

Short communication

Spray-pyrolyzed silicon/disordered carbon nanocomposites for lithium-ion battery anodes

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Abstract

A new and effective approach to prepare carbon-coated Si nanocomposites as high capacity anode materials for lithium-ion batteries with markedly improved electrochemical performance is described. Initially, nanosized Si particles (<100 nm) were mixed with different concentrations of the carbon source precursor, citric acid in ethanol solution via ultrasonication. Spray pyrolysis of these mixtures at 400 °C in air resulted in an amorphous carbon coating on the spherical Si nanoparticles. High-resolution transmission electron microscopy (HRTEM) analysis confirms a homogeneous layer of amorphous carbon coating of ~10 nm. These resultant nanocomposites show excellent cycling performance, especially when the disordered carbon (DC) content is above 50 wt.%. The 44Si/56DC nanocomposite shows the highest specific capacity retention of 1120 mAh g⁻¹ after 100 cycles. The carbon-coating on the nanocrystalline Si particles appears to be the main reason for the good cyclability, suggesting the excellent potential of these Si/DC-based nanocomposites for use as alternative anodes for lithium-ion batteries.

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1. Introduction

In order to develop high capacity anode materials for enhancing the performance of lithium-ion batteries, silicon (Si) and a variety of metals that alloy with lithium, such as Sn, Sb, and Al, were studied and found to be promising candidates as anode materials [1–4]. Among them, Si appears to be the most attractive candidate due to its large theoretical lithium insertion capacity of 4200 mAh g⁻¹ [1]. However, silicon undergoes a rapid capacity fading upon cycling due to its morphological deterioration, caused by volume expansion (>400%) during the alloying/de-alloying process [5]. A promising approach to overcome this detriment is to create a composite nanostructure in which silicon particles are homogeneously dispersed in a ductile and electrochemically active matrix [6,7]. Small volume expansion, coupled to a relatively lightweight

and good electronic conductivity makes carbon the best matrix.

Therefore, we suggest the addition of a carbon source to enhance the electronic conductivity of Si and also increase its specific capacity and cycle life. This concept has proven to be successful in other studies [8,9]. Our work here is based on the novel concept of spray-pyrolyzing Si in air with a low temperature carbon source without oxidizing the Si nanoparticles. In this work, we produced Si/disordered carbon (DC) nanocomposites using an in situ spray pyrolysis approach and investigated their electrochemical performance as anode materials for Li-ion batteries.

2. Experimental

Citric acid (C₆H₈O₇) was dissolved in 200 mL of absolute ethanol (99.99 wt.%) with continuous stirring. Subsequently, nanocrystalline Si powder was mixed into the initial citric acid/ethanol solution by ultrasonication for 90 min. Four types of composite materials were prepared by mixing the initial solutions with nanocrystalline Si powder (<100 nm) in weight ratios (Si: citric acid) of 1:1, 1:3, 1:6 and 1:10, respectively.

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Finally, the composites were obtained in situ via spraying of the Si/citric acid/ethanol suspensions at 400 °C using a flow rate of 4 mL min⁻¹ in a vertical type spray pyrolysis reactor. In this instance, citric acid was chosen as the carbon source due to its low decomposition temperature (175 °C) and low oxygen content. Meanwhile, ethanol acts not only as an efficient solvent, but also as a reducing agent to protect the nanocrystalline Si particles from oxidation during the spray pyrolysis process.

Thermogravimetric analysis (TGA) was performed to determine the amount of carbon in the composite materials. Powder samples were analyzed by X-ray diffraction (XRD), using the diffractometer method with Cu K α radiation and a graphite monochromator. Scanning electron microscopy (SEM) was performed using a JEOL JSM 6460A scanning electron microscope. Transmission electron microscopy (TEM) investigations were performed using a JEOL 2011 analytical electron microscope. TEM samples were prepared by deposition of ground particles onto lacey carbon support films.

The anode was prepared by mixing carbon-coated Si powders with 10 wt.% carbon black and 10 wt.% polyvinylidene fluoride (PVDF) binder in *N*-methyl-2-pyrrolidinone (NMP) solvent to form a homogeneous slurry, which was then spread onto a copper foil. The coated electrodes were dried in a vacuum oven at 110 °C for 24 h and then pressed. Electrochemical characterizations were carried out using coin cells (CR 2032) assembled in an argon-filled glove box. The electrolyte used was 1 M LiPF₆ in a 50:50 (w/w) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) provided by Merck KgaA. Subsequently, electrochemical tests were performed by galvanostatically charging/discharging the cells in the range of 0.02–1.20 V at a constant current density of 100 mA g⁻¹ via a Neware battery tester.

3. Results and discussion

For quantifying the amount of disordered carbon in the Si/DC nanocomposites, TGA analysis was carried out in air. The samples were heated from 60 to 800 °C at a rate of 5 °C min⁻¹. Fig. 1 shows a typical TGA analysis of the Si/DC nanocomposite samples along with those of nanocrystalline Si powders. As can be seen in Fig. 1, the bare Si powders started to oxidize slowly in air at temperatures above 500 °C, with rapid oxidation above 650 °C. Meanwhile, the Si/DC composite material shows rapid mass loss between 150 and 480 °C. As the bare Si powder remains stable in this temperature range, any weight change corresponds to the oxidation of disordered carbon. Therefore,

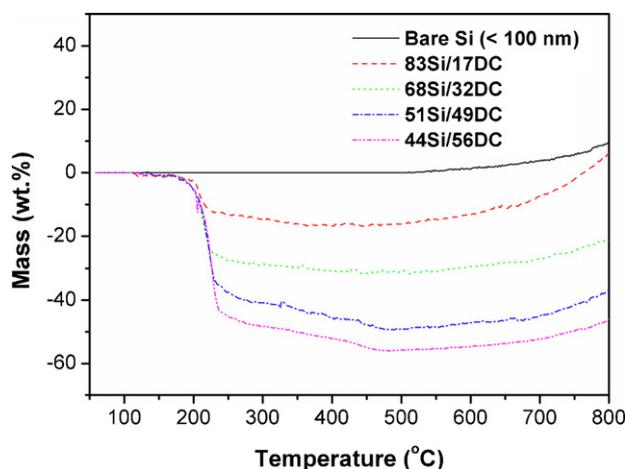


Fig. 1. Thermogravimetric analysis (TGA) curves for bare silicon powder (solid line) and Si/DC nanocomposites (dotted lines) with different Si/DC ratios.

the change in weight before and after the oxidation of carbon directly translates into the amount of disordered carbon in the Si/DC nanocomposites. Using this method, it was found that the amounts of disordered carbon in the composite were 16.78, 31.68, 49.37, and 55.98 wt.% for the precursor solutions with weight ratios (Si/citric acid) of 1/1, 1/3, 1/6, and 1/10, respectively. Table 1 summarizes the actual carbon content in the spray-pyrolyzed Si/DC nanocomposites. The carbon concentrations obtained after spray pyrolysis were below the targeted levels. All samples undergo between 28 and 40 wt.% carbon losses during the spray process. This can be explained by the following reaction during the spray pyrolysis process:

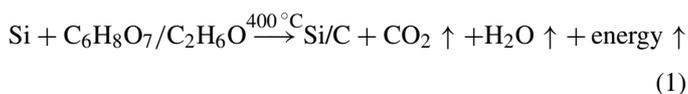


Fig. 2 shows XRD patterns of the nanocrystalline Si precursor powder (a) purchased from Nanostructured and Amorphous Materials Inc., the different Si/DC nanocomposites (b–e) prepared by spray pyrolysis at 400 °C in air, and pure spray-pyrolyzed amorphous carbon (f) made from citric acid. XRD pattern (a) in Fig. 2 shows a pure Si phase (JCPDS Card 01-0787). Meanwhile, XRD patterns (b–e) of the Si/DC nanocomposites in Fig. 2 show only the Si peaks, indicating that there was no bulk SiO₂ crystalline phase formed during the spray pyrolysis process at 400 °C in air. Moreover, no diffraction lines from crystalline carbon (graphite) were observed, indicating the amorphous nature of the carbon in the nanocomposites.

Table 1
Theoretical and actual carbon content in Si/DC nanocomposites spray-pyrolyzed at 400 °C in air from starting solutions with different concentrations of Si/citric acid^a

| Starting solution, Si/citric acid ^a (w/w) | Theoretical weight % of carbon | Actual weight % of carbon (via TGA) | Mass loss % of carbon during spray pyrolysis |
|--|--------------------------------|-------------------------------------|--|
| 1/1 | 27.27 | 16.78 | 38.47 |
| 1/3 | 52.94 | 31.68 | 40.16 |
| 1/6 | 69.23 | 49.37 | 28.69 |
| 1/10 | 78.95 | 55.98 | 29.09 |

^a C₆H₈O₇.

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