Materials Letters 184 (2016) 169–172

Contents lists available at ScienceDirect

Materials Letters

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

Porous carbon networks containing Si and SnO_2 as high performance anode materials for lithium-ion batteries

Jiayu Yu, Tao Sun, Qi Yang*, Jinxin Ma

School of materials engineering, Shanghai University of Engineering Science, Shanghai 201620, China

ARTICLE INFO

Article history:
Received 1 June 2016
Received in revised form
1 August 2016
Accepted 11 August 2016
Available online 11 August 2016

Keywords:
Silicon
Tin dioxide
Network structure
Porous materials
Carbon based materials
Energy storage and conversion

ABSTRACT

Porous carbon networks containing Si and SnO_2were synthesized by annealing the films formed by knife coating suspension with Si, $SnCl_2$, polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA) and N,N-Dimethylformamide (DMF) in vacuum. The Si-SnO_2-C composite was constructed by interconnected amorphous carbon branches containing nano-pores with a size of 1–5 nm, Si and SnO_2 nano-particles with a size of 30–50 nm. The composite demonstrates high performance as lithium-ion batteries (LIBs) anode. It delivers a high capacity of 1359.12 mA h g^{-1}after 200 cycling at a current density of 0.5 A $g^{-1}$and excellent rate capability of 512.16 mA h g^{-1}at a current density up to 20 A g^{-1}.

1. Introduction

With development of pure electrical vehicles, next generation electrode materials of lithium ion batteries (LIBs) with higher capacity, better cyclic and rate performance have attracted more and more attention. As well known, Si is regarded as a promising candidate anode material for next generation LIBs because it has the highest theoretical capacity of 4200 mA h g^{-1} which is much higher than the common used graphite. However, the main challenges for its commercial usage are its low electrical conductivity, its rapid decay of capacity upon cycling caused by the drastic volume change and unstable solid electrolyte interphase (SEI) during charge-discharge processes [1–3]. The preparation of carbon based composites with Si nano-particles encapsulated inside was well known as an effective strategy to solve these issues because carbon has excellent electrical conductivity, its volume does not change greatly during lithium intercalation and de-intercalation, and carbon layer on the surface of Si nano-particles can improve their SEI stability [1–3]. Presently, the most common used technique to prepare Si-C composite anode materials is electrospinning which can prepare carbon based fibers containing Si nano-particles [1–3].

Recently, extensive research efforts have been devoted to synthesize three dimensional (3D) hierarchical materials on the surface of Cu foils as LIBs anodes [4,5]. The 3D network structure can provide large specific surface area and outstanding mechanical property for the electrodes which enhance their reversible lithium ion storage capacity [4–7]. The integrated anodes usually are binder-free and conductive-free, which is benefit for the increase of their specific capacity [6,7]. For carbon based composite anodes, the micro-pores in carbon matrices will further increase their specific capacity and shorten lithium-ion diffusion distance, which leads to notable increase of their capacity especially under high current density.

In this paper, a novel and simple route was developed to synthesize Cu-supported Si-SnO_2-C composite with porous network structure as an integrated anode by knife coating suspension containing Si nano-particles, $SnCl_2$, polyacrylonitrile (PAN), poly (methyl methacrylate) (PMMA) and N, N-dimethylformamide (DMF) on the surface of Cu foils, and subsequently annealing the obtained Cu-supported films in vacuum. The volatilization of PMMA will leave space in carbon matrices formed by carbonization of PAN to achieve the 3D network structure of the composite. The pyrolysis of $SnCl_2$ will lead to nano-pores in carbon matrices. The produced SnO_2 is also electro-active material, which avoids the capacity decrease caused by residue of pore forming agent.

2. Experimental

2.1. Synthesis of samples

Si powder with a diameter of 30–50 nm was purchased from Shanghai Yunfu Nanotechnology Co. Ltd. $SnCl_2 \cdot 2H_2O$, PAN

---

* Corresponding author.
E-mail address: qiiyang@163.com (Q. Yang).

http://dx.doi.org/10.1016/j.matlet.2016.08.047
0167-577X/© Published by Elsevier B.V.

(MW = 150,000), PMMA (MV = 100,000) and DMF were provided by Sinopharm Chemical Reagent Co. Ltd. In a typical procedure, 0.1 g $SnCl_2 \cdot 2H_2O$, 0.2 g PAN and 0.1 g PMMA were dissolved in 6 g DMF to form a homogenous solution; subsequently, 0.1 g Si powder was added into the solution and ultrasonically vibrated for 10 min to produce stable suspension; the suspension was knife coated on the surface of Cu foils, and then annealed at 400 °C for 1 h in vacuum; finally, the obtained black coatings on the surface of Cu foils were ready for further characterization and testing.

2.2. Samples characterization

X-ray diffraction (XRD; X'Pect Pro MPD), X-ray photoelectron spectroscopy (XPS; VG Scientific ESCALAB 220IXL) and energy dispersive X-ray spectroscopy (EDX; JEOL 2011) were employed for composition and crystal structure analysis. Field emission scanning electron microscopy (FESEM, Hitachi S4800) and transmission electron microscopy (TEM, JEOL 2011) were conducted to observe morphologies and micro-structures of the samples. The coatings were scraped off from the surface of Cu foils for XRD and XPS testing. The Cu-supported composite was immersed into ethanol, and then ultrasonically vibrated for 10 min. The obtained black suspension was dropped on Cu grids for TEM observation.

2.3. Electrochemical measurements

The electrochemical measurements were performed by using CR-2032 coin cells. The Cu-supported Si-SnO_2-C composite was used as working electrode. The electrolyte consisted of a solution of 1 M $LiPF_6$ in the mixture of ethylene carbonate (EC):diethyl carbonate (DEC):ethyl methyl carbonate (EMC) with a volume ratio of 1:1:1, containing 2 vol% vinylene carbonate (VC). The cyclic and rate performance measurements were carried out on a Neware BTS3000 CT2001A battery tester.

3. Results and discussion

Fig. 1a shows the XRD pattern of the Si-SnO_2-C composite. All diffraction peaks are assigned to cubic Si phase (JCPDS no. 89-5012). No peaks related to SnO_2 and carbon can be observed, indicating the SnO_2 and carbon in the composite have amorphous structure. XPS testing was conducted to further analyze the elemental compositions and the chemical states of the composite. From Fig. 1b to d, it can be seen the Si2P peaks at 99.58 and 103.54 eV are assigned to Si and Si-O bond which is attributed to the structure with Si nano-particles embedded in the carbon matrices and silica layers on the surface of Si nano-particles [8]; the Sn3d peaks at 487.08 and 495.52 eV are assigned to Sn^{4+} in SnO_2 [9,10]; the C1s XPS spectrum is fitted to three peaks at 284.52, 285.88 and 287.66 eV which correspond to graphitic carbon, disordered carbon and C-O bond, respectively [9,10]. The TGA curve of the Si-SnO_2-C composite, as shown in Fig. S1, indicates its carbon content is ~40 wt%.

Fig. 2a shows top-view SEM image of the Cu-supported Si-SnO_2-C composite. The composite consists of continuous 3D

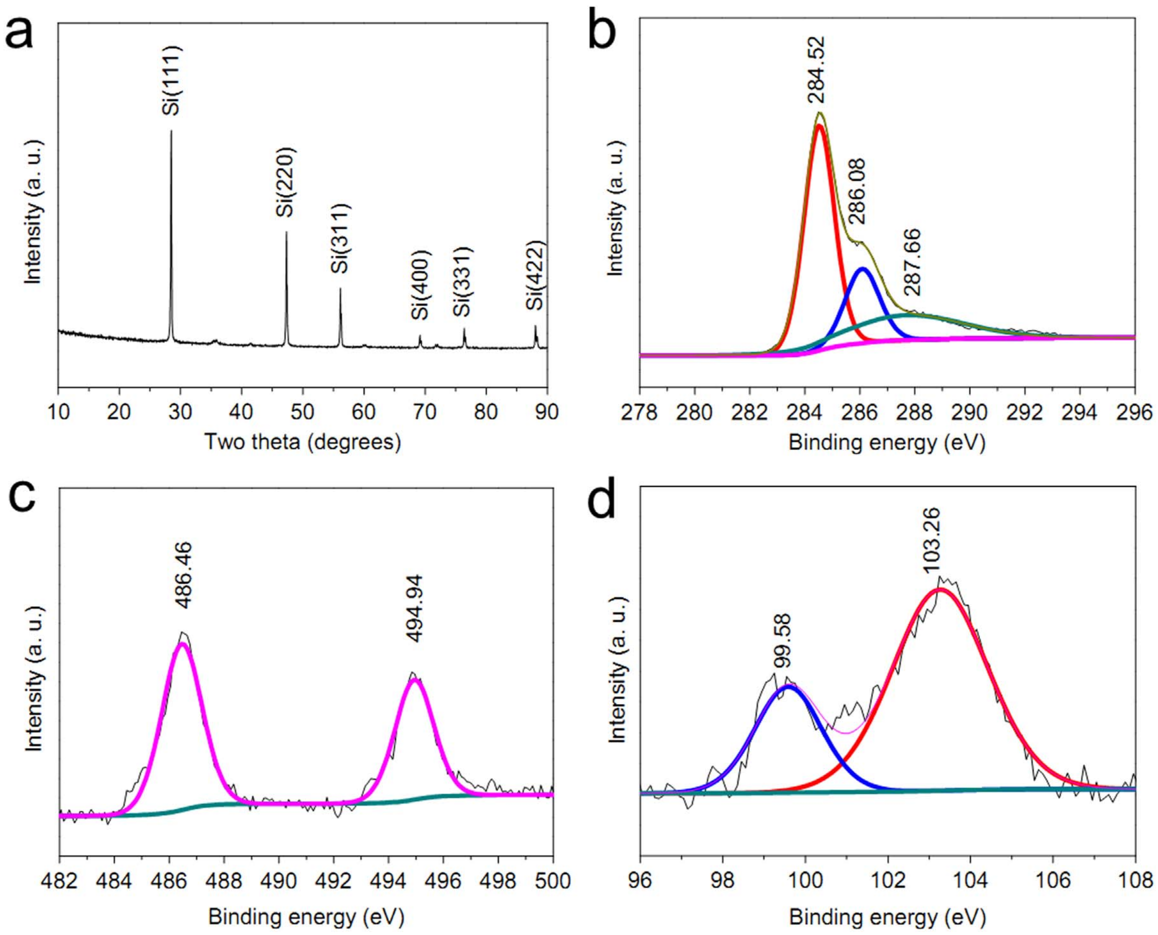

Fig. 1. Si-SnO_2-C composite: (a) XRD pattern, (b) XPS spectrum of Si2p, (c) XPS spectrum of Sn3d, (d) XPS spectrum of C1s.