19] reported a simple method to obtain N-doped SnO₂ particles with a micro/mesoporous structure through a one-step synthesis method using SnCl₄·5H₂O and hexamethylenetetramine. The resulting materials were found to increase the capacity and cyclability of the anodes. However, these previous studies focused on the synthesis of N-doped SnO₂ powders and those N-doping techniques are not suitable for applying to free-standing electrodes. Therefore, new Ndoping techniques need to be developed to make an electrical conducting layer on the surface of SnO2 particles. Plasma techniques are very simple and effective ways that can modify the surface properties of materials. It can be also used to dope ions and generate functional groups on the surfaces of solid materials using various gases such as O₂, N₂, CO₂, NH₃, etc. in a short time without any auxiliary washing/drying step, and it can easily control the degree of modification of the materials [20].

In this study, a new approach is introduced to modify SnO_2 freestanding anode materials for LIBs through a plasma-assisted N-doping technique. The SnO_2 free-standing anode materials were prepared by uniformly depositing SnO_2 nano-particles on electro-spun carbon nanofiber sheets using a hydrothermal method, followed by an ammonia plasma treatment. These free-standing SnO_2 anode materials were thoroughly characterized using SEM, TEM, XRD, and XPS and their microscopic electrical conductivities were measured using a SEM-FIB (3D Quanta) which used a four-point probe system. Coin cells were assembled using the SnO_2 free-standing materials as anode and their electrochemical performances were tested through cyclic voltammetry (CV), charge/discharge, rate capability, and long-term cycle tests.

2. Experimental section

2.1. Materials

Polyacrylonitrile (PAN, MW = 150,000 g mol⁻¹), polymethyl methacrylate (PMMA, Mw = 120,000 g mol⁻¹), N, N-dimethylformamide (DMF, 99.8%), tin(II) chloride dihydrate (SnCl₂·2H₂O), hydrochloric acid (HCl, 35%), mercaptoacetic acid, and urea were purchased from Sigma-Aldrich. For electrochemical tests, coin cell parts (CR2032) and pure Li metal foil were purchased from Welcos, Co., polypropylene separators (Celgard 2320) from Celgard, Inc., and an electrolyte composed of 1.3 M LiPF₆ in a mixed solution of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) at a 3:7 vol ratio including 5 wt% of fluoroethylene carbonate (FEC) additive from PANAX ETEC, Inc.

2.2. Synthesis of CNF

A polymer solution used for electrospinning was made by dissolving a given amount of PAN (13 wt%) in DMF while stirring for 24 h at 90 °C to obtain a homogeneous mixture. The mixture was then loaded into a 10 ml syringe having a stainless steel needle (27 G \times 13 mm). Electrospinning was carried out for 5 h under a positive voltage of 12 kV, a tipto-collector distance of 15 cm, and a jet rate of polymer solution of 0.2 ml h⁻¹. The resulting electrospun-PAN fiber sheets were stabilized at 250 °C for 2 h in air followed by a carbonization step at 700 °C for 1 h under a nitrogen atmosphere in a tubular furnace. The obtained CNF sheets were cut into 1 cm² squares and used as a support for free-standing electrodes.

2.3. Synthesis of SnO₂@CNF

A precursor solution for SnO₂ was prepared by dissolving 0.3 g of SnCl₂·2H₂O, 0.5 g of urea, 10 μ l of mercaptoacetic acid, and 0.5 ml of HCl in a 40 ml of deionized (DI) water while continuously stirring at room temperature. Subsequently, a piece of CNF sheet was immersed in the precursor solution and then transferred to a Teflon-lined stainless steel autoclave for a hydrothermal process to synthesize SnO₂ particles. The process was proceeded by placing the autoclave in an electric box furnace at 150 °C for 12 h. After the hydrothermal reaction was completed, the SnO₂-coated CNF sheet (SnO₂@CNF) was washed with DI water and dried in an electric oven at 60 °C for 12 h and then annealed at 300 °C for 1 h in air to oxidize the residual Sn and SnO to SnO₂. The loading of SnO₂ on a CNF sheet was calculated by measuring the weights of the sheet before and after SnO₂ deposition and the loading was set to be 1.5 mg cm⁻² in all electrodes.

2.4. Synthesis of N-doped SnO₂@CNF

The as-prepared SnO₂@CNF sheet was treated by RF (radio frequency) plasma generator (COVANCE-1MPR, Femto Science, Inc.) to implement N-doping into SnO₂ lattice. The SnO₂@CNF sheet was placed in a chamber of the RF plasma generator at 5.0×10^{-2} torr, and then ammonia gas was supplied to the chamber at a flow rate of 50 sccm while maintaining the pressure around 5.0×10^{-1} torr. The power of RF plasma generator was set at 200 W and the treatment time was adjusted from 5 to 20 min to investigate the effects of N-doping on the electrical conductivity and electrochemical performances of SnO₂ anode materials. The whole fabrication process consisting of three steps is schematically illustrated in Scheme 1.

The ammonia plasma-treated SnO₂ anode materials are denoted as 5N-SnO₂@CNF, 10N-SnO₂@CNF, 15N-SnO₂@CNF, and 20N-SnO₂@CNF according to the plasma treatment time of 5, 10, 15 and 20 min, respectively.

2.5. Materials characterization

Morphologies and structures of the anode materials were observed using field emission-scanning electron microscopy (FE-SEM, Inspect F50) operated at 15 kV, transmission electron microscopy (TEM, FEI Tecnai F20, Tecnai) operated at 200 kV, X-ray diffraction (XRD, Rigaku Ultima IV with Cu K α radiation ($\lambda = 0.15406$ Å)), and X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe, Ulvac-PHI with Al K α (h $\nu = 1486.6$ eV) source). The electrical conductivity of a SnO₂-coated carbon nanofiber in a free-standing CNF sheet was measured using a nano manipulator (MM3A EM) installed in an SEM-FIB system (Qunata 3D) with a semiconductor device analyzer (B1500A) [21–23].

2.6. Electrochemical performance

The electrochemical measurements were carried out using CR2032 coin cells that were fabricated in a dry room with a dew point below -60 °C. All galvanostatic charge/discharge tests were conducted using a battery test system (Maccor 4300 K). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out using an Autolab PGSTAT30 electrochemical workstation. CV was conducted to characterize the redox behaviors of the cells over a potential range of 0.1 V–3.0 V (vs Li⁺/Li) at various scan rates.



Scheme 1. Illustration of the fabrication process of free-standing nitrogen-doped SnO₂ anode material and its role in the LIB reactons.

3. Results and discussion

Fig. 1a shows a SEM image of a CNF sheet fabricated by electrospinning of PAN followed by carbonization at 700 °C. The CNF sheet consists of carbon fibers having a smooth surface and an average diameter of about 800 nm. SnO₂ particles were formed uniformly on the surface of CNFs through a hydrothermal process (Fig. 1b) and the particles look like nanosize petals with an average thickness of about 8.70 nm (Fig. 1c). The XRD spectra in Fig. 1d reveals that all the diffraction peaks represent the tetragonal rutile structure of SnO₂, indicating a pure SnO₂ crystalline structure [9].

To observe the morphological changes of SnO₂@CNF anode materials by ammonia plasma treatment, TEM analysis was carried out. Fig. 2a shows a highly crystalline structure of the pristine SnO₂ corresponding to the characteristic lattice fringe of 0.337 nm which can be assigned to the interplanar distance of (110) plane in rutile SnO₂. However, after ammonia plasma treatment amorphous regions (circled in green) and defects (circled in red) are formed due to the doping of nitrogen atoms as shown in Fig. 2b–e and Fig. S1b–e. These amorphous regions expand and the number of defects increase with increasing the plasma treatment time, leading to a less crystalline structure having many defects.

Surface composition and redox states of the N-doped SnO_2 materials were measured through XPS analysis. Fig. 3 shows the variation of binding energy in Sn 3d spectra of the material after ammonia plasma treatment for 10 min. The pristine SnO_2 formed on a CNF sheet ($SnO_2@CNF$) has binding energies of 486.8 and 495.2 eV at Sn 3 d5/2 and 3 d3/2, respectively. However, after plasma treatment both binding energies slightly shift by about 0.5 eV to lower energies of 486.3 and 494.7 eV, respectively, because of the formation of multiple oxidation states including Sn^{2+} by doping nitrogen atoms into SnO_2 lattice [18].

For more precise evaluation of the effect of N-doping on the surface composition of SnO₂, O 1s spectra analysis was conducted as shown in Fig. 4. The core level spectra of O 1s in the pristine and ammonia plasma-treated SnO₂ anode materials are fitted into three types of oxygen chemical states of 530.6, 531.3, and 532.4 eV that are attributed to lattice oxygen (OL), oxygen vacancies (VO), and chemisorbed oxygen (O_C), respectively. The O_L peak corresponds to the O^{2-} state with the lowest binding energy, which is related to non-stoichiometric oxygen from oxygen defects (V_{O}^{0} , V_{O}^{+} , and V_{O}^{++}) [19]. As shown in Fig. 4a–e, V_{O} peak area gradually increases from 22.2% to 67.8% with increasing ammonia plasma treatment time. It may be because the more negative N^{3-} replaces O^{2-} to occupy the regular lattice sites in SnO₂, which causes a charge imbalance and lattice distortion to form oxygen vacancies [18,21]. In addition, the N 1s spectra in Fig. 4f certainly show the increasing nitrogen content in the N-doped SnO2 material with increasing plasma treatment time. In contrast, the C 1s spectra in Fig. S2 show the contents of C-N bonding in all samples remain invariant, meaning nitrogen is not doped into CNFs during the plasma treatment because the CNFs are completely covered with SnO₂ particles.

Electrical conductivities of the N-doped SnO_2 anode materials were measured using a nano-manipulator installed in an SEM-FIB system (Quanta 3D) with a semiconductor device analyzer. The stand-alone anode materials prepared in this study have a three-dimensional



Fig. 1. SEM images and XRD patterns of anode materials: (a) before and (b) after deposition of SnO₂ particles and (c) a high magnification image of SnO₂ particles on a CNF. (d) XRD patterns of a CNF and a SnO₂@CNF anode material (JCPDS: 00-001-0657).



Fig. 2. TEM images of the anode materials before and after ammonia plasma treatment: (a) pristine, (b) 5N-, (c) 10N-, (d) 15N-, and (e) 20N-SnO2@CNF.



Fig. 3. Sn 3 d peaks of the SnO₂ anode materials before and after ammonia plasma treatment.

network with randomly interconnected carbon fibers. A conventional electric tester is only able to measure the bulk electrical conductivity of the CNF sheet covered with SnO2 particles. Therefore, the electrical conductivity of a single fiber in a CNF sheet was measured using a SEM-FIB system on a micron size level while excluding the interference by adjacent carbon fibers. A single fiber was selected and then the four probes of the nano-manipulator were placed at four different points of the fiber as shown in Fig. 5a, and its electrical conductivity was obtained using a DC-based current-voltage curve shown in Fig. 5b. The electrical conductivity of the plasma-treated SnO2@CNF material dramatically increases with increasing the plasma time, with the highest value marking a 21 times jump from that of the pristine material: 0.06×10^{-6} , $0.21 \times 10^{-6}, 0.32 \times 10^{-6}, 0.85 \times 10^{-6}, and 1.28 \times 10^{-6}$ S m⁻¹ for the plasma time of 0, 5, 10, 15 and 20 min, respectively. The increased conductivity is attributed to the enhanced electron transfer rate due to the oxygen vacancy and reduction of the band gap generated by Ndoping [18,19,24]. In addition, all the current vs. voltage (I-V) profiles are not linear but display upwardly parabolic shapes, revealing the semiconductor-like properties of the N-doped SnO_2 materials [30]. The line profiles of I-V curves are not smooth but have some noises, which might be generated by varying contact resistances during the measurements. These noises, however, do not affect the trend of conductivity change with respect to the plasma treatment time.

To investigate the effects of ammonia plasma treatment on the electrochemical performance of SnO_2 anode material, CV analysis was carried out using coin cells assembled with SnO_2 materials as cathode and Li foils as anode. The CV profiles were collected over a potential window of 0.01–3.00 V (vs. Li⁺/Li). Fig. S3 shows the first and the second cycle of the CV profiles of the coin cells with different anodes at 0.1 mV s⁻¹. In the first cycle of the pristine $SnO_2@CNF$, two cathodic and anodic peaks are observed. The cathodic peak around 0.83 V is for the conversion of SnO_2 to Sn and Li₂O. Another broad cathodic peak starting from 0.7 V is associated with a multi-step alloying reaction between Li and Sn to make Li_xSn alloy. The anodic peak around 0.55 V



Fig. 4. XPS spectra of the $SnO_2@CNF$ materials according to ammonia plasma treatment time: O 1s peaks for (a) pristine, (b) 5N-, (c) 10N-, (d) 15N-, and (e) 20N- $SnO_2@CNF$; (f) Comparison of the N 1s peaks for various plasma treatment time.



Fig. 5. Measurement of electric conductivities of SnO₂@CNFs in the electrodes using four-point probes installed in an SEM-FIB system: (a) A four-point probe configuration, (b) Measured I-V curves of the anode materials.

can be ascribed to the dealloying of Li_xSn into Li⁺ and Sn, and another stretched anodic peak starting from 0.98 V corresponds to the formation of SnO₂ due to the oxidation of Sn. In the second cycle, the main difference with the first one is the absence of cathodic peak at around 0.83 V while a broad cathodic peak at around 1.06 V is observed, which may be ascribed to the conversion of SnO₂ to Sn and Li₂O.

The more detailed investigation on the electrochemical activities of N-doped materials was carried out by taking CVs at various scan rates. As shown in Fig. 6a–e, the intensities and integral areas of cathodic and anodic peaks gradually increase with increasing the ammonia plasma treatment time. Additionally, the cathodic peaks for the 5N- and 10N-SnO₂@CNF shift to higher potentials than that of the pristine one as shown in the insets of Fig. 6a–c whereas the cathodic peaks for 15N- and 20N-SnO₂@CNF shift toward lower potentials (Fig. 6d and e). These results imply that the N-doping provides a highly electrical conducting

layer that can allow the faster electron transport rates and reaction kinetics. However, it appears that excessive N-doping may deteriorate the performance of SnO_2 anode by increasing the unreactive area consisting of Sn-N bonds [18,24].

In order to further understand the activities of the materials, lithium ion diffusion coefficients at the anode electrodes were calculated using Randles-Sevcik equation based on CV profiles taken by varying the scan rate (ν) [25]:

$$i_p = 0.4463 n^{3/2} F^{3/2} R^{-1/2} T^{-1/2} A D^{1/2} C \nu^{1/2}$$
(3)

where i_p is the peak current, F is the Faraday constant of 96,485 C mol⁻¹, n is the charge transfer number, A is the electrode surface area of 1.0 cm², R is the gas constant of 8.314 J mol⁻¹ K⁻¹, T is the absolute temperature of 298.15 K, C is the concentration of lithium ions in the electrode of 0.046 mol cm⁻³, and ν is the scan rate. Fig. 6f shows the



Fig. 6. CV profiles of anode materials at 0.25, 0.5, and 1.0 mV s⁻¹: (a) pristine, (b) 5N-, (c) 10N-, (d) 15N-, and (e) 20N-SnO₂@CNF; (f) The Randles-Sevcik plots of the linear relationships between peak current (i_p) and square root of the scan rate ($v^{1/2}$) for the plasma-treated anode materials.

chemical diffusion coefficients (D^{1/2}) of Li ions at discharge states that are calculated to be 3.338×10^{-4} , 6.011×10^{-4} , 6.459×10^{-4} , 7.969×10^{-4} , and 9.413×10^{-4} cm² s⁻¹ for the corresponding plasma treatment times, respectively. These results reveal that the increased electrical conductivity by N-doping contributes to the lithium ion diffusivity into the SnO₂ material. However, the elevated ion diffusivity does not guarantee the improvement of anode performance because of the expanded unreactive area as explained above.

Fig. 7a–e shows conversion and deconversion reversibility of the anode materials in terms of capacity retentions over a potential window

from 1.20 V to 3.00 V for the initial five cycles. In view of the charge/ discharge cycles, the reversibility of the anode in terms of the capacity retention increases with increasing the plasma-treatment time up to 10 min (10N-SnO₂@CNF). As shown in Fig. 7c, both the charge (conversion reaction) and discharge (deconversion) profiles for the last four cycles overlap very closely with one another, indicating that the anode material exhibits the highest capacity retention and suffers almost no capacity fading. Whereas the profiles for 15N- and 20N-SnO₂@CNF that were plasma-treated for 15 min and 20 min, respectively, become widely separated indicating lower capacity retentions and faster



Fig. 7. Charge-discharge profiles of the anode materials in the initial five cycles at 0.1 A g⁻¹: (a) pristine, (b) 5N-, (c) 10N-, (d) 15N-, and (e) 20N-SnO₂@CNF.

capacity fading as shown in Fig. 7d and e. These results imply that the electrical conducting layer formed on the N-doped SnO₂ can help improve the capacity retention by allowing the faster electron and ion transports. However, excessive N-doping can cause deficiency of oxygen content in the converting reactions of Sn and Li₂O back into SnO₂, leading to a decrease in the capacity retention [19].

Electrochemical performances of the plasma-treated SnO2@CNF anodes were evaluated through charge/discharge measurements with increasing the current density stepwise up to as high as 5 A g^{-1} in a potential window of 0.01–3.00 V (vs. Li⁺/Li). As shown in Fig. 8, all the anode materials exhibit similar specific capacities of about 1100 mA h g^{-1} at a low current density of 0.1 A g^{-1} . However, the specific capacity gaps among the electrodes become to widen with increasing the current density. Moreover, at a higher current density of 3.0 A g^{-1} , the pristine and 20N-SnO2@CNF anode materials rapidly fade away while the 5N-, 10N-, and 15N-SnO₂@CNF electrodes maintain relatively high capacities of 554, 767, and 401 mAh g^{-1} , respectively. At an even higher current density of 5.0 A g^{-1} , the 10N-SnO₂@CNF anode only survives showing a specific capacity of 533 mAh g^{-1} , which may be ascribed to the enhanced reversibility in charge/discharge reactions due to the optimized electrical conducting layer formed on the surface of SnO₂ anode material. Another noteworthy thing in this figure is the initial capacities of the materials at the 1st cycles at a current density of 0.1 A g⁻¹, where the pristine anode shows a higher capacity than those of the other N-doped ones. This is presumably because the electrochemically inactive N-doped SnO₂ layer brings about the reduction of capacity. However, as the cycles go on or at higher currents, most of the N-doped electrodes display higher capacities than that of the pristine one because the positive effects of the N-doped SnO₂ outweighs the negative effects. As the thickness of the N-doped layer is estimated to be a few atomic layers thick, the capacity loss may be negligibly small and thus it can be compensated by the improved performance due to increased electrical conductivity.

Long-term cycle tests were also carried out at a current density of 0.1 A g⁻¹ in order to compare the cycle stabilities of all anodes as shown in Fig. 9a. The tests were conducted at a low current density of 0.1 A g⁻¹ over 100 cycles because the current density was most adequate for the comparison of various electrodes having different performances. The 10N-SnO₂@CNF anode presents the highest specific capacity of 909 mAh g⁻¹ after 100 cycle, and it also shows the highest CEs of 62.0 and 99.3% at the 1st and the 100th cycle, respectively, as compared with other electrodes in Fig. S4 and Table S1. Meanwhile, 5N- and 15N-SnO₂@CNF show worse performances than 10N-SnO₂@CNF, furthermore, the pristine and 20N-SnO₂@CNF rapidly fade away in the 83th



Fig. 8. Rate capability tests of the coin cells with various anode materials during charge and discharge cycles at 0.1, 0.5, 1.0, 3.0, and 5.0 A g^{-1} : Open symbol = charge, closed symbol = discharge.

and 57th cycles, respectively. These results are coincident with the rate capability test in Fig. 8.

Consequently, the electrochemical performance tests in terms of CV, rate capability and long-term stability verify that the N-doped SnO₂ can significantly improve the anode performance presumably by accelerating the electron/ion transport rates through the conductive skin layer of SnO₂, leading to an enhanced utilization of SnO₂, the faster reaction rate between lithium ions and SnO₂, and improved reversibility of the charge/discharge reactions.

After reviewing all the data obtained through the physical/electrochemical characterizations and charge/discharge performance tests of N-doped SnO₂ anode materials, a mechanism is proposed explaining the roles of N-doped SnO₂ layer in the electrochemical reactions and how it affects the performance of the anode as follows (Fig. 9b): Basically the SnO₂ material is electrically nonconductive and thus the conventional SnO₂ anodes are generally made by mixing SnO₂ powders with carbon powders to give electric conductivity to the electrode. However, in the case of SnO₂ particles coated on a stand-alone carbon sheet, the SnO₂ particles are directly exposed to the liquid electrolyte. Therefore, the transport of electrons and Li ions through the interface between the electrolyte and the nonconductive SnO₂ are delayed, and thus a high over-potential can be generated as schematically depicted in Fig. 9b-1. This could be solved by forming an electric conductive skin layer on the surface of SnO₂ particles through nitrogen doping as depicted in Fig. 9b-2. The N-doping is implemented by replacing O^{2-} with N^{3-} in the SnO₂ lattice to create Sn-N bonds through an ammonia plasma treatment (Figs. 3 and 4). The electric conductivity of the N-doped SnO₂ increases with increasing the degree of N-doping (Fig. 5). The enhanced electric conductivity of SnO₂ anode can result in a significant performance improvement in terms of Li ion diffusivity, reversibility of the reactions, rate capability and long-term cycle stability (Figs. 6-9). However, as the N-doped SnO₂ layer is not active toward the reactions with Li ions, it can negatively affect the capacity of anode. As the degree of N-doping increases the thickness of unreactive N-doped layer becomes larger, which increases the travel length for Li ions to reach the active SnO₂ core. The expanded travel length results in an increased over-potential and a deteriorated reversibility of the reactions between Li ions and active SnO₂. Therefore, the thick electrical conducting layer of SnO₂ formed by excessive N-doping may deteriorate the electrochemical reactions as depicted in Fig. 9b-3, leading to a poor anode performance. This means there are pros and cons of N-doped SnO2. In conclusion, there is an optimal degree of N-doping in SnO2 as verified in the tests of reversibility, rate capability and long-term charge/discharge cycles (Figs. 7-9). In this study, 10N-SnO₂@CNF that was obtained by a plasma treatment for 10 min showed the best performance.

Comparative assessment with other reports reveals that the N-doped $SnO_2@CNF$ free-standing anode material synthesized in this work exhibits a relatively good performance superior or at least comparable to those of the SnO_2 -based anode materials in the literature as shown in Fig. 9c.

4. Conclusion

This study has successfully demonstrated a novel method for improving the performance of free-standing anode materials consisting of carbon nanofibers decorated with SnO₂ nano petals that were modified using an ammonia plasma treatment technique. In-depth characterization confirmed that the electrical conductivities of the N-doped SnO₂ materials were enhanced by forming oxygen vacancy in the lattice of SnO₂. The electrical conductivity of the N-doped SnO₂ increased with increasing the plasma treatment time in the range from 5 to 20 min. In case of 20N-SnO₂@CNF that was treated for 20 min, its electrical conductivity was raised by 21.3 times (1.28×10^{-6} S m⁻¹) of the pristine SnO₂ material (0.06×10^{-6} S m⁻¹). However, excessive N-doping was found to form a thick N-doped SnO₂ layer consisting of unreactive Sn-N bonds which could increase the over-potential in the electrochemical



Fig. 9. (a) Long-term cycle tests of the coin cells with various anode materials at 0.1 A g^{-1} ; (b) Schematic illustrations of the behaviors of lithium ion and electron on the surfaces of SnO₂ anodes depending on the thickness of conductive N-doped layer: (b-1) without a conducting layer, (b-2) thin conducting layer, and (b-3) thick conducting layer; (c) Performance comparisons of the anode materials in this work with the SnO₂-based anode materials in the literature.

reactions to result in a substantial deterioration of reaction reversibility and capacity retention of the battery during charge/discharge cycles. Therefore, the degree of N-doping into SnO₂ anode material should be optimized to balance the electric conductivity and reaction activity at the skin layer of SnO₂ particles. The best performing 10N-SnO₂@CNF obtained by a 10 min plasma treatment exhibited the highest specific capacity of 533 mA h g⁻¹ at a high current density of 5.0 A g⁻¹ while other SnO₂ anodes displayed almost zero capacities at the same current. It also showed a very stable cycling performance on a long-term test, displaying a specific capacity of 909 mAh g⁻¹ after 100 cycles.

Overall, it is confirmed that the performance of SnO_2 anode material can be significantly enhanced by N-doping through increasing the electrical conductivity of SnO_2 . It is believed that this N-doping method using a plasma technique suggests a novel and facile way to effectively enhance the performance of SnO_2 anode material for LIBs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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