Preparation of Si/C composite nanofibers by electrospinning method using as the lithium-ion battery anode

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Keywords: Lithium-ion battery anode; Si nanoparticles; Carbon coating; Electrospinning.

Abstract. Si was a promising anode material for next-generation LIBs due to its extremely large capacity of 4200mAh/g ($Li_{4.4}Si$ phase). However, during repeated lithium insertion/extraction processes, the accompanied huge volume change (400%) induced the structural failure of the active material and resulted in rapid capacity fading. To overcome this problem, Si/C composite nanofibers with porous structure were prepared through a facile electrospinning method. The inclusion of carbon not only worked as a stable electric conductive pathway but also buffered the volume expansion of silicon during the process of charging and discharging. The first discharge capacity of the composite nanofiber (26wt.% and 50wt.% Si) electrode reaches 1840mAh/g, 2042mAh/g, and it delivered a charge capacity of 1461mAh/g, 1644mAh/g at the first cycle, corresponding to an initial coulombic efficiency of 79% and 80%. In contrast, the cell with the pure Si nanoparticle exhibited an initial discharge/charge capacity of 18 and 13mAh/g, respectively, which was much lower than the composite nanofiber electrode.

Introduction

Lithium-ion batteries (LIBs) have been widely used in many types of portable devices due to their high specific energy, high battery voltage, and long cycle life. As the conventional anode materials, the commercialized carbon has a lower theoretical specific of 372mAh/g[1, 2], which cannot satisfy the high specific capacity requirement for the future use. Therefore, alternative high capacity anode materials are strongly required. Silicon has high theoretical specific capacity (4200mAh/g) [3] and low working potential, which can be used as the lithium-ion battery anode materials in the future.

However, in the process of charging and discharging, Si has large volume changes (400%) [3].This huge volume change gives rise to the collapse of electrodes and insulation of active material, eventually resulting in rapid capacity fading and poor cycle performance. How to improve specific capacity of silicon and make the cycle performance of silicon-based anode materials better become the research focus. Many Si-based materials with different morphologies such as nanoparticles, nanofibers, nanotubes, nanorods and nanowires [4] were prepared. Si-based nanofibers can not only provide higher electric conductivity, but also can effectively slow down the huge volume changes [5, 6]. In this paper, the Si/C composite nanofibers were prepared by the electrospinning method. Different mass Si was dispersed into the carbon nanofibers, which possessed good elasticity to maintain the structure integrity [7] and stable electrically-conductive networks.

Material and Methods.

Si powder (0.20g, 0.40g, 100nm in diameter, Nanostructured & Amorphous Materials, Inc) and polyvinylpyrrolidone（1.0g, PVP K90, Pfaltz & Bauer Inc）were dispersed in ethanol (10ml) with magnetic stirring for 12h and kept in the ultrasonic bath for 20min. Electrospinning was carried out to form Si/C nanofibers with a 0.4 mL/ h flow rate, 17cm needle-to-collector distance, and 22kV voltage. Electrospun Si/C nanofibers were first stabilized in air at 250 ℃ for 30 min (heating rate was 5 ℃ /min) and then carbonized at 650 ℃ for 7h in argon (heating rate was 2 ℃ /min) to form Si/C nanofibers. For comparison, Si without the carbon coating were also prepared. The crystal structures of the treated powders were analyzed by X-ray diffractometry (XD3). The morphologies of the particles were characterized by scanning electron microscopy (SEM, FEI, XL 30S-FEG).

The electrode was prepared by mixing 80wt.% active material with 10wt.% acetylene black and 10wt.% polyvinylidene difluoride (PVDF) binder, coating the mixture on an copper foil, and then cutting the sheet into pieces with 1 cm×1 cm, which was dried at 120 ℃ for 12h to achieve the anode. The CR2032 coin cell was assembled in an Ar-filled Mikrouna glove box by using the prepared electrode as anode, lithium film as the counter electrode, Celgard 2400 as separator and 1MLiPF6 in EC:DMC (1:2 in volume) as electrolyte. The electrochemical performance was investigated by carrying out galvanostatic charge–discharge experiments between cut-off potentials of 0.02 and 2.0 V at constant current densities of 42mA/g using Land cell test system (Land CT2001A, China).

Results and Discussion

Figure.1 showed the XRD patterns of the pure Si powder, Si/C composites with 26wt.% and 50wt.%. The pure Si (Fig.1a) presented well-defined peaks at 2θ of 28.4°, 47.4°, 56.2°, 69.2°, 76.5°and 88.1°, which were assigned to the (111), (220), (311), (400), (331) and (422) planes of crystalized Si, respectively (JCPDSNo.27-1402) [8]. After sintering at 650 ℃ in argon, the structure of the Si powder coated by carbon unchanged since no apparent changes could be observed for all XRD diffraction peaks (Fig. 1b and c). The carbon was not detected because of its amorphous structure.

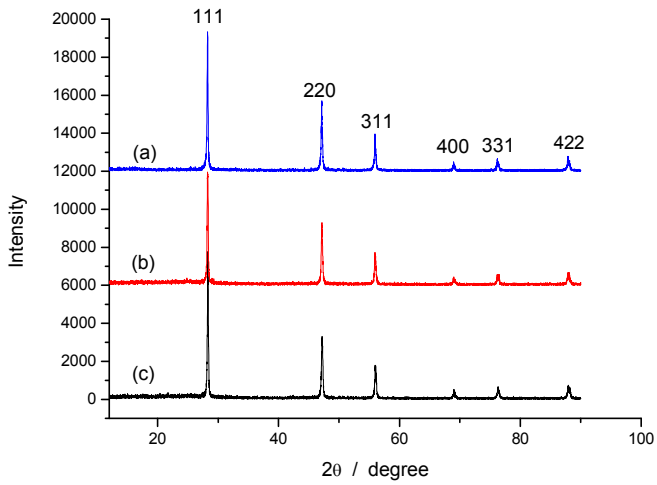

Figure 1: X-ray diffraction patterns of (a) Si nanoparticles, (b) Si/C composite with 26wt.% Si (c) Si/C composite with 50wt.% Si

Figure.2a showed the plane-view SEM images of the Si/C nanofibers (26wt.% Si) before sintering. From the surface direction, the sample exhibited an interconnected network structure composed of nanofibers with diameters of 1μm, and the fiber surface appeared uneven due to the presence of Si nanoparticles. This network structure was good for the cycling stability of Si because it had excellent structural buffering effect to absorb the mechanical stress induced by the volume changes of Si [3, 9].

Fig. 2b showed the Si/C composite (26wt.% Si) sample with aggregated porous structure, the porous structure could accommodate the Si volume expansion in the process of charging and discharging process. As shown in Fig. 2c for the Si/C composite (50wt.% Si) sample, some Si aggregated into bigger particles with the size of 2–3 um due to the Si content increasing. At the same time, carbon flakes in size around 1 um appeared in the composites, which was helpful for the conductivity improvement.

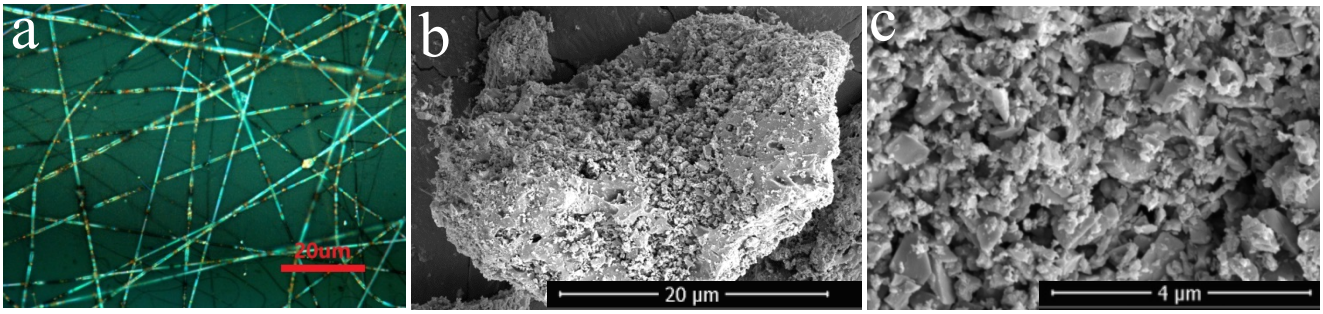

Figure 2: Images of the Si/C composite with 26wt.% Si (before sintering (a), after sintering (b))and 50wt.% Si sample sintered(c)

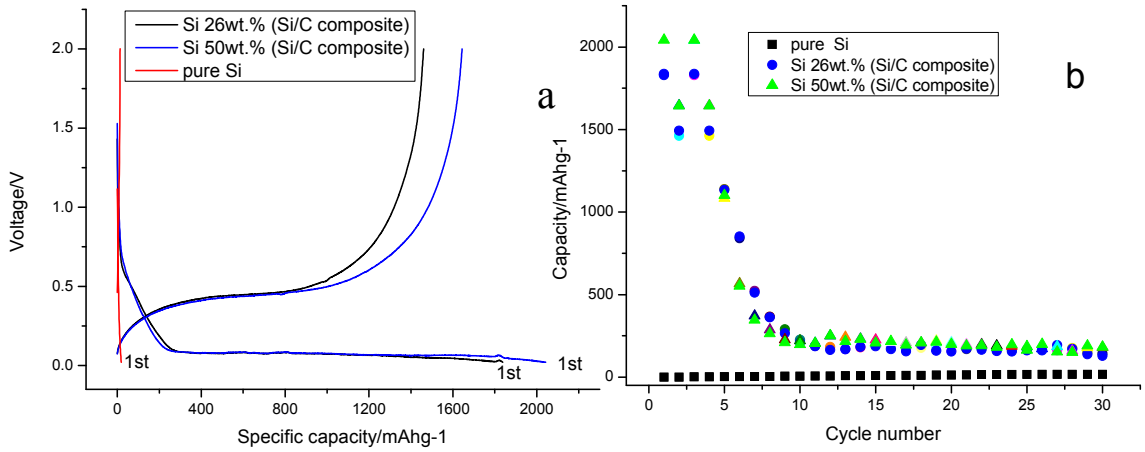

Figure 3: Voltage profiles (a) and Cycling performance (b) for the pristine Si and Si/C composite at 42 mA /g

Figure.3a showed the typical voltage profiles of the pure Si and the Si/C (26wt.% and 50wt.%Si) composite nanofiber electrode cycled between 0.02 and 2.0 V at 42 mA/g, respectively. The first discharge capacity of the composite (26wt.% and 50wt.% Si) electrode reaches 1840mAh/g, 2042mAh/g, and it delivered a charge capacity of 1461mAh/g, 1644mAh/g at the first cycle, corresponding to an initial coulombic efficiency of 79% and 80%. The low efficiency for the first charge/discharge could be mainly due to the larger surface area of the carbon-coated Si nanoparticles with porous nanofiber structure and formation of irreversible solid electrolyte interphase (SEI) layer[5, 10] in the first discharge process. In contrast, the cell with the pure Si nanoparticle exhibited an initial discharge/charge capacity of 18 and 13mAh/g, respectively, which was much lower than the composite electrode. The results provided clear evidence that the carbon-coated Si nanoparticles with porous nanofiber structure can enhance Li storage properties.

Figure.3b displayed the cycling performances of the Si/C composite (26wt.% and 50wt.%Si) electrodes and Si nanoparticle electrode. It could be seen that the capacity of the pure Si electrode decreased to about 17mAh/g after 30 cycles. As shown in Fig. 3b, the Si/C anode retained the reversible discharge capacity of 183mAh/g at the 30th cycle. In all 30 cycles, Si/C composite nanofibers had higher capacities and better capacity retentions than the pure Si due to the protection of Si with carbon.

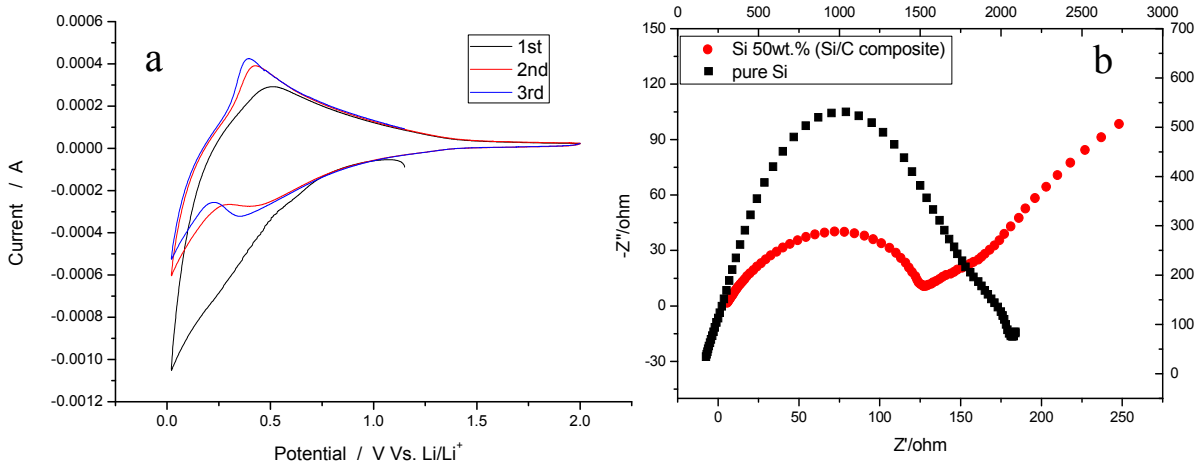

Figure 4: (a)Cyclic voltammograms of the Si/C composite (26wt.%) nanofiber electrode between 0.02 and 2.0 V (vs. Li/Li^+) at room temperature and the impedance spectra; (b) The impedance spectra of the Si/C composite (50wt.% Si) nanofiber electrode.

Figure.4a showed the C-V profiles of the Si/C composite (50wt. % Si) electrode measured between 0.02 and 2.0 V (versus Li/Li+) at a scanning rate of 0.1mV/s for the first 3 cycles. For the composite nanofibers, there is a broad cathodic peak between 0.25 and 0.70 V at the first cycle, which was resulted from the decomposition of the electrolyte and the formation of SEI film [1, 10]. It could be found that the cathodic peak of the third cycle became smaller and narrower compared with that of the first and the second cycle, indicating that the SEI formation is reduced. For the third cycle, the anodic peak at 0.39V corresponded to the alloying and de-alloying process of Li–Si alloys, which became clearer than those in the first cycle. The anodic current peaks exhibited an enhanced intensity from the first cycle to the third cycle, which could be attributed mainly to the gradual formation of the complete amorphization that depended on the migration rate of Li-ions into the silicon host [10].

Fig. 4b showed the impedance spectra of the pure Si and the Si/C composite nanofiber (50wt.% Si) electrode with the first cycle. The electrochemical impedance spectra consist of one depressed semicircle and a line. The semicircle at high frequency can be ascribed to the charge transfer resistance, which is related to the electrochemical reaction between the particles or between the electrode and the electrolyte. The sloping line is related to lithium-ion diffusion in the active material [11, 12]. As shown in Fig. 4b, the charge transfer resistance of Si/C composite nanofiber anode was 90 Ω at the first cycle, whereas it increased greatly to 2070 Ω for the pure Si. The improvement in the electrochemical performance for Si/C composite could be attributed to good electrical contact between the active materials and carbon during the lithium insertion and extraction cycles.

Conclusion

Si/C composite nanofibers with porous structure were prepared through a facile electrospinning method. The inclusion of carbon not only worked as a stable electric conductive pathway but also buffer the volume expansion of silicon during the process of charging and discharging. The first discharge capacity of the composite nanofiber (26wt.% and 50wt.% Si) electrode reaches 1840mAh/g, 2042mAh/g, and it delivered a charge capacity of 1461mAh/g, 1644mAh/g at the first cycle, corresponding to an initial coulombic efficiency of 79% and 80%. In contrast, the cell with the pure Si nanoparticle exhibited an initial discharge/charge capacity of 18 and 13mAh/g, respectively, which was much lower than the composite nanofiber electrode. In all 30 cycles at the current of 42mA/g, Si/C composite nanofibers had higher capacities and better capacity retentions than the pure Si due to the protection of Si with carbon. According to the impedance spectra, the charge transfer resistance of Si/C composite nanofiber anode was 90 Ω, whereas it increased greatly to 2070 Ω for the pure Si.

Acknowledgements

This work was supported by the Natural Science Foundation of Shandong Province (ZR2014EMQ005, ZR2010EQ001), the Project of Shandong Province Higher Educational Science and Technology Program (Grant No. J14LJ08， J15LA13), the Taishan Scholars Program of Shandong Province (ts20120528), China.

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