Oxygen-doped carbon host with enhanced bonding and electron attraction abilities for efficient and stable SnO₂/carbon composite battery anode

Zhen Geng^{1,2}, Bing Li¹, Hezhi Liu³, Hong Lv¹, Qiangfeng Xiao⁴, Yongjun Ji^{3*} and Cunman Zhang^{1*}

ABSTRACT The coupling between electrochemically active material and conductive matrix is vitally important for high efficiency lithium ion batteries (LIBs). By introducing oxygen groups into the nanoporous carbon framework, we accomplish sustainably enhanced electrochemical performance for a SnO₂/carbon LIB. 2–5 nm SnO₂ nanoparticles are hydrothermally grown in different nanoporous carbon frameworks, which are pristine, nitrogen- or oxygen-doped carbons. Compared with pristine and nitrogen-doped carbon hosts, the SnO₂/oxygen-doped activated carbon (OAC) composite exhibits a higher discharge capacity of 1,122 mA h g⁻¹ at 500 mA g⁻¹ after 320 cycles operation and a larger lithium storage capacity up to 680 mA h g⁻¹ at a high rate of 2,000 mA g⁻¹. The exceptional electrochemical performance originated from the oxygen groups, which could act as Lewis acid sites to attract electrons effectively from Sn during the charge process, thus accelerating reversible conversion of Sn to SnO₂. Meanwhile, SnO₂ nanoparticles are effectively bonded with carbon through such oxygen groups, thus preventing the electrochemical sintering and maintaining the cycling stability of the SnO₂/OAC composite anode. The high electrochemical performance, low biomass cost, and facile preparation renders the SnO₂/OAC composites a promising candidate for anode materials.

Keywords: tin oxide, nanoporous carbon, functional groups, anode materials, lithium-ion batteries

INTRODUCTION

As one of the most widely commercialized energy storage devices, lithium-ion batteries (LIBs) have attracted intensive interest during the past decades due to the ad-

vantages of light weight, environmental benignity, high energy density and high power density [1]. Although graphite is the dominated anode material for commercial LIBs, its low theoretical capacity (372 mA h g⁻¹) seriously hinders the development of LIBs with higher energy density [2]. Many efforts have devoted to exploring other high-capacity anode materials.

Among many kinds of anode materials, tin oxide (SnO₂) is regarded as a promising candidate considering its natural abundance, environmental benignity, and high theoretical capacity (782 mA h g⁻¹) [3–6]. However, similar to other anodes with high capacity such as silicon [7–9], large volume change (more than 300%) during lithiation and delithiation process leads to severe pulverization of electrode, aggregation of SnO₂ particles and formation of unstable solid electrolyte interphase (SEI) film, thus resulting in fast capacity fading. So far, two main strategies have been applied to resolve the above-mentioned problems. One effective way is to synthesize the nanostructured SnO₂, including one dimensional (1D) nanorods/nanotubes/nanowires, 2D nanosheets and 3D hollow or porous nanostructures [10–13]. The other approach focuses on developing hybrid nanostructure by embedding active SnO₂ nanoparticles into conductive carbonaceous matrix such as porous carbon and graphene [6,14–16]. It is well demonstrated that the carbon-based hosts play crucial roles as ideal volume change buffers and good electron conductors.

Another drawback of SnO₂ based anodes is poor initial Coulombic efficiency (CE) due to the irreversible conversion reaction during the initial electrochemical process, resulting in the insufficient utilization of SnO₂ and

¹ Clean Energy Automotive Engineering Center, Tongji University, Shanghai 201804, China

² Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

³ State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

⁴ General Motors Research and Development Center, Warren, MI 48090, USA

* Corresponding authors (emails: yjji@ipe.ac.cn (Ji Y); zhangcunman@tongji.edu.cn (Zhang C))

additional consumption of cathode materials [17]. The electrochemical processes can be summarized by the equations as follows [10,11]:

In the initial lithiation process, SnO_2 is irreversibly converted to Sn (Equation (1)) due to the strong stability of Li_2O , resulting in large capacity loss and low initial CE (<50%). Subsequently, reversible alloying/dealloying reaction between Sn and Li (Equation (2)) contributes to the dominant capacity. If the conversion reaction of Equation (1) is reversible, the theoretical specific capacity can be increased from 782 (based on 4.4 Li ions) to 1,493 mA h g^{-1} (based on 8.4 Li ions), which would significantly improve the capacity of SnO_2 .

Recently, SnO_2 anodes with higher experimental capacity than theoretical capacity were reported in SnO_2 /carbon nanocomposites, which was attributed to the synergetic effects benefit from unique hybrid nanostructure [18–23]. However, the detailed mechanism still remains unclear. In another attempt, higher experimental capacity is obtained by ternary composites SnO_2 /carbon/transition metal oxides (e.g., Co_3O_4 , Fe_2O_3), where transition metal oxides nanoparticles can promote the decomposition of Li_2O and also accelerate reversible conversion of Sn to SnO_2 [24,25]. It is well documented that Lewis acid can promote catalytic oxidation reaction by electron extraction as the electron acceptor, which has been widely used in homogeneous catalysis [26]. Besides, it is reported that tiny size of Sn nanoparticles (<5 nm) also could reduce the activation energy for Li_2O decomposition, thus boosting the partial conversion of Sn to SnO_2 [20]. Therefore, it could be an effective way to achieve reversible oxidation conversion of Sn to SnO_2 by introducing Lewis acid groups into carbon host and combining with tiny size of SnO_2 nanoparticles.

Taking these into account, SnO_2 /carbon composites are synthesized here by a simple hydrothermal approach, where tiny SnO_2 nanoparticles (2–5 nm) are effectively confined within the nanoporous carbon framework. Besides, Oxygen functional groups are herein introduced into nanoporous carbon matrix as Lewis acid sites in the form of carboxyl, hydroxyl and ester, which can effectively abstract electrons from Sn during the charge process, thus accelerating reversible conversion from Sn to SnO_2 and resulting in high initial CE. Meanwhile, SnO_2 nanoparticles are effectively bonded with carbon through such oxygen groups, thus realizing homogeneous anchor

of SnO_2 nanoparticles. Besides, nitrogen groups (e.g., pyridine-N and pyrrolic-N) as Lewis base sites are also introduced into porous carbon as a comparison. The oxygen doped nanocomposites exhibit excellent electrochemical performance, in terms of large specific capacity, high rate capability and long cycling stability.

EXPERIMENTAL SECTION

Preparation of nanoporous carbon materials

Original nanoporous carbon was prepared by potassium hydroxide (KOH) chemical activation with biomass corncob as the carbon source and KOH as the activating agent, according to previous reports [27,28]. The pristine carbon sample was hereafter denoted as corncob-derived activated carbon (CAC).

Based on CAC, oxygen doped activated carbon was prepared by nitric acid oxidation. The CAC was impregnated in concentrated nitric acid at 60°C for 2 h and then washed with adequate deionized water. The dried sample was collected and denoted as OAC.

Based on CAC, nitrogen doped active carbon was prepared by a two-step method. The first step was the above-mentioned nitric acid oxidation; the second step was ammonia (NH_3) treatment (the OAC sample was placed in a ceramic crucible and then annealed under NH_3 atmosphere at 800°C for 3 h). The final sample was denoted as NAC.

Preparation of SnO_2 /carbon composites

SnO_2 /carbon composites were synthesized by a simple hydrothermal approach. Firstly, 0.15 g carbon was ultrasonically dispersed into 30 mL stannate aqueous solution (0.15 g SnCl_2 with a purity of >99.995%, 0.3 mL HCl (38 wt%) and 0.3 g urea, purchased from Sigma-Aldrich). The mixture was stirred for 2 h, then the solution was transferred into 50 mL Teflon-lined stainless steel autoclave. The solution was subsequently heated to 180°C for 12 h in an oven. After rinsed with large amount of distilled water and ethanol to remove the chlorate ions, dried samples were calcined in air at 230°C for 5 h. Finally, SnO_2 /carbon composites were obtained. According to pore volume of the obtained carbons, SnO_2 /carbon composites were prepared with the optimal SnO_2 content of 50 wt%, denoted as SnO_2 /CAC, SnO_2 /OAC and SnO_2 /NAC respectively.

Materials characterization

The textural properties of the samples were performed by N_2 sorption at 77 K using a Micromeritics ASAP2020

Table 1 Textural and chemical characteristic of the as-obtained carbon samples

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{t} ($\text{cm}^3 \text{g}^{-1}$)	C (wt%)	N (wt%)	O (wt%)	H (wt%)
CAC	2762	1.49	90.89	<0.3	8.01	0.76
OAC	2532	1.21	77.56	0.6	20.45	1.39
NAC	2724	1.46	88.02	6.11	4.74	1.13

S_{BET} , specific surface area calculated by BET equation at $P/P_0 = 0.02\text{--}0.25$, correlation coefficient of BET curves for all samples is more than 0.9999; V_{t} , total pore volume estimated from the adsorption amount of N_2 at $P/P_0 = 0.98$.

over a wide relative pressure ranging from about 10^{-6} to 1.0. The surface area was calculated using the Brunauer-Emmett-Teller (BET) equation based on adsorption data in the partial pressure (P/P_0) ranging from 0.02 to 0.25 and the total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of 0.98. Pore size distributions (PSDs) were calculated by using the Density Functional Theory (DFT) Plus Software (provided by Micromeritics Instrument Corporation), which was based on the calculated adsorption isotherms for pores of different sizes. All samples were degassed at 300°C for 600 min prior to the measurements.

The scanning electron microscopy (SEM, FEI SIRION 200/INCA, OXFORD) and transmission electron microscopy (TEM, JEM-2100F, JEOL) were used to determine the morphologies and texture of the samples. The crystal structure of SnO_2 /carbon composites was characterized by X-ray diffraction measurement (XRD, Rigaku DLMAX-2200). Elemental analysis (Elementar, vario ELIII) and X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI 5000 Versa Probe) were employed to determine the element contents and surface functional groups. Thermogravimetric analysis (TGA) of all SnO_2 /carbon composites was carried out with a thermogravimetric analysis instrument (TGA, STA 409 PC Luxx, Germany) under air atmosphere. A high accuracy balance (METTLER TOLEDO with 0.00001g accuracy) was used to diminish the experimental error.

Cell fabrication and electrochemical measurement

The electrochemical performance of the composite electrode was measured using coin-type cells assembled in an argon-filled glove box. The working electrodes were prepared by pasting slurries onto Cu foil current collector, and dried at 90°C for 24 h under vacuum before testing. The slurry was made by mixing active material (SnO_2 /carbon composites), conductive materials (Super P carbon black) and binder (poly-vinylidifluoride, PVDF) in a weight ratio of 80:10:10 in *N*-methyl-2-pyrrolidone (NMP). The mass loading of active materials for all pre-

pared electrodes was $\sim 2 \text{ mg composites per cm}^2$. The specific capacity calculated here was based on the mass of SnO_2 /carbon composites. The electrolyte was 1 mol L^{-1} LiPF_6 dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 vol/vol) and the separator was glass fiber from Whatman. Lithium foil is used as the counter electrode.

Galvanostatic cycling tests of assembled cells were carried out on a Land CT2001A system (Wuhan Jinnuo Electronics, Ltd., Wuhan, China) in the potential range of 0.01–3 V (vs. Li^+/Li). The cyclic voltammetry (CV) measurements were carried out on a Solartron 1860/1287 Electrochemical Interface (Solartron Analytical, Oak Ridge, TN) in the potential range of 0.01–3.0 V at a scan of 0.2 mV s^{-1} (vs. Li^+/Li). All the electrochemical tests were conducted at room temperature (25°C).

RESULTS AND DISCUSSION

As shown in Table 1, large amounts of functional groups leave from CAC due to severe activation at high temperature, and just a few oxygen groups remain (Fig. 1a). Based on CAC, large amounts of oxygen groups are doped into carbon host by nitric acid oxidation (sample OAC). It is well documented that nitric acid treatment produces mainly oxygen groups into carbon, which improves surface chemical property of carbon matrix [29]. Table 1 shows oxygen content of carbon host significantly increases from 8 wt% (CAC) to 20.45 wt% (OAC), which mainly exists as Lewis acid groups (e.g., carboxyl, hydroxyl and ester) (Fig. 1b).

According to previous studies, oxygen groups in biomass play crucial roles on nitrogen doping using NH_3 as nitrogen source [30]. Treating CAC with NH_3 would lead to reduced nitrogen content ($< 2 \text{ wt\%}$) because of the elimination of oxygen groups during KOH activation. Based on above, the modified nitrogen doping method with two-step was developed, i.e., large amounts of oxygen groups were firstly doped into CAC by nitric acid oxidation, then nitrogen doping was further carried out by NH_3 treatment, thus obtaining NAC with high nitro-

Figure 1 O 1s XPS spectra of (a) CAC, (b) OAC and (c) NAC; (d) N 1s XPS spectra of NAC.

gen content. It provides a highly effective method to prepare nitrogen doped carbons based on existing porous carbons. XPS characterization shows the Lewis base groups mainly present in the form of pyridinic-N and pyrrolic-N (Fig. 1d). Meanwhile, large amounts of oxygen groups are consumed and finally only C–O group remains with the content of 4.74 wt% (Fig. 1c).

As shown in Fig. 2a, nitric acid oxidation destroys nanoporous structure of CAC, resulting in the slight decrease of surface area of OAC ($2,532 \text{ m}^2 \text{ g}^{-1}$, Table 1). NH_3 plays dual roles of activating agent and nitrogen source during the further treatment of OAC with NH_3 [30], thus leading to the increase of surface area of NAC. As shown in Fig. 2b, the PSDs of OAC and NAC are similar than that of CAC, ranging from 0.5 to 4 nm. Based on above, a series of ACs with similar surface area and pore structure but different surface chemical properties are fabricated, i.e., acidic for OAC, neutral for CAC and basic for NAC based on Lewis acid-base theory.

As shown in Fig. S1 (see Supplementary information), there are large amounts of irregular granules in CAC, due to irregular characteristic of corncob powders. In Fig. 3a, numerous slit-shaped nanopores are formed in CAC,

which is the characteristic of amorphous carbon. As shown in Fig. 3b, the morphology of representative sample SnO_2/CAC composite is unchanged, compared with the original CAC sample (Fig. S1), which indicates most of SnO_2 nanoparticles are restricted to grow within the carbon host. In Fig. 3c, element mapping shows SnO_2 is homogeneously distributed in the carbon framework, which is beneficial for alleviating aggregation of SnO_2 nanoparticles and pulverization of electrode during the lithiation and delithiation process. At the same time, conductive nanoporous structure can facilitate the penetration of electrolyte into the hybrid nanostructure to enhance Li ions accessibility. As shown in Fig. 3d, SnO_2 nanoparticles with the diameter ranging from 2 to 5 nm are uniformly dispersed on CAC. It is worth noting that so tiny SnO_2 nanoparticles could reduce the activation energy for Li_2O decomposition reaction and boost the partial conversion of Sn to SnO_2 during the charge process [20]. The interplanar spaces of the nanoparticles are measured to be 0.33, 0.26 and 0.17 nm, corresponding to the (110), (102) and (211) crystal planes of tetragonal rutile SnO_2 , respectively (Fig. 3e) [20,25]. Besides, layer nanostructure of graphite is also detected at the edge of

Figure 2 (a) N₂-sorption isotherms and (b) pore size distributions of all the as-obtained samples.

Figure 3 (a) TEM image of CAC; (b) SEM image of SnO₂/CAC; (c) element mapping of SnO₂/CAC; (d) and (e) HRTEM image of SnO₂/CAC.

carbon host due to the carbon atom restructuring caused by KOH activation, which is beneficial for conductivity improvement of carbon host.

The crystal structure of nanocomposites is examined by XRD patterns, as shown in Fig. 4a. It can be seen that

XRD patterns of three composites are quite similar. All intensive peaks match well with rutile SnO₂ (JCPDS No. 41-1445), illustrating that SnCl₂ is completely transformed to well-crystallized SnO₂. Based on the Scherrer equation, the particle sizes of SnO₂/CAC, SnO₂/OAC and

Figure 4 (a) XRD patterns and (b) TGA curves of all the as-obtained samples.

SnO₂/NAC are calculated to be 5.23, 4.91, and 4.53 nm, respectively, consistent with the TEM observation (Fig. 3d, Figs S2 and S3). It indicates that different surface chemical property for carbon hosts has no obvious effects on the distribution and size of SnO₂ nanoparticles.

The accurate content of SnO₂ in composites is measured by thermal gravimetric analyses (TGA) conducted in air. As shown in Fig. 4b, three composites contain the similar SnO₂ content, i.e., 47 wt% for CAC, 50 wt% for OAC and 49 wt% for NAC. Weight loss process represents the combustion process of carbon host in air. Exothermic peak has a shift to some extent, which is mainly attributed to different oxygen content of three composites (i.e. 20.45 wt% for OAC, 8.01 wt% for CAC, 4.74 wt% for NAC in Table 1). Oxygen groups play a role of combustion-supporting agent in combustion engineering [31]. Thus, combustion is more sufficient with increasing oxygen content, resulting in exothermic peak shifts to lower temperature.

Interaction between SnO₂ nanoparticles and functional groups results in totally different electrochemical performance of SnO₂/carbon composites. Among them, SnO₂/OAC presents the obviously enhanced performance. Charge-discharge curves during the first 150 cycles of SnO₂/OAC at a current density of 500 mA g⁻¹ (activated at the first 3 cycles using 200 mA g⁻¹) are shown in Fig. 5a. The SnO₂/OAC electrode delivers the discharge and charge capacity of 1,745 and 1,183 mAh g⁻¹ for the first cycle, respectively. It is worth mentioning that the initial CE of SnO₂/OAC is 67.8%, which is higher than that of SnO₂/CAC (60.4%) and SnO₂/NAC (57.9%) electrodes, as shown in Figs S4 and S5, respectively. According to initial electrochemical process (Equations (1) and (2)), totally 8.4 mole Li-ions are utilized during the first lithiation process if one mole of SnO₂ involves in the reaction. However, due to irreversibility of the reaction in

Equation (1), at least 4 mole Li-ions are inactivated in the following delithiation process, leading to a low initial CE (~52%). Higher initial CE of SnO₂/OAC implies probable partial reversible conversion from Sn to SnO₂. The 32.2% capacity loss is generally attributed to irreversible formation of the SEI layer on the surface of the nanocomposites and partial irreversible conversion of Sn to SnO₂ [11,20,25]. The CE is further increased to almost 100% for subsequent cycles (Fig. 5e), indicating the excellent reversibility of the electrode.

Fig. 5b shows CV curves of the first four cycles of SnO₂/OAC electrode within the potential range of 0.01–3 V at a scanning rate of 0.2 mV s⁻¹. In the first cathodic cycle, a cascade of reduction wave is observed, corresponding to (from higher to lower potential) the reduction of SnO₂ to Sn, the formation of SEI film, and alloying reaction of Sn with Li to form Li_xSn alloy [32]. In the first anodic cycle, the peak at 0.5 V responds to the dealloying process to form Sn, and the peaks at 1.3 and 2.5 V could be assigned to the partial conversion reaction of Sn to SnO₂ accompanied with the decomposition of Li₂O [25]. The subsequent CV curves are almost identical, indicating reversible and stable electrochemical performance of SnO₂/OAC composite.

Fig. 5c shows the galvanostatic cycling performances of SnO₂/carbon composites. It is found that at the same current density (500 mA g⁻¹), SnO₂/OAC exhibits the best cycling stability with a high discharge capacity of 930 mA h g⁻¹ at 150th cycle, suggesting high reversibility and utilization of SnO₂. After stabilizing for 60 cycles, SnO₂/CAC shows a fast capacity fading. Among them, SnO₂/NAC shows the worst cycling performance, presenting a serve capacity fading. In addition, as shown in Fig. 5d, SnO₂/OAC composite also displays an excellent rate performance at a current density from 100 to 2,000 mA g⁻¹, superior to SnO₂/CAC and SnO₂/NAC.

Figure 5 (a) Discharge-charge profiles of SnO₂/OAC for 150 cycles; (b) CV curves of SnO₂/OAC at a scanning rate of 0.2 mV s⁻¹ for 4 cycles; (c) cycling performance of all samples at 500 mA g⁻¹; (d) rate performance of all samples; (e) long cycling performance and Coulombic efficiency of SnO₂/OAC at 500 mA g⁻¹.

Remarkably, a high lithium storage capability of 680 mA h g⁻¹ at a high rate of 2,000 mA g⁻¹ can still be obtained for the SnO₂/OAC composite. Moreover, the specific capacity can be restored to around 1,100 mA h g⁻¹ when the current rate is reversed back to 100 mA g⁻¹. More interestingly, starting from the 150th cycle, the discharge capacity of SnO₂/OAC increases gradually to 1,122 mAh g⁻¹ for 320 cycles, as shown in Fig. 5e. The increasing capacity could be explained by gradually reversible conversion of Sn to SnO₂, extra in-

terfacial charge storage between SnO₂ and carbon, as well as the reversible formation of a polymeric layer at the electrode-electrolyte interface [21–23].

To the best of our knowledge, the electrochemical performance of the SnO₂/OAC is one of the best of the reported SnO₂ based anode materials, in terms of large specific capacity, high rate performance and long cycling stability [10–12,14–17,24]. Besides, other advantages, e.g., low biomass cost and facile preparation method, also make SnO₂/OAC composites become an ideal candidate

Figure 6 (a) Differential charge capacity *versus* voltage plots of all samples for 150th cycle at 500 mA g⁻¹; (b) CV curves of all samples at a scanning rate of 0.2 mV s⁻¹ for 2nd cycle.

for anode materials in applications.

Obvious performance differences among three samples indicate that functional groups play crucial roles in the electrochemical performance of SnO₂/carbon composites, considering the similar SnO₂ content, size and distribution of nanoparticles and surface area of carbon host. O-containing groups play a positive role, opposite to N-containing groups. The excellent electrochemical performance of SnO₂/OAC can be attributed to several possible reasons: (1) microporous carbon host effectively buffers the volume changes of SnO₂ nanoparticles during the lithiation and delithiation process; (2) carbon host prevents the aggregation of SnO₂ nanoparticles during cycling; (3) SnO₂ nanoparticles are bonded with carbon through oxygen groups such as carbonyl and carboxylic groups, thus realizing homogeneous anchor of SnO₂ nanoparticles [20]; and (4) reversible conversion of Sn to SnO₂ during the delithiation process. It is easy to understand the first three reasons for the improved cycling performance and rate capability. However, reversible conversion of Sn to SnO₂ is still controversial. Although it is commonly believed that the conversion of Sn to SnO₂ is an irreversible reaction during delithiation process, there are some reports which attempt to probe the presence of partial conversion [19,20,25]. It is reported that the required activation energy for conversion of Sn to SnO₂ and Li₂O decomposition reactions would be reduced with the decrease of nanoparticle size [20]. In this case, SnO₂ nanoparticles for sample SnO₂/OAC and SnO₂/NAC (i.e., 2–5 nm) are small enough to promote reversible conversion of Sn to SnO₂, as previously reported by other groups. However, SnO₂/NAC shows so weak electrochemical performance, even weaker than pure SnO₂ powders [11], implying functional groups play crucial roles on the electrochemical performance of SnO₂/carbon composites. Nitrogen groups play a negative role, oppo-

site to oxygen groups, which could be attributed to effects of Lewis acid and base groups on electrons during the lithiation and delithiation process.

Oxygen groups are doped into CAC as Lewis acid groups, which is the electron acceptor during the electrochemical process. It is well documented that Lewis acid can promote catalytic oxidation reaction by electron abstraction as the electron acceptor, which has been widely used in homogeneous catalysis [26]. It can abstract electrons from Sn during the charge process combining with tiny SnO₂ nanoparticles, thus making the conversion from Sn to SnO₂ available and leading to the higher initial CE of SnO₂/OAC, compared with SnO₂/CAC and SnO₂/NAC. Fig. 6a shows differential charge capacity *versus* voltage plots of three samples after 150 cycles. Compared with SnO₂/CAC and SnO₂/NAC, peaks at 1.3 and 2.5 V for SnO₂/OAC demonstrate reversible conversion of Sn to SnO₂ by incorporating Lewis acid sites into carbon host, which is also demonstrated by CV curves at the 2nd cycle (Fig. 6b). At the same time, the strong interaction between SnO₂ and oxygen groups prevents the electrochemical sintering of SnO₂ nanoparticles [33–35]. Thus, high capacity can be kept at the high rate (Fig. 5d).

Fig. 7a shows TEM image of SnO₂/OAC after cycling, where uniform tiny SnO₂ nanoparticles (~2 nm) still maintain the homogeneous distribution due to the strong interaction between SnO₂ and oxygen groups. Compared with oxygen groups, nitrogen groups are doped into carbon in the form of pyridine-N and pyrrolic-N, considered as Lewis base groups. Opposite to oxygen groups, nitrogen groups as the electron provider make the conversion of Sn to SnO₂ harder, which could have repelled the interactions between Sn and nitrogen groups. Thus, Sn nanoparticles is easier to aggregate during the electrochemical process, which makes the capacity of SnO₂/NAC severely degrade, as demonstrated by TEM image of

Figure 7 HRTEM images of sample (a) SnO₂/OAC and (b) SnO₂/NAC charged to 3 V at 500 mA g⁻¹ after 150 cycles.

SnO₂/NAC after cycling (Fig. 7b). As shown in Fig. 7b, most of original SnO₂ nanoparticles (2–5 nm) are aggregated into big nanoparticles (5–10 nm) on the outer surface of carbon.

CONCLUSIONS

In summary, SnO₂/carbon composites were synthesized here by a simple hydrothermal approach, where tiny SnO₂ nanoparticles (2–5 nm) were effectively refined within the nanoporous carbon framework. Different kinds of functional groups were doped into carbon hosts to study the influence of surface chemical property of carbon host on the electrochemical performance of SnO₂/carbon composites anode. It indicates oxygen groups as Lewis acid sites effectively abstract electrons from Sn during the charge process, thus accelerating reversible conversion of Sn to SnO₂ and resulting in high initial Coulombic efficiency. Meanwhile, SnO₂ nanoparticles are effectively bonded with carbon through such oxygen groups, thus realizing homogeneous anchor of SnO₂ nanoparticles. The resulting SnO₂/OAC exhibits excellent electrochemical performance. The performance of the SnO₂/OAC is one of the best SnO₂ based anode materials, in terms of large specific capacity, high rate performance and long cycle stability. Besides, other advantages, e.g., low biomass cost, facile preparation method, also make SnO₂/OAC composites become an ideal candidate for anode materials. This work provides a new route about reversible conversion of Sn to SnO₂ by catalytic oxidation of Lewis acid groups. We believe it could be easily extended to other similar metal oxides anode materials, which is very meaningful for improving performance of anodes in LiBs.

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Zhen Geng obtained his PhD from Tongji University under the supervision of Prof. Cunman Zhang, in 2016. From 2014 to 2015, He worked as a visiting graduate student in the group of Prof. Yunfeng Lu, at the University of California, Los Angeles. Currently, he is working as a post-doctoral researcher at the Institute of Physics, Chinese Academy of Science (CAS), under the supervision of Prof. Hong Li. His research interest mainly focuses on nano-materials for energy storage, solid state electrolytes, lithium metal anode and solid state lithium batteries.

Yongjun Ji received his PhD degree from East China Normal University in 2012, under the supervision of Prof. Peng Wu. After postdoctoral research at Tsinghua University with Prof. Yadong Li, he joined the faculty of the Institute of Process Engineering, Chinese Academy of Sciences in 2014. He is currently an associate professor. His research interests include the synthesis and application of zeolite and nanomaterials.

Cunman Zhang is a professor in the School of Automotive Studies, Tongji University. His current research interests include the design and development of new energy storage systems for vehicles, the development and application of hydrogen infrastructure and energy storage materials.

基于具有增强键能和电子吸引双功能特性的氧掺杂碳载体制备高性能二氧化锡/碳复合负极材料

耿振^{1,2}, 李冰¹, 刘合之³, 吕洪¹, 肖强凤⁴, 纪永军^{3*}, 张存满^{1*}

摘要 通过电化学活性材料与导电载体材料复合制备纳米复合材料, 对于高能量锂离子电池的发展至关重要. 本文利用水热法将含氧官能团引入到纳米孔碳材料骨架上, 制备得到了骨架内均匀生长粒径为2–5 nm的SnO₂纳米颗粒的纳米孔碳材料, 作为SnO₂/碳复合负极材料其电化学性能显著提高. 与原始(CAC)、氮掺杂碳(NAC)载体相比, 氧掺杂碳载体(OAC)制备得到的SnO₂/碳复合材料表现出更优异的电化学性能. SnO₂/OAC在500 mA g⁻¹充放电速率下, 320圈后其放电容量保持在1122 mA h g⁻¹; 2000 mA g⁻¹下其容量仍保持680 mA h g⁻¹. SnO₂/OAC优异的电化学性能主要归因于: 氧官能团作为Lewis酸, 可以在充电状态下从Sn纳米颗粒处吸引电子, 促进Sn向SnO₂的可逆转化; 同时, 由于氧官能团的存在, SnO₂纳米颗粒被有效地限制在了碳载体骨架内, 有效抑制了充放电过程中SnO₂纳米颗粒的团聚, 从而提高了SnO₂/OAC复合负极材料的电化学稳定性. 综上, 优异的电化学性能、低的生物质成本以及简易的制备方法使得SnO₂/OAC复合材料成为一种非常有潜力的锂电池负极材料.