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One-step synthesis of a silicon/hematite@carbon hybrid nanosheet/silicon sandwich-like composite as an anode material for Li-ion batteries

Abstract

Silicon and hematite, both important functional materials with high theoretical capacity, have been intensively investigated separately for application as anode materials in lithium ion batteries (LIBs). The main challenges associated with these anode materials are their low electronic conductivity and structural degradation caused by large volume expansion during cycling, which are not tolerable for future LIBs with high energy density and large power output. Active particles anchored on a porous conductive skeleton are widely used for improving the electrochemical performance of silicon as well as that of hematite. Herein, we develop a novel-structured carbon-silicon-hematite anode material via a single-step technique that addresses these problems. In the resultant architecture, silicon nanoparticles are sandwiched between the iron-oxide-embedded porous carbon sheets. The flexible and conductive carbon sheets improve the conductivity and accommodate the volume changes of the embedded hematite and silicon nanoparticles, and thus maintain the structural and electrical integrity. Meanwhile, the void space between the carbon layers leaves enough room for the expansion and contraction of silicon during the lithiation and delithiation processes. High capacity ($\sim 1980 \text{ mA h g}^{-1}$ at 750 mA g^{-1}) and long cycle life (250 cycles) have been achieved for this sandwich-like carbon-silicon-hematite electrode.

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One-Step to Synthesize Silicon/Hematite@Carbon Hybrid Nanosheets/Silicon Sandwich-Like Composite as Anode Materials for Li-ion Batteries

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Abstract

Silicon and hematite, both important functional materials with high theoretical capacity, have been intensively investigated separately for their applications as anode materials in lithium ion batteries (LIBs). The main challenges associated with these anode materials are their low electronic conductivity and structural degradation caused by large volume expansion during cycling, which are not available for future LIBs with high energy density and large power output. Active particles anchored in a porous conductive skeleton are widely used for improving the electrochemical performance of silicon as well as the hematite. Herein, we develop a novel structured carbon-silicon-hematite anode via a single-step technique that tackles these problems. In the resulted architecture, silicon nanoparticles sandwiched between the iron oxide embedded porous carbon sheets. The flexible and conductive carbon sheets improve the conductivity and accommodate the volume change of the embedded silicon and hematite nanoparticles and thus maintain the structural and electrical integrity. Meanwhile, the void space between carbon layers leaves enough room for the expansion and contraction of silicon during the lithiation and delithiation process. High capacity ($\sim 2000 \text{ mAh g}^{-1}$ at 750 mAh g^{-1}) and long cycle life (200 cycles) have been achieved for this sandwich-like carbon-silicon-hematite electrode.

Keywords: Hematite; Silicon; Sandwich-like structure; Anode; Lithium ion batteries;

1. Introduction

Conventional lithium ion batteries (LIBs) based on carbon anodes, such as commercial graphite microspheres and mesophase carbon microbeads (MCMB), with theoretical capacity of about 372 mAh g⁻¹, have now seen the limit of meeting the needs of high-energy storage.¹⁻⁴ To meet the increasing demand for energy storage capability, novel electrode materials with higher capacity, low cost, and the ability to be produced at large scale are of great interest.⁵

Silicon (Si) and hematite (α -Fe₂O₃) have long been regarded as an appealing anode materials for LIBs because of their much higher theoretical capacities ($\approx$ 4200 and 1007 mA h g⁻¹, respectively) than that of commercially used ones, nontoxicity and natural abundance.^{3,6-14} Despite of all these advantages, the full utilization of silicon or α -Fe₂O₃-based batteries to date has been hindered by a series of obstacles, including the poor cycle life and rate performance, resulted from its large volumetric expansion during the cycling and low ionic/electronic conductivity.¹⁵⁻¹⁹ Hence, great efforts have been made to further improve their electrochemical performance by using various silicon-containing (silicon nanowires,^{10,20-21} silicon nanotubes,²² porous structures silicon,²³ and carbon coated silicon²⁴⁻²⁵) or α -Fe₂O₃-containing (Fe₂O₃ nanorods,¹⁵ Fe₂O₃ nanotubes,²⁶ Fe₂O₃ nanosheets,⁶ graphene@Fe₂O₃ composite⁹) materials. Among them, porous carbon@Si or carbon@ α -Fe₂O₃ composites in which the active particles are coated or embedded in porous conductive carbon skeleton are quite promising, because the void space allows the expansion of silicon and α -Fe₂O₃ during the lithiation/ delithiation processes thus maintain the structural and electrical integrity.⁷ For instance, Cui et al., was demonstrated a carbon@void@Si (yolk-shell) composite system having a high capacity of $\sim$ 2800 mAh/g.²⁷ α -Fe₂O₃/reduced graphene oxide (rGO) nanocomposites ($\sim$ 1100 mAh/g) were fabricated by Zhang et al.,²⁸ through a facile microwave hydrothermal method in which the α -Fe₂O₃ nanoparticles are uniformly anchored on the graphene

nanosheets. Therefore, the problem of silicon and α -Fe₂O₃ can be tackled by combining porous structure and incorporation of carbon in one structure. To the best of our knowledge, the composite anodes explored so far contain either silicon or α -Fe₂O₃ along with carbon, and no reports are available wherein both the materials are utilized in one system. It is therefore envisioned that advances in LIBs technology can be achieved by incorporating both silicon and α -Fe₂O₃ in one porous carbon skeleton.

Herein, we report a facile one-step synthesis of a carbon-silicon-hematite (C-Si-Fe₂O₃) composite. In our case, silicon nanoparticles (Si NPs) sandwiched between α -Fe₂O₃ embedded porous carbon sheets (C@Fe₂O₃). The electronic conductivity of both silicon and α -Fe₂O₃ NPs can be improved by the conductive carbon layers.²⁹⁻³⁰ Meanwhile, the flexible carbon sheets are adaptable and can freely switch between the expansion and contraction of the active particles upon lithiation and delithiation.^{28,31} Besides, the space between the carbon layers allows the Si NPs to expand freely.³² More importantly, the C@Fe₂O₃ layers can prevent Si and α -Fe₂O₃ nanoparticles from aggregation. These unique characteristics facilitate the collection and transport of electrons, resulting in high capacity and good cycling stability.³³⁻³⁴

2. Experiment section

2.1. Material synthesis

In this work, 0.36 g of iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 1.33 mmol, Sigma-Aldrich, 98%) was dissolved in 1.22 g of oleic acid (Sigma-Aldrich). The resulting mixture was aged at 85 °C for 3 h, and then mixed with 600 mg Si (~100 nm). The mixture was heated to 600 °C at the heating rate of 5 °C min⁻¹ under Ar atmosphere for 3 h and then washed with distilled water to get the final material (C-Si-Fe₂O₃). For the comparison, carbon coated silicon (C-Si) composite was fabricated for which 600 mg Si was mixed with 1.22 g of oleic acid. Then, the mixture was heated to 600 °C at the heating rate of 5 °C min⁻¹ under Ar atmosphere for 3 h to get C-Si.

2.2. Characterization

The products, C-Si-Fe₂O₃, C-Si and Si NPs, were analyzed by X-ray diffraction (XRD; GBC MMA) with Cu K α radiation; Raman spectroscopy (JobinYvon HR800) employing a 10 mW helium/neon laser at 632.8 nm; field emission scanning electron microscopy (FESEM; JEOL 7500) and transmission electron microscopy (TEM; JEOL ARM-200F) with high-resolution TEM (HRTEM). Elemental CHN (Carbon-Hydrogen-Nitrogen mode) analysis was conducted for determining the carbon content in C-Si-Fe₂O₃. The X-ray photoelectron spectra (XPS) experiment was carried out using Al K-alpha radiation and fixed analyser transmission mode. The pass energy was 60 eV for the survey spectra and 20 eV for specific elements.

2.3. Electrochemical measurement

The tests were conducted by assembling coin-type half cells in an argon-filled glove box. Lithium foil was employed as both reference and counter electrode. The working electrode consisted of 70

wt.% active material (C-Si-Fe₂O₃, C-Si and Si NPs, respectively), 20 wt.% carbon black, and 10 wt.% carboxymethyl cellulose (CMC) binder. The electrolyte was 1.0 M LiPF₆ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Electrochemical cycling of coin cells was conducted at 750 mA g⁻¹ using galvanostatic mode in the potential window of 10 mV to 2.8 V (vs. Li/Li⁺). Cyclic voltammetry was performed using a Biologic VMP-3 electrochemical workstation between 0.01 and 2.8 V at a scan rate of 0.1 mV s⁻¹.

3. Results and discussion

Fig. S1 shows a typical SEM image of Si NPs, which are in the size range of around 100 nm. The obtained C-Si composite in Fig. 1a exhibits an interconnected network, forming a continuous three dimensional (3D) structure. The higher magnification image of C-Si (Fig. 1b) shows that Si NPs were well connected with each other through the carbon coating layers. Compared with C-Si, C-Si-Fe₂O₃ (Fig. 1c) shows a significantly different structure. It can be seen, C-Si-Fe₂O₃ possesses a layer-by-layer assembled structure. Si NPs are dispersed between the Fe₂O₃ embedded carbon (C@Fe₂O₃) layer and these C@Fe₂O₃ layers prevent the aggregation of Si NPs and α -Fe₂O₃ nanoparticles during the annealing process. More importantly, portions of carbon sheets stacked reconstitute to form a porous conductive network, and this unique interconnected 3D nanostructure not only improves the electronic conductivity, but also provides void space to accommodate the volume change of Si NPs and α -Fe₂O₃ during cycling while maintaining the mechanical stability.³² Fig. 1d shows the enlarged image of C@Fe₂O₃ layer, where uniformly embedded α -Fe₂O₃ NPs in the size range of 30-40 nm were clearly seen on the carbon layers.

Fig. 1. SEM images of C-Si (a and b), and C-Si-Fe₂O₃ (c and d)

The energy dispersive X-ray (EDX) data in Fig. S2a shows that only carbon and silicon can be found in this sample (Cu peaks arise from the specimen holder). Fig. S2b shows the TEM image of C-Si. It can be seen, C-Si is composed of carbon coated Si NPs in a size range of 80-130 nm and all of these particles are interconnected with surface coated amorphous carbon (AC) stemmed from oleic acid. The enlarged TEM image of C-Si (Fig. 2Sc) shows that the thickness of the carbon coating layer on the silicon surface is around 10-15 nm. The carbon (Fig. 2Sd) and silicon (Fig. 2Se) elemental mapping images indicate that the Si NPs are homogenously coated with the interconnected carbon coating layer and every single silicon nanoparticle is separated from each other due to the outer carbon shell (please see Fig. 2Sf). Fig. 2a shows that carbon, silicon and iron can be found in C-Si-Fe₂O₃. The elements mapping images (Fig. 2c to 2f) show that, even after the ultrasonication used to disperse the C-Si-Fe₂O₃ composite for TEM characterization, α -Fe₂O₃ particles with a size range of 26-30 nm are still firmly attached to the carbon sheets and Si NPs are

also dispersed uniformly between C@Fe₂O₃. This unique structure helps to prevent α -Fe₂O₃ and Si NPs from agglomeration and enables a good dispersion of these active particles over the carbon sheets support. Besides, very thin carbon coating layers can be seen on the surface of Si NPs. The mechanism for the formation of this structure can be explained to be as following. The iron–oleate complex was first synthesized during the aging period and then uniformly mixed with Si NPs. Upon heating under inert atmosphere, the metal–oleate complex was converted to form the two-dimensional hematite/carbon hybrid nanosheet structure, and thin carbon coated Si NPs were sandwiched between these hybrid nanosheets.³⁴⁻³⁵

Fig. 2. C-Si-Fe₂O₃: EDX (a), TEM (b), carbon (yellow), silicon (red) and iron (green) elemental mapping images (c, d, e and f).

Fig. 3a shows the XRD patterns of C-Si-Fe₂O₃, C-Si and Si NPs. For all the samples, there are three distinct diffraction peaks at 2θ values of 28.3, 47.0, and 55.8°, which can be assigned to (111), (220), and (311) planes of silicon phase (JCPDS NO. 27-1402) respectively.¹⁶ Besides the silicon phase, in the sample C-Si-Fe₂O₃, all the peaks at about 24.1, 33.1, 35.6, 43.3, 49.5, 54.1, 57.5, 62.3, and 65.3° can be assigned to lattice planes (012), (104), (110), (202), (024), (116), (018), (214), and

(300), respectively, of α -Fe₂O₃ (JCPDS No. 33-0664).²⁸

Fig. 3b shows their Raman spectra. For all the silicon-based samples, the strong peaks at about 500 cm⁻¹, are ascribed to Si and SiO.³⁶⁻³⁷ The peak at around 1350 cm⁻¹ (D-band) are associated with the vibration of carbon atoms with dangling bonds in plane terminations of the AC,³⁸ while the strong peak at about 1590.0 cm⁻¹ (G-band) can be assigned to the vibration of sp²-bonded carbon atoms in a two-dimensional hexagonal lattice,³⁹ namely the stretching modes of C=C bonds in typical graphite. For the carbon-based samples, a low-intensity and weak G-band peak suggest a structural imperfection of the graphene sheets such as small crystal domain size or defects.⁴⁰⁻⁴² Therefore, the carbon inside C-Si-Fe₂O₃ and C-Si belongs to AC and has a low graphitization degree. Compared with Si NPs, it can be seen that the peaks around 292 and 606 cm⁻¹ of C-Si-Fe₂O₃ are having better intensity. This increased intensity is due to the overlap of peaks of α -Fe₂O₃ and silicon at these positions, indicating the existence of α -Fe₂O₃. In agreement with the XRD results, this indicates that the C-Si-Fe₂O₃ composite was successfully synthesized via the facial one-step method.

The components of C-Si-Fe₂O₃ were further confirmed by X-ray photoelectron spectra (XPS) spectrum, suggesting the presence of Si, C, O, and Fe elements in the sample (see Fig. 3c). A high resolution spectrum of Fe 2p is displayed in figure 3d, showing two peaks at about 712.0 and 725.0 eV, corresponding to Fe 2p_{3/2} and Fe 2p_{1/2}.⁴³ The carbon content of C-Si-Fe₂O₃ was measured using a carbon-hydrogen-nitrogen (CHN) analyzer. 15 wt.% of carbon was found in C-Si-Fe₂O₃. Based on the ratio of FeCl₃·6H₂O and Si NPs, the α -Fe₂O₃ and silicon content of C-Si-Fe₂O₃ was calculated to be around 20 and 65 wt%, respectively.

Fig. 3. XRD patterns (a), Raman spectra (b) of all the samples, the wide XPS spectrum of C-Si-Fe₂O₃ (c) and the high resolution XPS spectrum of Fe 2p (d).

Fig. 4a shows the charge/discharge curves of C-Si-Fe₂O₃ and C-Si at a current density of 750 mA g⁻¹. The discharge and charge capacities in the first run are about 2846.5 and 1911.4 mAh g⁻¹ for C-Si-Fe₂O₃, and 3404.3 and 2206.9 mAh g⁻¹ for C-Si, thus their initial coulombic efficiency is 67.2 and 64.8 %, respectively. The low initial coulombic efficiency of the synthesized C-Si-Fe₂O₃ may be because of the secondary reactions such as electrolyte decomposition between electrode and electrolyte that often results in a high irreversibility (low columbic efficiency).⁴⁴⁻⁴⁶

Fig. 4b gives the representative first three consecutive cyclic voltammetry (CV) curves of C-Si-Fe₂O₃ in the voltage range of 0.01–2.8 V at a scan rate of 0.1 mV s⁻¹. During the first discharge process, two reduction peaks at 1.48 and 0.68 V can be observed, which could be related

to a multi-step electrochemical reduction process.^{6,47-48} Specifically, the small cathodic peak at 1.48 V can be respectively ascribed to the initial lithium intercalation and the phase transition from hexagonal $\text{Li}_x(\text{Fe}_2\text{O}_3)$ to cubic $\text{Li}_2(\text{Fe}_2\text{O}_3)$.⁴⁹⁻⁵⁰ Besides, another cathodic peak located around 0.68 V, which disappears from the second cycle, can be attributed to the further reduction of the $\text{Li}_2(\text{Fe}_2\text{O}_3)$ into Fe^0 , as well as the formation of SEI layer.⁵¹ Thus, the reactions are speculated to be as following formulas.

In addition, another cathodic at 0.18 V appears since the second cycle, attributed to the alloying of lithium with silicon.⁵² The subsequent broad anodic peaks during the charge process are observed at 1.60 and 1.93 V, indicating the multiple step oxidation of Fe^0 .^{26,49,53} Meanwhile, the other oxidative peaks located at about 0.31 and 0.48 V are due to the extraction of lithium ions from the carbon and dealloying of Li_xSi .^{7,30} The general overlapping of charge curves implies the good reversibility and stability of the electrochemical reaction.⁶ These results nearly coincide with the voltage plateaus in the galvanostatic discharge–charge curve (Fig. 4a) and consistent with its good cycling performance as discussed below. However, compared with C-Si- Fe_2O_3 , the first three CV curves of C-Si in Fig. S3 are quite different. Only the reduction peaks below 0.3 V and anodic peaks around 0.5 V can be found.

The cycling performance in Fig. 4c shows the charge/discharge capacity of C-Si- Fe_2O_3 at a current density of 750 mA g^{-1} for 200 cycles. It can be seen, the charge capacity is $1911.4 \text{ mAh g}^{-1}$ at the first cycle and $2015.4 \text{ mAh g}^{-1}$ after 200 cycles, suggesting that C-Si- Fe_2O_3 has a high capacity and good cycling stability. Meanwhile, a small decrease of reversible capacity is observed during the first 50 cycles. After that, the capacity starts to increase slowly and reaches the plateau

after the 100 cycle. It is known that the capacity of AC is around 600.0 mAh g^{-1} .⁵⁴ Thus, the improved capacity for C-Si-Fe₂O₃ is attributed to the contribution of silicon and α -Fe₂O₃ nanoparticles, and the capacity of silicon, α -Fe₂O₃ and AC is calculated to be around 2730.0, 200.0 and 90.0 mAh g⁻¹ (based on the CHN data). Therefore, the theoretical capacity of C-Si-Fe₂O₃ is around 3020.0 mAh g⁻¹ and the capacity retention is about 66.7 % even after 200 cycles.

Fig. 4d shows the rate performance of samples at different current densities. The charge capacities of C-Si-Fe₂O₃ and C-Si at the first 0.75 A g^{-1} after 20 cycles are 1472.0 and 1148.3 mAh g⁻¹, respectively, and the retention of the capacity at 1.5, 3.0, and 6.0 A g^{-1} is 96.2, 66.0, and 50.4 % for C-Si-Fe₂O₃, higher than those of the C-Si (61.2, 12.8, and 5.8%), especially at the current densities of 3.0 and 6.0 A g^{-1} , indicating the better rate performance of C-Si-Fe₂O₃. More importantly, compared with C-Si, after the high rate charge and discharge, a much higher reversible capacity of C-Si-Fe₂O₃ can still be maintained for the next 150 cycles. Fig. S4 shows the electrochemical impedance plots of C-Si-Fe₂O₃ and C-Si. It can be seen, the solution resistance of C-Si-Fe₂O₃ is less than C-Si, suggesting that C-Si-Fe₂O₃ has a better electronic conductivity and rate performance.⁷

The enhanced electrochemical properties of the porous C-Si-Fe₂O₃ could be attributed to its unique architecture: (1) the sandwich nanoarchitecture helps to prevent α -Fe₂O₃ and Si NPs from agglomeration and enables a good dispersion of these active particles over the carbon sheets support; (2) multilayered structure can form a porous, highly conducting 3D network that can serve as a structural scaffold to improve the electronic conductivity, strengthen the mechanical properties and also provides better room for the huge volume change of Si NPs and α -Fe₂O₃ during cycling;^{5,55-56} and (3) nano-sized α -Fe₂O₃ particles ($\approx 30 \text{ nm}$) uniformly embedded on the carbon layers will enhance the diffusion process, which leads to the less tortuosity of electrode and higher electrolyte

diffusion thus enhancing the rate performance.⁵⁷

Fig. 4. Electrochemical properties: (a) the initial discharge-charge of C-Si-Fe₂O₃ and C-Si, (b) the first three consecutive CV curves of C-Si-Fe₂O₃ at a scan rate 0.1 mV s⁻¹, (c) cycling property for C-Si-Fe₂O₃ between 2.8 and 0.01 V at the current density of 750 mA g⁻¹, and (d) the rate performance of C-Si-Fe₂O₃ and C-Si at different current densities.

4. Conclusions

In summary, we have demonstrated a facile and scalable method for preparing a novel nanoarchitecture of carbon@silicon@hematite (C-Si-Fe₂O₃) composite employing the one-step self-assembled method. Silicon nanoparticles sandwiched between the nanosized iron oxide embedded carbon layers, and more importantly, portions of these carbon sheets stacked reconstitute to form a porous conductive network. Rationally designed unique 3D porous carbon network

enhances the electrical conductivity and enables this C-Si-Fe₂O₃ composite to buffer the volume change of silicon and α -Fe₂O₃ during the cycling much more effectively. Compared with the commercial graphite microspheres (372 mAh g⁻¹), C-Si-Fe₂O₃ shows much higher capacity and better rate performance. Clearly, the simplicity and scalability of this fabrication process and the excellent electrochemical property will make C-Si-Fe₂O₃ anode material promising for the practical application in the next generation Li-ion cells.

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