Silicon nanoparticles prepared from industrial wastes as high-performing anode materials for lithium ion batteries

Qian He[a,b], Jing Yu[b], Yanhong Wang[b,c,*], Ziyi Zhong[d], Jiaxing Jiang[a,*], Fabing Su[b,c,e,**]

[a] Key Laboratory for Macromolecular Science of Shaanxi Province, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, Shaanxi 710062, China
[b] State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[c] Zhongke Langfang Institute of Process Engineering, Fenghua Road No 1, Langfang Economic & Technical Development Zone, Hebei Province 065001, China
[d] Colleague of Engineering, Guangdong Technion Iarael Institute of Technology (GTIIT), 243 Daxue Road, Jinping District, Shantou 515063, China
[e] Institute of Industrial Chemistry and Energy Technology, Shenyang University of Chemical Technology, Shenyang 110142, China

A B S T R A C T

Silicon (Si) nanostructures are considered to be the most promising anode materials for next-generation lithium batteries (LIBs) because of the very high theoretical capacity of Si. However, how to achieve a large-scale and cost-effective manufacture of them is still a big challenge. In this work, we report a facile and scalable method for preparation of two crystalline Si nanoparticle samples of 3P-2h (derived from a mixture of Cu, CuO and Cu_2O catalyst) and S21-2h (derived from Cu_2O catalyst). These Si samples are extracted from the wastes after reacting a metallurgical-grade Si with hydrogen chloride (HCl) gas catalyzed by the Cu catalysts. The latter is the typical industrial process used for production of organosilane monomers. The synthesized Si nanoparticles had a size of 100–300 nm. When used as anode materials for lithium ion batteries, 3P-2h delivered a reversible capacity of 636 mAh g^{-1} while S21-2h showed a reversible capacity of 529 mAh g^{-1} at 50 mA g^{-1} after 50 cycles, better than that of the bulk Si sample. These improved electrochemical properties are attributed to the formed nanostructure and the void spaces among the Si nanoparticles which can buffer the volume expansion and shorten the diffusion path of Li-ion. This work demonstrates the feasibility for a facile, green and scalable preparation of Si nanoparticles as high-performing anode material from industrial waste.

1. Introduction

Silicon (Si) is believed to be very promising anode materials due to its abundance in nature, low working potential and ever-known highest theoretical capacity (4200 mAh g^{-1}), which is much higher than that of the present commercial graphite anode material (theoretical capacity 372 mAh g^{-1}) [1–8]. However, the large volume changes (upon to 300%) of Si anodes materials during lithium insertion and extraction processes often lead to high internal stress, electrode pulverization and gradual loss of electric contact between Si and the current collector [9–12]. In the last decade, intensive efforts have thus been made to resolve the problem via reducing particle size [12,13], designing varies morphology and structure [14], using new kind of binders [15], surface coating [16] and hybridizing with other materials [12], and it is generally concluded that formation of nanostructured silicon is essential to Si based anodes used for the next-generation lithium batteries.

Therefore, in these years many Si nanostructures have been developed for the purpose of accommodating the Si volume changes so as to prevent the cracks formation and improve their conductivity [17]. These nanostructured Si materials include Si nanotubes [18], Si nanowires [19], Si nanospheres [20], Si/C nanoparticles [21], Si/C nanopheres [22], porous Si [23], and so on. For example, Park et al. prepared Si nanotubes by reductive decomposition of a silicon precursor, which exhibited an initial reversible capacity of 3247 mAh g^{-1} with a Coulombic efficiency of 89%, and a capacity retention of 89% even after 200 cycles [18]. Chockla et al. fabricated Si nanowires by the supercritical fluid-liquid-solid process which showed a capacity of more than 800 mAh g^{-1} at a rate of C/20 without addition of any conductive substance or binder [19]. Yao et al. reported a kind of novel interconnected Si hollow nanospheres which had a capacity of 1420 mAh g^{-1} at C/2 after 700 total cycles, and a Coulombic efficiency as high as 99.5% [20]. Choi et al. prepared single crystal Si

nanoparticles covered with nitrogen-doped carbon layers using a laser photopylysis method technique and formed a nitrogen-doped carbon layer on them, which exhibited a specific capacity of 967.1 mAh g^{-1} and a capacity retention of 87.3% after 300 cycles at 1 C [21]. Li et al. fabricated core-shell Si/C nanospheres by a magnesium thermal reduction/glucose carbonization process using sodium chloride (NaCl) as the template, which showed a capacity of 1018 mAh g^{-1} at 1 A g^{-1} after 200 cycles [22]. Cheng et al. developed a kind of novel porous Si films by electrochemical etching method that showed a high reversible specific capacity over 2500 mAh g^{-1} after 60 cycles at 0.1 C [23].

By briefly comparing these reported nanostructures, it seems that Si nanoparticles are more promising anode materials for LIBs than the other nanostructures of Si. The reported methods employed to fabricate Si nanoparticles mainly include magnesiothermic reduction, etching of SiO$_2$, plasma deposition, high-energy ball-malling and so on. Substantial progress has been made for the preparation of these Si nanoparticles in these years. For example, Favors et al. prepared 3D network of Si nanoparticles via the magnesiothermic reduction process, which exhibited achieved a remarkable electrochemical performance with a capacity of 1024 mAh g^{-1} at 2 A g^{-1} after 1000 cycles [24]. Zhong et al. made mesoporous Si nanoparticles through magnesium-thermal reduction which retained a high capacity of 1444 mAh g^{-1} at 400 mA g^{-1} capacity after 100 cycles [25]. Yi et al. prepared Si−C micro-sized particles via HF-etching SiO$_2$ building blocks sized at 10 nm, and the resulted products showed a fare reversible capacity of 1459 mAh g^{-1} at 1 A g^{-1} after 200 cycles [26]. Hou et al. synthesized Si nanosphere-porous carbon composites by using the radiofrequency induction thermal plasma system and ball-milling post process, the composites showed a capacity of 500 mAh g^{-1} at 210 mA g^{-1} after 50 cycles [27]. Genki et al. synthesized Si nanoparticles from Si bar electrode via solution plasma, which had diameters ranging from 50 to 1000 nm [28]. Gauthier et al. reported Si nanoparticles (a crystallite the size of ~10 nm) through high-energy ball-milling, which showed more than 1170 mAh g^{-1} at 480 mA g^{-1} capacity at 600 cycles [29]. Yim et al. prepared silicon power (with an average size of 0.73 μm) by ball-milling crystalline silicon for 100 h and 200 h, the power ball milled for 200 h exhibited have the lowest first-cycle irreversible capacity and the highest reversible capacity reaching over 500 mAh g^{-1} after 50 cycles at C/12 [30]. Heet al. developed a facile and large-scale approach for preparing micro-sized porous silicon by acid etching the economic-effective metallurgical Fe−Si alloy, and the products exhibited an excellent reversible capacity of 1250 mAh g^{-1} after 100 cycles at 500 mA g^{-1} [31]. In general, these methods are still quite costing and difficult to be scaled up.

Previously, our group reported fabrication of several high-performing anode materials including a scalable synthesis of the interconnected porous Si/C porous composites and Si/C nano-branches by Rochow reaction [32,33], and carbon-coated porous silicon composites by reaction of Si particles with alcohols over Cu-bases catalysts. Here we report a new facile and scalable method for preparing Si nanoparticles by reacting silicon with HCl gas over Cu-based catalyst particles, which is the well-known route used to produce organosilane monomers in chemical industry. After the reaction, the Si nanoparticles were extracted from the solid residua waste and used as anode materials, which showed a high reversible capacity and good cycle life.

2. Experimental

2.1. Material synthesis

Typically, 10 g of the commercial metallurgical grade Si power and 0.3 g of the Cu-based catalyst powder were ball-milled for 2 h to form a mixture. In this step, we use two different catalysts 3P (mixture with Cu, CuO and Cu$_2$O) and S21 (Cu$_2$O compound) to make two different samples. The mixture was pretreated at 450 °C for 2 h under an Ar/H$_2$ (9:1, v/v) gas flow in a tube furnace to form a contact mass. 4 g of the

contact mass was coated with foamy copper, which was then loaded in the quartz reactor. The reactor system was purged with purified N$_2$ at a flow rate of 25 mL min^{-1}. Subsequently, N$_2$ was turned off and commercial HCl gas with a flow rate of 25 mL min^{-1} was introduced into the reactor to react with the contact mass at 300 °C for 2 h. The waste contact mass (solid residue after the reaction) was denoted as 3P-2h and S21-2h.

2.2. Characterization

X-ray diffraction pattern (XRD) were recorded on a PANalytical X'Pert PRO MPD using the Kα radiation of Cu (λ = 1.5418 Å). The microscopic features of the samples were observed by field-emission scanning electron microscopy (SEM) (JSM-7001F, JEOL, Tokyo, Japan) with energy dispersive X-ray (EDX) spectroscopy and transmission electron microscopy (TEM) (JEM-2010F, JEOL, Tokyo, Japan). A Raman spectroscopy (Renishawin Via plus, England) with an excitation wavelength of 514.5 nm and a beam spot size of 1–2 μm was used to characterize the samples.

2.3. Electrochemical measurement

The working electrode was prepared by mixing the active materials, acetylene black, and alginic acid sodium salt in a weight ratio of 4:4:2 with water as a solvent. The resulting slurries were cast onto copper current collectors. The foils were rolled into 16 μm thin sheets, and then dried at 40 °C for 24 h. The foils were cut into disks which were 14 mm in diameter, and then dried at 120 °C under vacuum for 24 h. CR2016 coin-type cells were assembled in an argon-filled glove box with lithium foils as the counter electrodes and polypropylene macroporous films (Celgard 2400) as separators. The liquid electrolyte was 1 mol L^{-1} LiPF$_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v). The galvanostatic charge and discharge tests were carried out by the NEWARE-BTS-5 V/10 mA testing instrument (NewareCo., Ltd., Shenzhen, China) in a voltage range between 0.005 and 2.0 V at the current density of 50 mA g^{-1}. Cyclic voltammetry (CV) tests were carried out between 0.005 and 2.0 V at a scan rate of 0.2 mV s^{-1} using CHI660D electrochemical workstation. Electrochemical impedance spectroscopy (EIS) measurements were carried out on CHI660D electrochemical workstation in the frequency range from 100 kHz to 10 mHz at an ac-oscillation of 5 mV. All the electrochemical performances were measured at room temperature.

3. Results and discussion

The material preparation process is illustrated in Scheme 1. The commercial metallurgical-grade bulk Si powder (Scheme 1a) and Cu-based catalyst particles are ball-milled to form Cu−Si mixtures (Scheme 1b). After pretreated at 450 °C in Ar/H$_2$ (9:1, v/v) gas, Cu$_x$Si species is formed at the interface between bulk Si and Cu-based catalyst particles within the contact mass (Scheme 1c), which reacts further with HCl gas to produce organosilane monomers (Scheme 1c and d), and meanwhile, generating the waste contact mass (Scheme 1d and e), which is composed of unreacted Si and Cu mixtures (marked by red in Scheme 1c). The reaction pathway of Cu$_x$Si with HCl is shown in Scheme 2. After etching off the Cu catalyst residual by acid, nanostructured silicon particles are obtained (Scheme 1e to f).

Fig. 1 shows SEM images of the metallurgical-grade bulk Si and the obtained samples Si nanoparticles, and Si and Cu elemental mapping of the Si nanoparticles. It can be seen from Fig. 1a and b that bulk Si particles have a size range of about 10–100 μm before reaction. After the catalytic reaction and removal of the Cu-based catalysts, it is observed that many interconnected Si nanoparticles are generated (Fig. 1c–f) with sizes around 100–300 nm. The elemental mapping images (Fig. 1g–i) taken from the Si nanoparticles show that Cu and Si are distributed in the interphase, and Cu is located over the surface of