Preparation and Properties of Silicon Carbon Composites Using the Thermal Plasma Method

Yakun Fan1,*, Xiaohan Wan1, Wenhui Ma1,2,*, Xin Huang1, Zhengjie Chen1

1National Engineering Laboratory for Vacuum Metallurgy, Kunming University of Science and Technology, Kunming 650093, China
2State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, China

*Corresponding author e-mail: mwhsilicon@126.com, 664144605@qq.com

Abstract. Silicon-carbon composites were prepared from industrial silicon powders and graphite powder using the thermal plasma method. The structure and properties of the composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET), Raman spectroscopy, and constant current charge-discharge tests. The results revealed that spherical nano-silicon/graphene can be prepared when the carbon content in raw materials is more than 30%. The size of the nano-silicon/graphene prepared by the one-step method was about 6.6nm×10.6um, and inserted nano-silicon were ~30nm. The nano-silicon/graphene composites were used as negative active materials to make lithium-ion batteries. The first specific capacity was 339 mAh/g. The constant current charging and discharging tests were carried out at 1 C. The first discharge specific capacity was about 339 mAh/g and a reversible capacity of 150 mAh/g was retained after 50 cycles at a current density of 1000 mAh/g.

1. Introduction

Silicon is one of the most abundant elements in nature, and will not produce pollution at the time of being utilized. Silicon is a pretty promising anode material for lithium-ion batteries because its theoretical capacity will arrive at 4200 mA h/ g when the alloy Li4.4Si is formed by silicon (Si) and lithium (Li) atoms. In addition, Si has a lower Li insertion potential of silicon potential than that of graphite carbon (C). As a result, Si-based electrodes have gained more and more attention recently.[1-4]

However, there is a significant change in volume during Lithium-ion insertion/extraction, which results in serious structural failure and loss of electrical contact throughout the anode.[5-6] Nanostructured Si and its nano-composites are thought to be able to tackle these problems.[7-8] Several methods have been used to prepare Si/C composites, such as pyrolysis, mechanical milling, and chemical vapor deposition (CVD).[9-10]

Here, we propose a one-step synthesis of global Si/C nano-composites using a thermal plasma approach. Having metallurgical silicon (MG-Si) as the Si precursor and graphite as the C precursor is cheaper, safer, and less toxic than silane (SiH4). [10] Nano-Si/C composites were prepared in a plasma furnace and the Si/C composites obtained under suitable conditions showed more
satisfactory capacities than graphite and good cycling performance, which suggests great potential for the commercial application of advanced Lithium-ion batteries.

2. Experimental section

2.1. Material synthesis
Nubby MG-Si powders (D_{50} = 16 \text{ um}, \text{purity} = 99.6\%) were purchased from Yunnan Great Union Group Co., Ltd., China and used as raw materials. The graphite powder was purchased from a market with a purity of 98.0\% and particle size of 200 mesh. Fig.1 shows the DC thermal plasma reactor in our laboratory, which consists of a power supply, gas system, powder feeder and diverter. Firstly, plasma gas (Ar_2, 99.9\%) was introduced into the reactor in order to exhaust the air and cooling water was inputted. The plasma furnace was then started, abundant heat was generated, and the raw materials were set into the temperature field by the powder feeder. Finally, Si/C nano-composites were prepared in the low temperature zone and collected via the diverter.

![Fig.1. The DC thermal plasma reactor in our laboratory.](image)

2.2. Characterization
The microscopic features of the samples were observed using a high-resolution transmission electron microscope (HRTEM, FEI Tecnai G2 TF30, and 300 kV) equipped with selected area electron diffraction (SAED). XRD characterization was obtained using a Bruker D4 with Cu K\(\alpha\) radiation at a wavelength of 1.5406 Å. Atomic force microscopy (AFM) measurements were performed with an Agilent 5500 atomic force microscope (Agilent Technologies, USA).

2.3. Electrochemical measurements
The working electrode was prepared by mixing the active Si/C nano-composites, super P, and polyvinylidene fluoride (PVDF) in a weight ratio of 7:2:1, with N-methylpyrrolidone (NMP) as a solvent. The slurry was cast onto a copper foil and then dried at 80\(^\circ\)C under a vacuum for 12 h. The foils were rolled into 30 \text{ um} thin sheets, and then cut into disks of 14 mm in diameter. CR2032 coin-type cells were assembled in an Ar-filled glove box with Li foils as the counter electrodes and polypropylene microporous foils (Celgard 2400) as separators. The electrolyte was LiPF_6 (1 \text{ mol} \ast \text{L}^{-1}) in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v). The galvanostatic charge and discharge tests were carried out using a CT2001A LAND testing instrument in the voltage range between 0.01 and 3.0 \text{ V}.

3. Results and discussion
The morphology and structure of the products were characterized by TEM, EDS, and SAED in Fig. 2(a-d). Fig.2 (a) shows the TEM images of Si/C composites prepared with a carbon content of 30 wt.\%.

As can be seen from the figure, there are several transparent flakes with a size of about 6.6 \text{ um} \times 10.6
um, which are attached by some spherical particles. Two points were selected from the flakes to analyze the elementary composition, as shown in Fig. 2 (b). Obviously, they are Si and C. Fig. 2 (c) presents the HRTEM image of nano-silicon, with the particle size ranging from 10 nm to 30 nm. An area was chosen from Fig. 2 (a) to confirm that the composites consisted of crystalline silicon (111) and silicon carbide (111), and graphene with the help of SAED in Fig. 2 (d).
Fig. 2. (a): TEM of Si/C nano-composites; (b): EDS of Si/C nano-composites; (c): HRTEM of Si/C nano-composites; (d): SAED of Si/C nano-composites.

Raman spectroscopy characterizations of the fabricated composites were implemented at 532 nm in Fig. 3. The peak located at ~510 cm$^{-1}$ is attributed to silicon.[11] The peaks at ~1350 cm$^{-1}$, ~1580 cm$^{-1}$, and ~2700 cm$^{-1}$ are corresponding to the D, G, and 2D peak of the produced graphene, respectively.[12] According to Ferrari’s research, there is an upshift of the 2D graphene peaks of the graphene with increasing layers, and for more than 5 layers there is no distinguishable difference compared to bulk graphite.[13] The 10 cm$^{-1}$ upshift may be due to the small size effect, and the remarkable shape difference of the 2D peak in Fig. 3 indicates that the layers of the produced graphene are less than 5.

Fig. 3. Raman spectra of graphite/silicon and nano-silicon/graphene composites.

AFM characterization was conducted to research the thickness of the obtained graphene in Fig. 4. Layers of graphene were calculated according to the thickness of a single-layer graphene sheet of 0.34 nm. Fig. 4 suggests that the maximum thickness of the produced graphene was about 1.3 nm, and indicates maximum layers of four. [14] This is consistent with the Raman spectra result in Fig. 3.
Fig. 4. AFM images and corresponding height profiles of the produced graphene

The XPS spectra and curve-fitted peak components of the Si 2p region are shown in Fig.5. The peak located at 98.3 eV (FWHM=1) is attributed to Si-Si bonds; the peak located at 99.3 eV (FWHM=0.8) is attributed to Si-C bonds, which is consistent with the SAED image result in Fig.2(d); and the peak located at 102.5 eV (FWHM=1.5) is attributed to Si-O bonds owing to oxygen in the air.[15]

Fig. 5. XPS spectra and curve-fitted peak components of the Si 2p region

The cycle performance of the cell is shown in Fig.6. The first discharge specific capacity was about 339 mAh/g, a reversible capacity of 150 mAh/g was retained after 50 cycles at the current density of 1000 mAh/g, and the decay rate of the discharge capacity was about 45%. The large irreversible capacity is attributed to the formation of SEI film consuming part of the Lithium-ion during the first
charge and discharge, and part of the Li\(^+\) cannot be removed after being embedded in nano-Si/graphene composites, forming irreversible embedding.[16]

![Charge/discharge capacity](image)

Fig.6. cycling performance of the produced nano-silicon/graphene composites

4. Conclusion
In the present study, a nano-silicon/graphene structure was prepared in a plasma atmosphere that contained high-octane plasma argon. This resulted in silicon/carbon particles nucleating and anisotropic growth. High concentrations of gaseous Si particles completed the nucleation process in the high temperature zone of the plasma, and then the initial nucleation agglomerated and developed to nanoscale nano-silicon/graphene composites. [17, 18]

Consequently, we produced global nano-Si/graphene composites using a thermal plasma approach. The size of the nano-silicon/graphene prepared using a one-step method was about 6.6 \(\mu\)m \(\times\) 10.6 \(\mu\)m, and inserted nano-silicon were \(\sim\)30nm. The specific area was about 147.160 m\(^2\)/g, which appears to provide more space for Li\(^+\) embedding and releasing. Finally, the nano-Si/graphene composites showed a good electrochemical activity of Lithium-ion storage.

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