Enhanced cycle-capacity of micron scale silicon anode materials for lithium-ion batteries using embedded nanoparticles

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ABSTRACT: Micron scale Silicon (Si) powders embedded with nanoparticles were fabricated by dealloying methods and extracted from antimony (Sb)-inoculated Aluminum-10 wt.% Silicon (Al-10Si) alloys. From TEM observation, most of these nanoparticles were not connected with adjacent ones, with radii ranging from 3 to 10 nm. The cycling performance of Si powders with nanoparticles delivered a specific capacity of 105.2 mAh/g after 30 cycles at a current density of 0.05 mA/g, which was 40% higher than those without nanoparticles, due to the formation of preferential channels for electrolytes. Therefore, the micron size Si structures with nanoparticles have shown a potential as high-performance anode materials for lithium-ion batteries.

KEYWORDS: micron-size Si, nanoparticles, lithium-ion batteries, dealloying, anode, energy storage and conversion

INTRODUCTION

As one of the most promising anode materials for new generation lithium-ion batteries (LIBs), micron scale silicon (Si) has drawn a lot of scientific and technological attention due to its high theoretical specific capacity (∼4200 mAh/g) [1–3]. However, the commercial application of Si anode materials is hindered by its low electrical conductivity and short cycle life originated from the huge volume change (over 280%) and the pulverization during lithiation [4]. To overcome these challenges, innovative structural design concepts of Si anode materials have been proposed and implemented for battery applications, such as nanocrystallization [5], Si-C composites [6, 7], Si-C yolk-shell structures [8], oxide wall confinements [9], and porous structures [10, 11]. Each of these design concepts would lessen the mechanical and/or electrical instability of Si electrodes and enhance the cycling performance during lithiation. However, unlike other types of batteries [12], the high cost and potential safety issues, such as exploration of nanostructured Si, are still challenges for the commercial application of Si-based anode materials.

Micron size Si could make up for these deficiencies in performance, but it will suffer from the difficulty of inner structural modification for effective accommodation of large stress during lithiation. Generally,

complicate silicon-carbon composite of micro-size was constructed by an aggregation of silicon nanoparticles (∼100 nm) coated with conductive carbon layer to improve the mechanical and cycling performances [13] as an anode material for LIBs. Recently, micron scale eutectic Si particles embedded with Al-rich nanoparticles (radii of 3–10 nm) have been reported in inoculated Al-10Si alloys [14]. While embedded nanoparticles have a significantly smaller size than Si nanoparticles that form agglomerate superstructures (as noted in reference [13]), it is worth noting that Si powders that generate their own nanoparticles can be obtained with ease. In fact, melt reactions and dealloying can efficiently manufacture high-performance anode materials like nanoporous Ge at a low cost (as discussed in reference [15]). This paper presented the study of the microstructure and cycling performance of micron scale Si powders with nanoparticles. The results showed a significant improvement of embedded nanoparticles in the performance of micron scale Si powders as the LIB anode material.

METHODS AND EXPERIMENTS

Through the dealloying methods, micron scale Si powders with and without nanoparticles were extracted from as-solidified Al-Si alloys with a holding time of 10 and 60 min, respectively [14, 15]. After a precipitation
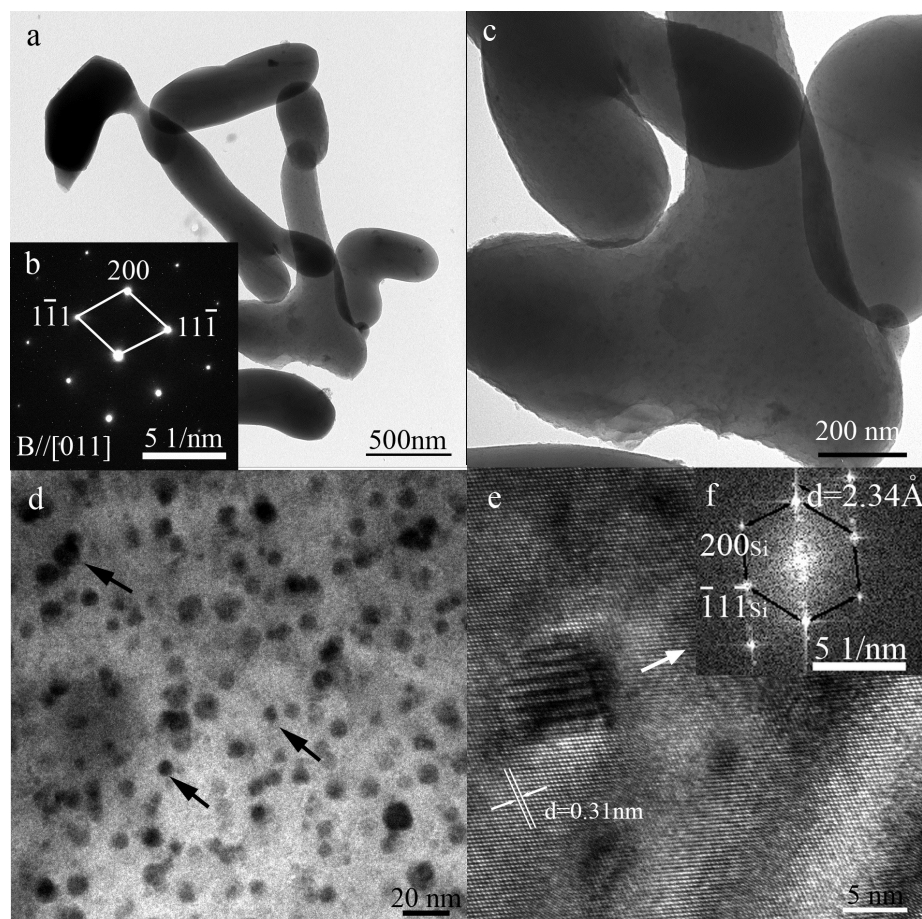
Fig. 1 As-prepared micron scale Si powders embedded with Al-doped nanoparticles: (a) bright-field TEM image; (b) diffraction patterns; (c) magnified bright field image; (d) nanoparticles; (e) atomic lattice image; and (f) FFT image of atomic lattice image of nanoparticles.

by gravity for about 24 h in deionized water, the supernatant liquid was centrifuged at 10,000 r/min and Si powders with an average radius of 1.0 µm were obtained for the Li-ion battery performance tests.

Morphologies and microstructure of micron scale Si powders were characterized by VEGA3 scanning electron microscope (TESCAN, Kohoutovice, Czechoslovakia) and Tecnai G2 F20 Spirit-TWIN field emission transmission electron microscopy (FEI Company, Hillsboro, OR, USA).

The Cu-supported Si-acetylene black-CMC composites with a weight ratio of 60:25:15 were used as working electrodes. Electrochemical performance was measured in coin-type cells, using a LAND-CT2001A tester (Wuhan, China) in the potential range of 0.01–1.5 V (vs. Li$^+$/Li). Lithium hexafluorophosphate (LiPF$_6$) 1 mol/l in ethylene carbonate/diethyl carbonate (EC/DEC) was the electrolyte solution (1:1 by volume), and a Celgard 2325 polypropylene membrane (Celgard, LLC, Charlotte, NC, USA) was the separator. More details could be referred in [16].

RESULTS AND DISCUSSION

Fig. 1(a) exhibits the morphology of micron scale Si powders. The short-rod like morphology is in good agreement with the microstructure of Si in as-casted Al-10Si alloys [14]. Titled to the silicon [13] zone axis, the pattern of the selected area electron diffraction (SAED) was indexed in Fig. 1(b). Fig. 1(c) is the enlarged view of Fig. 1(a), and more details could be found in Fig. 1(d). Many particles with radii ranging from 3 to 10 nm were embedded in the Si powders extracted from alloys with a holding time of 60 min, as denoted by the arrow in Fig. 1(d). Moreover, Fig. 1(d) also demonstrates that most of the nanoparticles did not contact with the adjacent ones. The typical lattice image of these nanoparticles was shown in Fig. 1(e). The spots corresponding to a distance of 0.234 nm in its FFT pattern indicated the existence of Al doping, as shown in Fig. 1(f), which could enhance the conductivity of Si powders as anode materials.

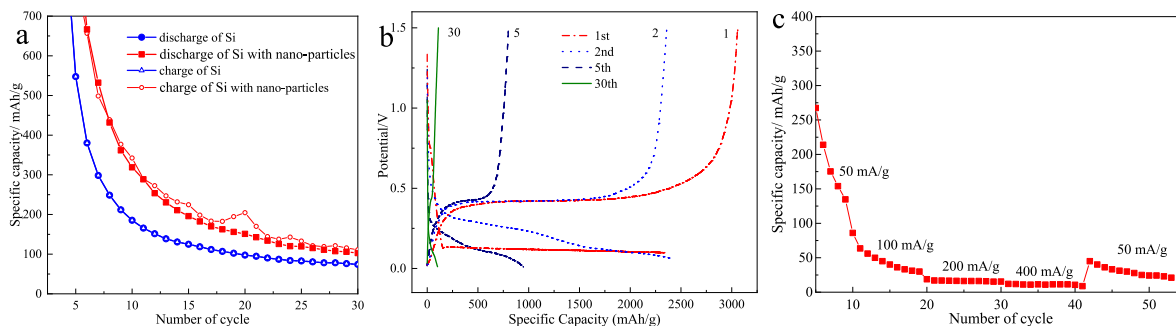Fig. 2(a) exhibits the cycling performance of the Si

Fig. 2 Cycling performance of micron scale Si embedded with nanoparticles: (a) comparison of the cycling stability of Si with and without nanoparticles at a current of 0.05 A/g; (b) initial discharge-charge curves of the Si with nanoparticles; and (c) rate performance of Si electrode with nanoparticles.
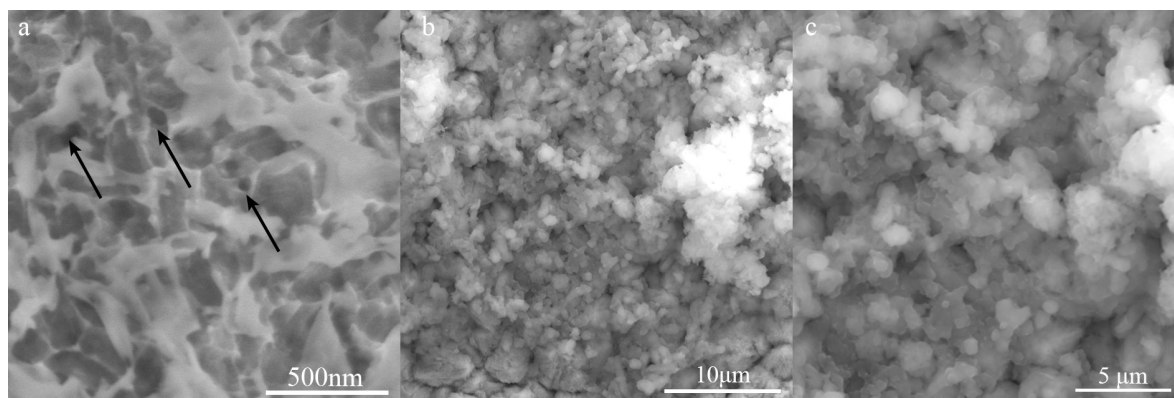

Fig. 3 Morphological observations of Si powders with nanoparticles after lithiation: (a) nanoscale holes induced by nanoparticles after one cycle; (b) the crack in the electrode; and (c) the pulverization of Si electrodes.

powders with and without nanoparticles as LIB anode materials. After 30 cycles at a current density of 0.05 A/g, the Si powders with and without nanoparticles retained specific capacities of 105.2 mAh/g and 75.2 mAh/g, respectively. The Si powders with nanoparticles had a specific capacity about 40% more than the without-nanoparticle powders. The improved specific capacity was not determined by the powder size since they were selected by the same technological process, and their sizes were the same. Taking the different microstructures inside Si powders into account, it was reasonable to conclude that the embedded nanoparticles were responsible for the increase of specific capacity.

During the electrochemical reaction of Si powders with embedded nanoparticles, the existence of Al element and the small radius of such nanoparticles led to the preferred dissolution. As depicted in Fig. 3(a), pores in the scale of several decade nanometers formed, which provided a preferential channel for electrolytes and enhanced mass transfer. For Si-based electrodes, pores with sizes ranging from 1 to 5 nm were effectively improve the specific surface area and could additionally provide a total pore volume needed

to enhance the cycling performance [16, 17]. However, such a channel might not be completely connected in the present Si powders with nanoparticles, since most of the nanoparticles seemed to be independent from adjacent ones (Fig. 1(d)). The incomplete connection might create a discontinuous channel for electrolytes and a difficulty in adapting to the large volume expansion and pulverization during lithiation, as shown in Fig. 3(b,c). In addition to the size of Si powders being far larger than the critical size of 150 nm [18], the discontinuous channel also explained why the stable specific capacity of Si with nanoparticles was not as high as the aggregated Si nanoparticles in reference [13].

As depicted in Fig. 2(b,c), the dependence between potential and specific capacity and rate capability was not as satisfied as that of cycle-capacity. Fig. 2(c) reveals rate capabilities with substantial reversible lithium storage capacities of 267.3, 40.1, 16.2, 11.3, and 31.1 mAh/g at current densities of 50, 100, 200, 400, and 50 mA/g, respectively. The dependences could mean that the micron scale Si powders should be further modified to enhance the cycling performance, such as introducing larger size nanoparticles to pro-

vide continuous nanoholes. Nevertheless, with simple fabrication, the present micron scale Si powders with nanoparticles could improve the cycling performance Si anode materials. The introduction of nanoparticles provided a potential method for the improvement of Si-based anode materials and their commercial application.

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