MANUFACTURE OF SI CORE/C SHELL NANOFIBERS AND THEIR ANODIC PROPERTIES

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Abstract
Due to their superior theoretical performances, the silicon-based materials have been intensively researched to replace the commercial graphite anode (372 mAh g^{-1}). However, the pulverization and following performance deterioration of silicon has emerged as a serious problem to develop the high performance anode. To overcome this demerit, considerable attempt has been made to develop composite anodes using the carbonaceous and silicon-based materials. In this work, silicon core/ carbon shell (Si core/C shell) nanofibers are manufactured using co-axial electrospinning of Si nanoparticles dispersed in styrene-co-acrylonitrile core solution and poly(acrylonitrile) shell solution and are subsequently carbonized. Then, the effect of the core-shell structure on the electrochemical performance is evaluated using galvanostatic charge-discharge test. By comparing the electrochemical performance of Si core/C shell nanofibers with that of Si/C solid composite nanofibers, it is demonstrated that the core-shell structure is an efficient structure to improve the electrochemical performance of Si/C composite anodes.

1 Introduction

There is a strong demand for high performance rechargeable batteries with high capacity and long lifespan as electronic devices consume much energy in maximizing their performance and electric vehicles have been affordable within a reasonable price. As such the silicon (Si)-based materials have been intensively researched given that the specific capacity of the crystalline Si (4200 mAh g^{-1}) is much larger than other active materials such as Sn (990 mAh g^{-1}) and transition metal oxide (MO, where M is Co, Cu, Ni or Fe) nanoparticles (700 mAh g^{-1}) [1-3]. The pulverization and resulting electrical contact loss of Si, however, are the main obstacles to the development of commercialized Si anode. The fabrication of the silicon-carbon composite electrode is considered as a promising method to overcome these problems because the excellent mechanical properties of the carbonaceous materials can mitigate the problems while the high performance is still maintained by Si.

Since the early 2000s, the simple mixture of silicon and carbon has been suggested as an effective composition method due to their relatively simple processings [4, 5]. Recently, the core/shell (or multi-layered) type Si/C composites have been developed as the anode materials of the lithium ion battery using sequential vapor deposition of Si and carbon [6-8] or co-axial electrospinning and subsequent thermal treatment [9, 10]. These two methods seem to be valid to improve the anode performance, however, it is not clear yet which one is better.

In this study, the effect of the core-shell structure on the electrochemical performance is investigated. The electrochemical performance of Si core/C shell nanofibers is compared with that of Si/C solid composite nanofibers.

2 Experimental

PAN (M_w = 200,000 gmol^{-1}, Misui chemical) is used as a shell solute, while styrene-co-acrylonitrile (SAN, AN 28.5 mol%, M_w = 120,000 gmol^{-1}, Cheil industries) is used as the sacrificial core solute carrying Si nanoparticles. *N, N*-dimethylformamide (DMF, purity 99.5%, Daejung chemical) is used as a dissolving agent of both SAN and PAN. The concentrations are set to be 30 and 20 wt.%, respectively. Si nanoparticles (0.5 g, D < 100 nm, Aldrich) are added to SAN solution (10 g). Details on the electrospinning conditions can be found in [11].

Si/C solid composite nanofibers are prepared using single nozzle electrospinning. For this, Si nanoparticles (0.5 g) are added to the PAN 20 wt.% solution (10 g). The precursor nanofibers are then thermally treated for the stabilization (270-300 ℃ for 1 h) and carbonization (1000 ℃ for 1 h) of the PAN shell.

The morphologies of the nanofibers are examined using a field emission scanning electron microscope (FE-SEM) (SUPRA 55VP, Carl Zeiss). The Si core/C shell structure is further investigated using a high resolution transmission electron microscope (HR-TEM, JEM-3000F). Wide angle X-ray diffraction (WAXD) (wave length: 0.154 nm, New D8 Advance, Bruker) is used to characterize the carbonized samples.

A two-electrode 2032-type coin cell is adopted to evaluate the electrochemical behaviors of the nanofibers. The anode cell consists of 60 wt.% of the nanofibers, 20 wt.% of acetylene black, and 20 wt.% of poly(vinylidene floride). A lithium foil is used as the counter and reference electrode for a half-cell configuration. The electrochemical performance is carried out at a current density of 50 mAg^{-1} for the voltage between 0.01 and 1.5 V.

3 Results and discussion

The morphologies of the Si core/C shell nanofibers and the Si/C composite nanofibers are firstly investigated (see Fig. 1). Both nanofibers consist of smooth strings and repeated beads like "beads on string". The average diameters of the string and bead of Si core/C shell nanofibers are 930 nm (± 82 nm) and 1287 nm (± 245 nm), respectively. The cross-sections of the Si core/C shell nanofibers clearly demonstrate the incorporation of Si nanoparticles. In the meantime, the average diameters of the string and bead of Si/C composite nanofibers are 710 nm (± 163 nm) and 1270 nm (± 319 nm), respectively. The bead morphologies of the Si/C composite nanofibers are more dendritic in comparison to the Si core/C shell nanofibers because their carbonized PAN shell is thinner than that of the Si core/C shell nanofibers. The thin shells of the Si/C composite nanofibers may not endure the stress caused by the large volume change during the lithium insertion and extraction. Note that the thickness of the PAN

shell is not a control parameter in Si/C composite nanofiber electrospinning. In contrast, the shell thickness of the carbonized PAN shell in the Si core/C shell nanofibers can be controllable [12]. There is a notable difference between the two nanofibers, i.e., difference between the string and bead diameters. The diameter difference of the Si core/C shell nanofibers is 27.7 %, while that of the Si/C composite nanofibers is 44.1%. The lower difference results from the molten and burnt-out SAN, which can move the lumps of Si nanoparticles during the thermal treatment. On the other hand, the Si lumps in the Si/C composite nanofibers cannot migrate during thermal treatment due to surrounding PAN molecules.
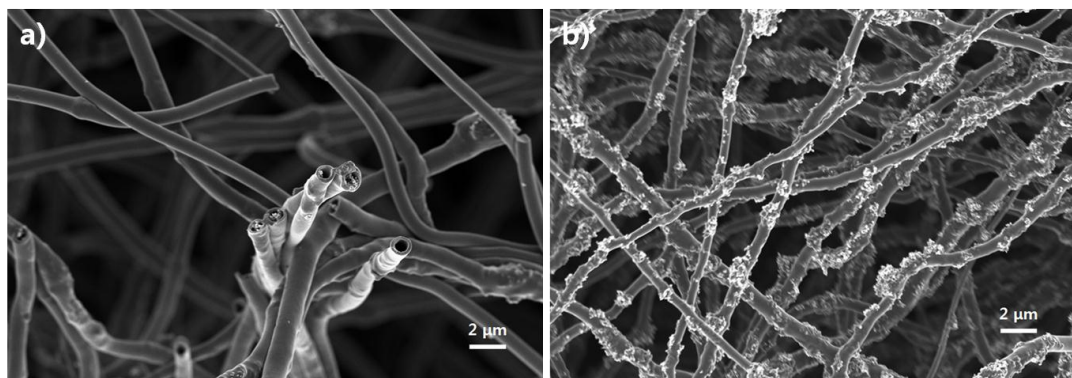

Figure 1. FE-SEM images of: a) the Si core/C shell nanofibers and b) the Si/C composited nanofibers.

The electrochemical performances of the two nanofibers are evaluated by using Galvanostatic charge-discharge. Fig. 2 shows the voltage profiles of the nanofiber anodes for the initial five cycles between 0.01 and 1.5 V at a current of 50 mAg^{-1}. In the voltage profiles of the Si core/C shell nanofibers (see figure 2 (a)), a hysteresis is not observed during these initial stages of the cycling test except the first discharge. On the first discharging, an inflection is developed at around 0.75 V, which is related to the formation of SEI layers of the carbon (0.75 V) and the silicon (0.62 V). A plateau is formed below 0.2 V, demonstrating the formation of the amorphous Si-Li compounds at the core and the reversible lithium insertion of the turbostratic carbon shell. From the second cycles, reversible charge and discharge behavior of the C shell are shown at below 0.1 and 0.09 V, respectively. In addition, several small inflections of the silicon are developed: 0.24 and 0.09 V during lithiation, 0.27 and 0.44 V during delithiation [9]. The voltage profiles of the Si/C composite nanofibers in figure 2 (b) show a trend similar to the Si core/C shell nanofibers.
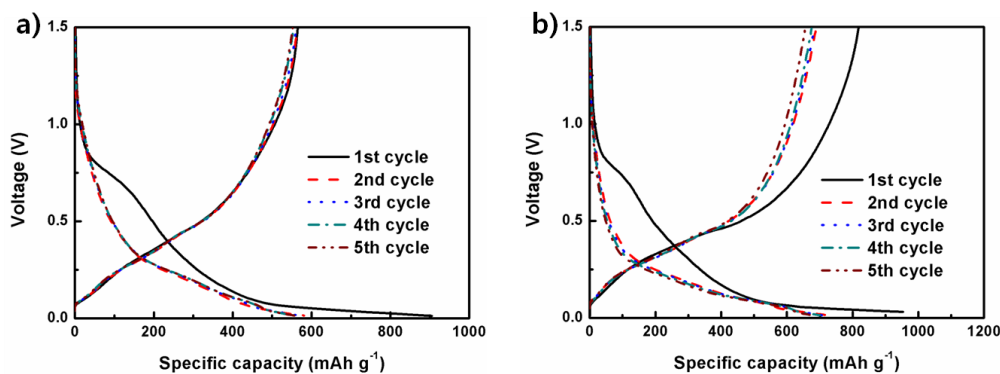

Figure 2. Voltage profiles of: a) the Si core/C shell nanofibers and b) the Si/C composited nanofibers.

Figure 3 shows the cycling performances of the two nanofibers. The red and blue symbols represent the Si core/C shell and the Si/C composited nanofibers, respectively. Although the initial performances of the Si/C composite nanofibers are better than those of the Si core/C shell nanofibers, the trend is reversed as the cycles proceed. The initial coulombic efficiency of the Si/C composite nanofibers (85.8%) is significantly higher than that of the Si core/C shell nanofibers (61.6%). The coulombic efficiency of the both nanofibers are maintained at 98% and 97% after the 10th cycle, respectively. The discharge and charge capacities of the Si core/C shell nanofibers are stably maintained at around 600 mAhg^{-1} upto 30 cycles with large capacity retention of 95.9%. The stable cycling performances result from the firm core/shell structure. The capacities of the Si/C composite nanofibers are, however, gradually decreased as the cycle proceeds. The capacity retention of the Si/C composite nanofibers is 53.6% after 30 cycles. The large capacity loss is due to the electrical contact loss, which may be caused by the destruction of the sheath of the beads. It can be concluded that the Si core/C shell nanofibers are more efficient and stable anode materials compared to the Si/C solid composite nanofibers.
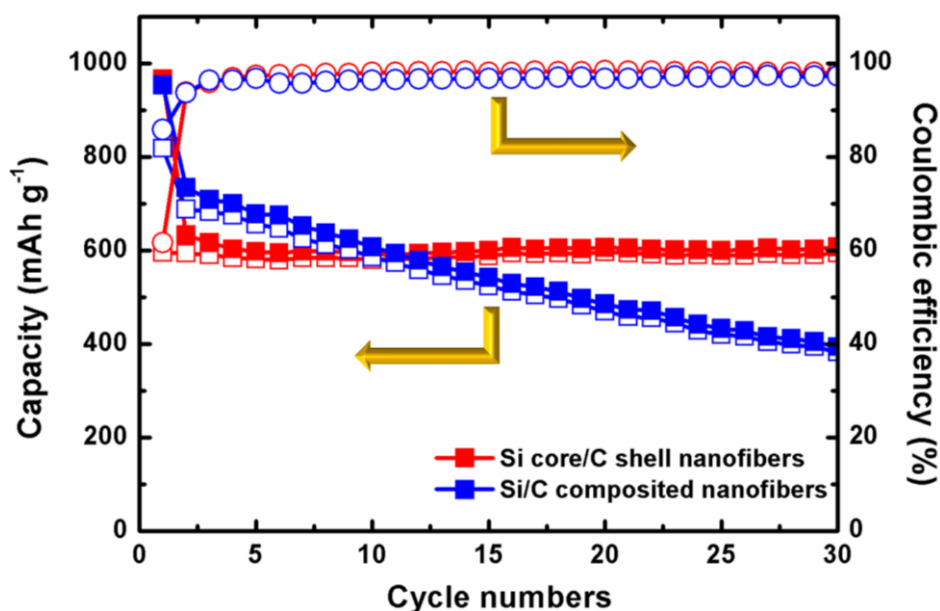

Figure 3. Cycling performances of the nanofibers.

4 Summary

Si core/C shell nanofibers and Si/C composite nanofibers have been successfully prepared using the co-axial and single nozzle electrospinning processes, respectively. The "beads on string" morphologies are commonly observed due to the incorporation of the Si lumps, but the Si core/C shell nanofibers show that the carbon shell perfectly wraps Si nanoparticles. The Si and carbon of both nanofibers react to lithium ions in an independent and stable manner during the lithiation and delithiation cycles. Although the initial performances of the Si/C composite nanofibers are better than those of the Si core/C shell nanofibers, the latter nanofibers is better than the former nanofibers. Therefore it can be claimed that the core-shell structure is more efficient structure to improve the electrochemical performance of Si and carbon composite anodes

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