



ELSEVIER

Contents lists available at ScienceDirect

Energy Storage Materials

journal homepage: www.elsevier.com/locate/ensm

Porous carbon nanocages encapsulated with tin nanoparticles for high performance sodium-ion batteries

Shuangqiang Chen^{1,2}, Zhimin Ao¹, Bing Sun, Xiuqiang Xie, Guoxiu Wang*

Centre for Clean Energy Technology, University of Technology Sydney, 15 Broadway, Sydney, New South Wales 2007, Australia

ARTICLE INFO

Article history:

Received 7 June 2016

Received in revised form

3 July 2016

Accepted 6 July 2016

Available online 26 July 2016

Keywords:

Sodium ion batteries

Anode

Tin nanocrystal

Carbon nanocage

Theoretical calculation

ABSTRACT

Sodium-ion batteries (SIBs) are recognized as an alternative to lithium ion batteries due to the abundance of sodium and potentially low cost of the whole battery system. One of the major challenges facing SIBs is to develop suitable anode materials with high capacity and long cycling life. Herein, we report the synthesis of porous carbon nanocage-Sn (PCNCs-Sn) nanocomposites as anodes of SIBs, demonstrating a high capacity of 828 mAh g⁻¹ at 40 mA g⁻¹. The electrodes also exhibited good rate capabilities (up to 3C) and superior cycling performances (1000 cycles). Post-mortem analyses verified the efficient volume change restriction by carbon nanocages and the well-preserved porous structure. Theoretical calculations indicated that the pulverization of bare Sn electrodes could be ascribed to strong bonds formed between amorphous carbon and the discharge product (Na₁₅Sn₄), which also deteriorated the conductivity. In contrast, the relatively weak interaction between Na₁₅Sn₄ and graphitic carbon can maintain superior conductivity and structural stability for better cycling performance.

© 2016 Published by Elsevier B.V.

1. Introduction

Lithium ion batteries (LIBs) have demonstrated great commercial success in powering portable electronic devices and electric vehicles [1–8]. With the increasing demand of large-scale energy storage, more attentions are shifting to alternative technologies, such as sodium-ion batteries (SIBs) due to the abundant resources of sodium [9–12]. However, sodium ion is almost three times heavier than lithium ion, and also much larger than lithium ion (1.06 Å in radius for Na⁺ vs. 0.76 Å radius for Li⁺) [9,13], which creates challenges for developing appropriate electrode materials for sodium-ion batteries. The large-scale practical application of SIBs has been hampered by several factors, including slow diffusion kinetics of Na⁺ ions, volume expansion during sodiation, and pulverization of electrodes during cycling, resulting in the fast capacity decay, low rate capability and low Coulombic efficiency [14–16]. Many cathode materials have been successfully developed, including simple transition metal oxides (V₂O₅), the bilayered Na₂V₂O₅, P2-Na_{0.66}Fe_{0.5}Mn_{0.5}O₂, Na_{0.8}Li_{0.12}Ni_{0.22}Mn_{0.66}O₂, Na₇V₃(P₂O₇)₄, Na_{0.44}MnO₂, P2-Na_xCoO₂, and O3-NaFeO₂ [17–25].

The development of appropriate anode materials for sodium-

ion storage is of paramount importance. Recently, several anode materials have been studied, including porous hard carbon [26–29], nitrogen-doped carbon nanofibers [12], metals and alloys (Sn, SnSb, Sb, Ge, Sn–Ge and Sn–Ge–Sb) [30–36], metal oxides/sulfides (TiO₂, SnO₂, Sb₂O₄, Sb₂S₃, SnS₂, WS₂ and MoS₂) [37–47], and phosphorus [48,49]. Among them, Sn is recognized as a promising anode material for SIBs due to the high theoretical capacity (847 mAh g⁻¹), environmental friendliness, non-toxicity and low charge/discharge potentials. However, bare Sn as anodes for SIBs is subjected to huge volume change during cycling. Chevrier and Ceder demonstrated that the calculated average sodiation potential is around 0.15 V, which is lower than the lithiation potential and the volume occupied by Na⁺ ions is twice as large, suggesting that more voids in host materials need to be provided to accommodate Na⁺ [50]. Using *in situ* transition electron microscopy (TEM), Wang et al. observed a two-step reaction during the sodiation of Sn, involving the transition from a two-phase reaction mechanism with a modest volumetric expansion of about 60% to a single-phase reaction mechanism with a huge volumetric expansion of about 420% after complete sodiation [51]. The huge volumetric expansion/contraction imposes strong mechanical pressure on Sn nanoparticles, generating many cracks and turning Sn into much smaller nanoparticles. Such pulverization of Sn leads to the continuous growth of solid electrode interfaces (SEI), which results in slow Na-ion kinetics and low Coulombic efficiency. Therefore, it induces rapid electrode failure as a result of the loss of inter-particle contact [51,52]. Many efforts have been devoted to control the large volume changes by using flexible materials, increasing the

* Corresponding author.

E-mail addresses: S.Chen@kf.mpg.de (S. Chen),Guoxiu.Wang@uts.edu.au (G. Wang).¹ These authors contributed equally.² Present Address: Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany.

conductivity through coating carbon layer or conductive polymers, and enhancing the kinetics by decreasing the particle size of Sn [26,53–57]. For example, to control the volume changes and enhance the electrochemical performance, Wang et al., using a facile soaking-chemical vapor deposition (CVD) technique, developed a free-standing carbon paper carried Sn@carbon nanotube nanopillars with a core-sheath structure, which delivered a reversible specific capacity of 644 mAh g^{-1} and maintained 399 mAh g^{-1} after 100 cycles with high Coulombic efficiencies [53]. To buffer the volume changes, Zhu et al. prepared binder-free flexible wood fiber-carried Sn nanoparticles by electrochemical deposition, which exhibited an initial discharge capacity of 339 mAh g^{-1} and maintained 145 mAh g^{-1} after 400 cycles [26]. In order to suppress the volume changes and control the particle aggregation of Sn nanoparticles, Liu et al. synthesized ultra-small Sn nanoparticles embedded in spherical carbon networks via an aerosol spray pyrolysis method, which exhibited an initial reversible specific capacity of 493.6 mAh g^{-1} at a current density of 200 mA g^{-1} [54]. Chen et al. developed nitrogen-doped carbon nanofibers encapsulated ultra-small tin nanoparticles ($< 5 \text{ nm}$) free-standing composites by electrospinning method, exhibiting a high reversible capacity of 633 mAh g^{-1} at the current density of 200 mA g^{-1} and long-term cycling life [58].

To enhance the electrochemical performance, we developed graphitic porous carbon nanocages (PCNCs) with the encapsulation of Sn nanoparticles by a template-assisted CVD and *in situ* reduction method. The PCNCs provide sufficient inner voids to restrict volume expansions of Sn during sodiation. Moreover, density functional theory (DFT) calculations demonstrate that amorphous carbon black as conductive agent would form strong covalent bonds with the sodiation product ($\text{Na}_{15}\text{Sn}_4$) and accelerate the pulverization of bare Sn electrodes. However, graphitic PCNCs as the host show weak interactions to $\text{Na}_{15}\text{Sn}_4$, which can maintain the good conductivity and structural stability of electrodes to improve cycling performances. When applied as anode materials, the as-synthesized PCNCs-Sn nanocomposites delivered a high initial reversible capacity (828 mAh g^{-1} at a current density of 40 mA g^{-1}), high Coulombic efficiencies, excellent cyclic performance, and good rate capability. The effort to combine fundamental research and theoretical simulation is expected to fully discover the potentials and optimize the performances of Sn as an anode material for high performance sodium-ion batteries.

2. Experimental

2.1. Preparation of mesoporous MnO nanocube template and porous carbon nanocage (PCNC)

All chemicals were used as received without further processing or purification. In a typical template synthesis procedure, mesoporous MnO nanocubes were prepared using a moderate method: $35 \text{ mmol Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 35 mL ethanol and $100 \text{ mmol } (\text{NH}_4)_2\text{SO}_4$ were dissolved in 350 mL of de-ionized water in a round flask with strong stirring and then placed into a preheated oil-bath tank ($50 \text{ }^\circ\text{C}$). $100 \text{ mmol } (\text{NH}_4)_2\text{CO}_3$ was dissolved in 350 mL of de-ionized water with strong stirring for 10 min. Then, the second solution was added drop-wised into the former solution under vigorous stirring and maintained for 12 h. After that, white precipitation of MnCO_3 was collected by filtration, washed with copious de-ionized water and dried at $80 \text{ }^\circ\text{C}$. The precursor was annealed at $600 \text{ }^\circ\text{C}$ with a temperature ramp of $2 \text{ }^\circ\text{C}/\text{min}$ and maintained for 4 h in air to obtain MnO nanocube templates. Fig. S1a–d (Supplementary materials, SM) show the low and high magnification scanning electron microscopy (SEM) images of porous MnO nanocube templates. Mesoporous MnO was placed in

a quartz tube furnace and heated to $600 \text{ }^\circ\text{C}$ at a temperature ramp of $5 \text{ }^\circ\text{C}/\text{min}$ in Ar. Then, acetylene (5% in Ar) was introduced with a flow rate of 100 sccm for 30 min. Carbon coated MnO nanocubes (C@MnO) were prepared. Afterward, PCNCs were obtained by etching C@MnO with 1 M HCl , washing and drying at $80 \text{ }^\circ\text{C}$ in a vacuum oven overnight.

2.2. Preparation of PCNCs-Sn nanocomposites

The as-synthesized PCNCs (20 mg) were dispersed in 10 mL 1, 5-pentanediol and ultrasonic treated for 10 min, Tin chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 0.178 g , Sigma-Aldrich) as the Sn precursor and sodium borohydride (NaBH_4 , 0.1 g , Sigma-Aldrich) as the reducing agent were separately dissolved in 40 mL 1, 5-pentanediol under strong stirrings. The well-dispersed PCNCs were added in tin chloride solution. The newly prepared sodium borohydride solution was slowly pumped into the PCNCs-tin chloride solution and purged continuously with argon while being stirred to prevent oxidation. The mixture was then heated to $80 \text{ }^\circ\text{C}$ for 2 h. The PCNCs-Sn composites were subsequently washed with ethanol several times by centrifugation, and dried in a vacuum oven at $60 \text{ }^\circ\text{C}$ overnight. For comparison, bare Sn nanoparticles were prepared with the same method without PCNCs.

2.3. Electrochemical measurement

The working electrodes were made from 80% of active materials, 10% of carbon black, and 10% of the binder (Polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP)). The slurry was pasted on copper current collectors using a medical blade. The work electrodes were dried in a vacuum oven at $80 \text{ }^\circ\text{C}$ overnight, followed by pressing at around $200 \text{ kg}/\text{cm}^2$. The mass loading of anode materials including bare Sn, PCNCs and PCNCs-Sn nanocomposites is around 1.5 mg on the copper current collector, respectively. CR2032 coin cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany), in which both the moisture and oxygen contents were controlled to be less than 0.1 ppm . Sodium cubes were applied as the counter and reference electrodes. Glass microfiber (Whatman) was used as separator. The electrolyte solution was composed of 1 M NaClO_4 dissolved the mixture of ethylene carbonate (EC) and propylene carbonate (PC) with a volume ratio of 1:1, and 5 vol% fluoroethylene carbonate (FEC) as electrode additive. For each electrode, around $30 \mu\text{L}$ electrolyte was added in the coin cell. Electrochemical measurements were performed using a LAND-CT2001C battery test system. The cells were galvanostatically discharged and charged in a voltage range of $0.01\text{--}2.0 \text{ V}$ at a current density of 40 mA g^{-1} . Higher current rates (80 mA g^{-1} , 160 mA g^{-1} , 320 mA g^{-1} , 640 mA g^{-1} , 1280 mA g^{-1} and 2560 mA g^{-1}) were also applied to evaluate the rate capabilities. The CV was measured on a CHI 660E electrochemical workstation at a scan rate of 0.1 mV s^{-1} . The electrochemical impedance spectra (EIS) were examined with a voltage amplitude 5 mV and frequency ranges from 106 to 0.1 Hz .

Full sodium-ion batteries, using PCNCs-Sn nanocomposites as anode and $\text{P2-Na}_{0.80}\text{Li}_{0.12}\text{Ni}_{0.22}\text{Mn}_{0.66}\text{O}_2$ as cathode, were assembled. A similar strategy was applied to prepare cathode electrode: $\text{P2-Na}_{0.80}\text{Li}_{0.12}\text{Ni}_{0.22}\text{Mn}_{0.66}\text{O}_2$ synthesized according to the previous report was mixed with carbon black and PVDF in the weight ratio of 80:10:10. The mass loading of cathode materials is around 7.5 mg on the aluminum current collector. The electrolyte and separator used were the aforementioned ones. Galvanostatic charge/discharge method was applied to measure the electrochemical performances between 0.01 V and 4.2 V at current densities of 80 mA g^{-1} , 160 mA g^{-1} , 320 mA g^{-1} and 640 mA g^{-1} , respectively.

Download English Version:

<https://daneshyari.com/en/article/1564564>

Download Persian Version:

<https://daneshyari.com/article/1564564>

[Daneshyari.com](https://daneshyari.com)