



Journal of Alloys and Compounds



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

Electrochemical behavior of nanoporous/nanofibrous Si anode materials prepared by mechanochemical reduction

Rongguan Lv, Jun Yang*, Pengfei Gao, Yanna NuLi, Jiulin Wang

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

ARTICLE INFO

Article history: Received 21 July 2009 Received in revised form 24 September 2009 Accepted 3 October 2009 Available online 13 October 2009

Keywords: Nanoporous/nanofibrous silicon Mechanochemical reduction Anode material Lithium-ion battery

1. Introduction

Rechargeable lithium-ion batteries are widely used for portable electronic devices duo to their high energy density and low maintenance requirement. However, the theoretical Li-storage capacity of commercial carbon anodes is limited to 372 mAh g^{-1} [1]. In recent year, there is a great interest in developing alternative anode materials to carbonaceous for lithium-ion batteries. Among them, Si is one of the most promising anode materials due to its high theoretical lithium storage capacity of 4200 mAh g⁻¹ and low electrochemical potential vs. Li/Li⁺ [2,3]. One of the major challenges associated with its practical application is the poor electrochemical reversibility upon cycling, deriving from the very large volume change during the lithium insertion/extraction process.

To improve the cycling stability of Si-based negative electrodes, the current strategies are focusing on two sides. One is to fabricate composite microstructures in which the Si particles are finely dispersed in various active/inactive matrixes. To date, carbon is one of the most effective matrixes to disperse Si. For instance, Si particles embedded in a disordered carbon matrix deriving from pyrolysis of various organic polymers were reported by many groups [4–7]. However, the capacity fade mostly remains remarkable. The other is to reduce the particle and crystallite size to the nanometer regime (such as nano-particles, nanowires, nanosized films, etc.). Recently, Si nanowires were prepared by using the VLS process and the electrode exhibited a reversible capacity of about 3100 mAh g⁻¹

ABSTRACT

A mixture of nanoporous and nanofibrous silicon (NPNF-Si) is prepared by the mechanochemical reduction of SiCl₄ using Li₁₃Si₄ as reducing agent in the presence of Super P carbon (SP) and the following thermal treatment and washing process. Morphologies and structures of the as-obtained composites are investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). After carbon coating via pyrolysis of polyvinyl chloride (PVC), the resulting NPNF-Si/SP/C composite is evaluated for the use as anode material in lithium-ion battery. It exhibits the first discharge capacity of 746.6 mAh g^{-1} at current density of 0.2 mA m g^{-1} and capacity retention of 91.1% after 30 cycles. The good electrochemical performance arises from the particular Si nano-structure, which can alleviate the volume effect during lithium insertion and extraction.

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at C/20 rate within 10 cycles [8]. Barbara reported on a new threedimensional Si nanowires (200-300 nm in diameter) synthesized by CVD method. This architecture can accommodate the large volume change during lithium insertion/extraction [9]. Si nanowires with homogeneous diameters of 10-20 nm have been synthesized by DC arc discharge method with metal catalyst [10]. It is also shown that some porous Si-based anode materials can effectively alleviate the volume expansion [11–14]. For example, Zheng et al. reported a nanoporous Si/graphite composite [11]. More nanosized Si composites have been prepared via ball-milling technique using various Si sources and reducing agents (such as C, Mg, Al, Li and so on) [15–19]. In view of the importance of the reducing agent for the mechanochemical reaction under ball-milling, we choose Li₁₃Si₄ as the reducing agent here, because it acts not only as the reducing agent but also as nucleation center for Si reduction from other Si source.

In this work, nanoporous and nanofibrous silicon/carbon black (Super P) composite (abbreviated as NPNF-Si/SP hereafter) was prepared via a mechanochemical reaction between SiCl₄ and Li₁₃Si₄ under ball-milling and subsequent thermal treatment and washing process. For the first time to our knowledge, Si nanofibers can be prepared by such a route. The microstructures and the electrochemical behaviors of NPNF-Si/SP anode materials were investigated.

2. Experimental

2.1. Material preparation

For the material preparation, $1.85\,ml\,SiCl_4$ (Aladdin-reagent Corp., China, 99.9% pure), $0.8394\,g\,Li_{13}Si_4$ powders (SIMIT, CAS, China) (i.e., with 20% excess SiCl_4 for

^{*} Corresponding author. Tel.: +86 21 54747667; fax: +86 21 54747667. *E-mail address:* yangj723@sjtu.edu.cn (J. Yang).

^{0925-8388/\$ -} see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2009.10.023

Table 1

Compositions of the com	posite samples in	weight percent.
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Sample	Si (wt.%)	SP (wt.%)	Carbon (wt.%)
Si	100	-	-
NPNF-Si/SP	80.8	19.2	-
NPNF-Si/SP/C	30.0	7.1	62.9

the redox reaction) and 0.2000 g carbon black named Super P (SP) (40 nm, Timical) were loaded in an 80 ml argon filled stainless-steel vial with eight 10 mm and seven 8 mm diameter hardened steel balls. Then the milling was performed on a Planetary Mono Mill P-6 (Fritsch, Germany) at a rotation speed of 450 rpm for 20 h. To remove the excessive SiCl₄, the as-milled composite was placed in a quartz tube in an argon filled glove box, and heated at the rate of 5 °C min⁻¹ under a constant flow of Ar and maintained at 700 °C for 6 h, then naturally cooled down to room temperature. The obtained NPNF-Si/SP mixed with LiCl was washed with deionized water and isolated by centrifugation for 4 times. By this process, LiCl was removed and NPNF-Si/SP composite was obtained. The sample was finally dried under vacuum at 100 °C for 4 h. For comparison, Si was prepared using the above-mentioned procedure without SP. The NPNF-Si/SP composite was added into the polyvinyl chloride (PVC, (CH₂-CHCl)_n, average Mw~233,000 Aldrich) solution (dissolved in tetrahydrofunan) and homogeneously mixed under ultrasonic action. After stirring for 1 h. the resulting slurry was spread onto a flat surface, dried at 80 °C, and then the precursor was heated at 5 °C min⁻¹ to 900 °C under Ar atmosphere. After pyrolysis at 900 °C for 2 h, the furnace was cooled automatically. The resulting composite was named as NPNF-Si/SP/C hereafter.

2.2. Characterizations

The resulting samples were analyzed by X-ray diffraction (XRD) on a Rigaku diffractometer D/MAX-2200/PC equipped with Cu K α radiation. The carbon contents of the composites were measured using a Carbon-Sulfur Analyzer (Dekai Instrument, China). The weight ratios of the composite samples are listed in Table 1, assuming no loss of silicon and SP during pyrolysis. The morphologies of the samples were observed by scanning electron microscopy (SEM) on a JEOL field-emission microscope (JSM-7401F) and transmission electron microscopy (TEM) on a JEOL high-resolution electron microscope (JEM-2010). The specific surface area and pore volume were determined from the results of N₂ adsorption/desorption experiments using ASAP2010M+C (Micromeritics Inc., USA).

2.3. Cells assembling and electrochemical test

The electrodes in thickness of ca. 30 μ m were composed of 80 wt.% active materials (the as-prepared composite), 10 wt.% polyvinylidene fluoride (PVDF) binder, and 10 wt.% SP as a conducting agent. The electrode performance was evaluated using CR2016 coin cells with ENTEK ET20-26 membrane separator, lithium-foil counter electrode, and electrolyte of 1 M LiPF₆ in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume ratio). The cells were assembled in an argon filled glove box (Mbraun, Unilab, Germany) with oxygen and water contents less than 10 ppm. The charge/discharge test of the cells was performed using LAND CT2001A system. The cells were charged (delithiation) and discharged (lithiation) in the galvanostatic mode at a constant current of 0.2 mA mg⁻¹ between 0.01 and 1.4 V vs. Li/Li⁺. The specific capacity was calculated on the basis of the total composite weight.

3. Results and discussion

Direct ball-milling of SiCl₄ and Li₁₃Si₄ led to the formation of coarse and clumpy powders. To solve this problem, SP was added as dispersing agent. At the same time, SP can improve the electronic conductivity and accommodate part of the volume change of silicon during lithium insertion/extraction. The XRD patterns of the NPNF-Si/SP and the NPNF-Si/SP/C are shown in Fig. 1. For NPNF-Si/SP composite, the main diffraction peaks at scattering angels (2θ) of about 28.4°, 47.4°, 56.2° and 69.2° correspond to (111), (220), (311) and (400) planes of silicon crystallites and the amorphous SP presents no diffraction response. The high temperature preparation of NPNF-Si/SP/C composite at 900 °C has almost no effect on the crystallinity of the sample. SiC phase is not observed. The broad peak near 24° is attributed to the carbon pyrolyzed from PVC.

On the basis of Sandu's work [16], we list the following mechanochemical reaction between SiCl₄ and Li₁₃Si₄: SiCl₄(1)+Li₁₃Si₄(s) \rightarrow Si(s)+LiCl(s). This redox reaction will produce nano-dispersed LiCl in composite. After washing by deion-



Fig. 1. XRD patterns of the composites of NPNF-Si/SP (a), and NPNF-Si/SP/C (b).

ized water, LiCl was completely removed from composite, thus nanosized pores are formed. Fig. 2 presents SEM images of as-prepared Si and NPNF-Si/SP. As shown in Fig. 2a, short Si fibers, irregular porous and compact Si particles coexist in the as-prepared Si powders. When SP was added for ballmilling, the longer Si nanofibers and more distinct nanoporous Si particles are obtained (see Fig. 2b). The Si nanofibers have diameters of 50–200 nm and lengths ranging from several ten nanometers to several micrometers. The mechanism of the Si nanofibers' growth remains unclear and requires further investigation. The nanoporous Si morphology is exhibited in the inset



Fig. 2. SEM images of Si (a), and NPNF-Si/SP (b).



Fig. 3. BJH pore size distribution for the NPNF-Si/SP.

of Fig. 2b. As determined by Brunauer–Emmett–Teller (BET) measurement, the specific surface area of the NPNF-Si/SP composite is $118.4 \,\mathrm{m^2 \, g^{-1}}$. The BET result demonstrates the formation of porous structure in the Si particles. BJH pore size distribution for NPNF-Si/SP composite is given in Fig. 3. The most pores distribute from 10 to 50 nm, which may accommodate the volume change.

A TEM image shown in Fig. 4(a) reveals that the nanoporous and nanofibrous parts are blended and enwound in the NPNF-Si/SP composite. The selected area electron diffraction (SAED) pattern (inset of Fig. 4(a)) and the energy dispersive X-ray (EDX) spectrum (Fig. 4(b)) were recorded simultaneously with TEM analysis. The SAED pattern indicates the polycrystalline nature of Si. The EDX result is shown in Table 2, which confirms the complete elimination of LiCl product from the composite. In addition, besides polycrystalline Si (59.6 at.%) and amorphous SP carbon (36.2 at.%), a small amount of oxygen (4.2 at.%) is detected. It should be related to oxidation of the fresh silicon during the sample preparation.

Fig. 5 shows the cycling stability for the different Si-based anode materials. The first discharge capacity of as-prepared Si sample is 2692.9 mAh g⁻¹ and its cycling stability is poor. In the case of the NPNF-Si/SP composite electrode, the first discharge capacity is 2012.5 mAh g⁻¹ and the first efficiency is 66.7%. The capacity loss in the first cycle mainly arises from the SEI formation relating with the specific surface area of 118.4 m² g⁻¹ [20,21]. Furthermore, after 9 cycles, the charge capacity of NPNF-Si/SP electrode becomes 449.4 mAh g⁻¹, which is higher than that of as-prepared Si electrode (200.9 mAh g⁻¹). The relatively good electrochemical

Table 2

EDX analysis results of NPNF-Si/SP composite after washing process.

Element	Weight%	Atomic%
С	20.01	36.2
0	3.05	4.2
Si	76.94	59.6



Fig. 5. Cycling behaviors of the Si-based electrodes at the constant current density of 0.2 mA mg⁻¹. Solid and hollow marks represent discharge and charge capacity, respectively.

performance of NPNF-Si/SP composite should be ascribed to the nanoporous and nanofibrous structure, which can suppress part of the volume change [9,11]. Additionally, nanosized dispersion of SP in NPNF-Si/SP composite is also beneficial to accommodate the volume change during lithium insertion/extraction.

In view that incorporation of pyrolyzed carbon with silicon remarkably improves the cycling stability of the Si-based material, the NPNF-Si/SP/C composite was prepared by carbon coating pyrolyzed from PVC. Fig. 5 shows that the first discharge capacity of NPNF-Si/SP/C electrode is 746.6 mAh g⁻¹ and the first efficiency is 68.8%. Apparently, the cycling stability of NPNF-Si/SP/C electrode has been improved distinctly compared with that of as-prepared NPNF-Si/SP electrode, which mainly derives from the enhanced electronic conductivity by incorporation of pyrolyzed carbon. Taking account of a Li-insertion capacity of ca. 290 mAh g⁻¹ for pyrolyzed carbon from PVC, about 70% of the theoretical capacity for Si can be effectively utilized. The architecture of NPNF-Si/SP/C composite can accommodate the volume change and preserve the integrity of the electrode structure. Then, 91.1% of the first charge



Fig. 4. TEM image of NPNF-Si/SP and the corresponding SAED pattern (inset) (a), and EDX spectrum of NPNF-Si/SP (b).



Fig. 6. Galvanostatic discharge-charge curves of the cell with NPNF-Si/SP/C in the potential region of $0.01-1.4 V (vs. Li/Li^+)$ at the current density of 0.2 mA mg^{-1} .



Fig. 7. Cyclic voltammograms (CVs) of the NPNF-Si/SP/C electrode measured in the voltage region of 0.01-1.5 V with a scan rate of 0.2 mV s⁻¹.

capacity is retained after 30 cycles with 0.30% of capacity loss ratio per cycle, but further improvements should be expected especially with respect to the charge capacity.

Fig. 6 presents galvanostatic discharge-charge curves of the cell with NPNF-Si/SP/C electrode. A sloping potential plateau in the first discharge process corresponds to the stage of Li-insertion into the pyrolyzed carbon in company with the SEI film formation in connection with the electrolyte decomposition, while the Li-insertion potential of Si at the first cycle is mainly below 0.1 V. The voltage trend of the first discharge is clearly different from the following cycles, relating to the typical phase transformation of Si from crystal to amorphous. Moreover, the charge capacity increases with cycling in the initial cycles. It means that the nano-structured silicon embedded in pyrolyzed carbon is not completely utilized at the beginning. After several cycles, lithium diffusion and electrochemical kinetics reach an optimal state. Additionally, the discharge potential plateau slightly drops with progressive cycle numbers, indicating an increased polarization due to the hindered electrochemical interface kinetics [22], which could result in capacity degradation.

Fig. 7 shows the cyclic voltammograms (CVs) of NPNF-Si/SP/C electrode measured at the scan rate of 0.2 mV s^{-1} . The initial potential of the electrode is about 2.0 V vs. Li/Li⁺ in the open-circuit state. In the case of the first reduction half-cycle (lithium insertion), three

cathodic peaks appear at around 0.90, 0.68 and 0.01 V, respectively. The first two low current peaks originate from the formation of SEI films, which disappear from the subsequent cycles. One additional cathodic peak at 0.20 V appears from the second cycle. Upon charging, two anodic peaks located at 0.34 and 0.50 V gradually evolve after the first cycle and become more distinct for the following cycles. These two anodic peaks correspond to the extraction of lithium from the silicon. Furthermore, the magnitude of the current peaks increased with cycling, correlating to the capacity's increase during the initial cycles in Fig. 6.

4. Conclusions

In summary, nanoporous and nanofibrous Si-based composite has been firstly prepared by mechanochemical reduction using SiCl₄ and Li₁₃Si₄ as starting materials with small amount of SP and subsequent thermal and washing treatments. As anode material for lithium-ion battery, the composite NPNF-Si/SP electrode showed fast capacity loss upon cycling. After carbon coating via the pyrolysis of PVC, the capacity retention was significantly improved. The initial discharge capacity of the composite NPNF-Si/SP/C electrode is 746.6 mAh g⁻¹, and the first coulombic efficiency is 68.8%. After 30 cycles, 91.1% of the first charge capacity remained. More investigation will focus on the Si structure optimization and the improvement in electrochemical reversibility.

Acknowledgements

This work was financially supported by National 863 Project (2006AA03Z232) and National 973 Programs (2007CB209700).

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