Silicon/Graphene/Carbon Hierarchical Structure Nanofibers for High Performance Lithium ion Batteries

Zhenjiang He^b, Xianwen Wu^{a,*}, Zhaojun Yi^b, Xinyu Wang^b, Yanhong Xiang^a

^a The Collaborative Innovation Center of Manganese-Zinc-Vanadium Industrial Technology, School of Chemistry and Chemical Engineering, Jishou University, Jishou 416000, P.R. China

^b College of Environmental Science and Engineering, Donghua University, Shanghai 201620, P.R. China

Abstract: Silicon/graphene/carbon composite nanofibers (Si@RGO@C NFs) with a hierarchical structure are prepared by encapsulating graphene coated Si nanoparticles in the interconnected carbon nanofibers based on an electrospinning technology. For the hierarchical structure, Si nanoparticles are embedded in the graphene and the core-shell structure formed, which is further wrapped by the carbon nanofibers. As lithium ion battery anode, the well-defined Si@RGO@C NFs demonstrates a reversible capacity of 1228 mAh g⁻¹ and a capacity retention of 72 % after 100 cycles with a current density of 800 mA g⁻¹. With the current density gradually increasing to 4000 mA g⁻¹, the electrode displays a specific capacity of 954 mAh g⁻¹, exhibiting superior rate capability compared to the Si nanoparticles. These excellent electrochemical properties are attributed to the hierarchical core shell structure and cross linked network for Si@RGO@C NFs.

Keywords: Carbon materials; Composite materials; Energy storage and conversion

1. Introduction

The capacity of the commercial graphite has reached its limit, which prevent lithium ion batteries to meet the increasing demand of higher energy density. Besides, the commercial or in-development cathode materials also display a low specific capacity [1-8]. Therefore, new anode

materials should be developed to substitute the current commercial electrode materials. Silicon is a promising candidate for anode material because of its high theoretical capacity (about 4200 mAh g⁻¹), low discharge voltage and natural abundance [9-14]. But a significant volume expansion and unstable solid electrolyte interphase (SEI) films occurred during the electrode process and results in particle fracture and loss of capacity with cycling [15-20]. Si nanoparticles (NPs) wrapped in carbon materials is an effective way to strengthen the electrochemical properties. Recently, porous carbon [17, 21], grapheme [18, 22], carbon nanofiber [23, 24] etc. have been utilized to accommodate the volume change of the SiNPs, thus effectively avoiding the direct contact between encapsulated SiNPs and the electrolyte and enabling the interfacial and structural stabilization of encapsulated SiNPs during cycling. Though all of these carbon materials have their own advantages, the enhanced electrochemical performance of SiNPs has been limited depended on single coating materials. However, there are only a few of research referred to wrapping SiNPs in two different coating materials, in which different coating materials can make their respective advantages complementary to each other, and then improve the electrochemical properties of SiNPs dramatically.

In this work, we fabricated Si@RGO@C NFs with a hierarchical structure by encapsulating graphene coated Si nanoparticles in the interconnected carbon nanofibers. Firstly, for the Si@RGO, Si NPs were encapsulated into graphene shells with sufficient elasticity to accommodate the strain associated with volume change and enhance the conductivity of lithium ions and electrons. And then these as prepared Si@RGO powders have been wrapped in carbon nanofibers based on an electrospinning technology. This type of composite nanofibers as anode material possesses the advantages of high capacity and long cycle life.

2. Experimental

To prepare the graphene coated Si nanoparticles (Si@RGO), 2 g Si nanoparticles is dispersed in the solution of graphene (200 ml, 1.0 mg ml⁻¹) with ultrasonic stirring over 2 h at room temperature, in which the graphene was prepared by the method published by Li[25]. After evaporating the solvent at 80 °C, the obtained powders (1 g) were mixed with polyacrylonitrile (2 g, 0.15 M MW, Sigma Aldrich) in N, N-dimethylformamide by stirring for 24 h at 60 °C. Then this solution was electrospun into nanofibers: applied voltage is 15 kV (Dongwen, P503-1ACDF); distance between the syringe needle containing the solution and the grounding collector (aluminum foil) is 15 cm; and pumping rate of syringe was 1 mL h⁻¹. As-fabricated composite nanofibers were annealed at 260 °C in air for 2 h and 600 °C in argon atmosphere for 8 h to obtain silicon/graphene/carbon nanofibers (Si@RGO@C NFs).

X-ray diffraction (XRD) and transmission electron microscope (TEM) were employed to identify the crystalline phase of Si NPs and Si@RGO@C NFs. The electrochemical performance was performed using a two-electrode coin-type cell (CR2025) of Li | LiPF₆ (EC: EMC: DMC = 1: 1: 1 in volume) | silicon nanoparticles or Si/C composite nanofibers. The Si@RGO@C NFs can be used as the electrode directly. Electrode film consisting of silicon nanoparticles anode material is prepared by a slurry coating technique and the typical active material loading is about 2 mg cm⁻²[26]. The assembly of the cells is carried out in an argon-filled glove box. The cells are charged and discharged over a voltage range of 0.01-2.0V versus Li/Li⁺ electrode at current densities of 400-4000 mA g⁻¹ at room temperature.

3. Results and discussion

The typical X-ray diffraction patterns of Si NPs and Si@RGO@C NFs are shown in Fig. 1. It

is seen that pure carbon nanofibers exhibit a diffraction peak at $2\theta = 25.0^\circ$, which is corresponding to the (002) layers of the graphite[24]. Si@RGO@C NFs present diffraction peaks at 2θ of 28.5° , 47.4° , 56.3° , 69.2° , 76.8° and 88.3° , which are ascribed to the (111), (220), (311), (400), (331) and (422) planes of Si crystals in nanofibers[28], respectively. Obviously, for Si@RGO@C NFs, the fluctuation of their XRD patterns at 2θ between 5° and 40° is resulted from the effect of carbon nanofibers.

Fig.1 XRD patterns of C NFs, Si NPs and Si@RGO@C NFs

Fig. 2 illustrates morphology and microstructure of Si NPs and Si@RGO@C NFs. The silicon nanoparticles have an average size of about 60 nm, as shown in Fig. 2 (a). The Si NPs show the clear particle edges and perfect crystallinity with a lattice spacing of 0.3123 nm originated from the Si (111), and the distinct lattice fringe extending to the particle boundary, as illustrated in Fig. 2 (b). A uniform graphene coating layer on the surface of Si NPs can be clearly seen from Fig. 2 (c) and (d). The existence of graphene can accommodate the strain associated with volume change and enhance the conductivity of lithium ions and electrons. TEM images of the Si@RGO@C NFs

clearly reveal that the diameter of Si@RGO@C NFs is about 500 nm, and the graphene coated silicon nanoparticles are well wrapped within the carbon nanofibers by electrospun, as shown in Fig. 2 (e). The stronger evidence has been provided in the Fig. 2(f), in which it is clear that the silicon nanoparticle is imbedded in the graphene and then carbon nanofibers. The compact fiber can further prevent electrolyte entering into the interior, and then avoided the formation of unstable solid electrolyte interphase (SEI) layer on the silicon surface [24]. We can expect the excellent electrochemical properties that illustrated by Si@RGO@C NFs.

Fig.2 TEM image of Si NPs (a) and (b), graphene coated Si NPs (c) and (d), Si@RGO@C NFs (e) and (f).

In order to evaluate electrochemical properties of Si NPs and Si@RGO@C NFs, galvanostatic cell cycling tests have been conducted within the voltage between 0.01-2.0V vs. Li/Li⁺ electrode. As shown in Fig.3 (a) and (b), Si NPs show a specific capacity of 3555 mAh g⁻¹, at 400 mA g⁻¹. However, the discharge capacity only represents 92 mAh g⁻¹ after 50 cycles at 800 mA g⁻¹, which is due to anode cracking and pulverization caused by large volume change on lithium ion insertion.

On the contrary, Si@RGO@C NFs exhibit a specific capacity of 1718 mAh g⁻¹, at 400 mA g⁻¹ and remain a relatively high specific capacity of 907 mAh g⁻¹ after 50 cycles at 800 mA g⁻¹. Furthermore, the comparison of the cycling stability of Si NPs and Si@RGO@C NFs can be clearly seen from Fig.3 (c). After 50 cycles, the capacity retention of Si NPs is only about 5.8 %, but Si@RGO@C NFs show specific capacities of 954 and 887 mAh g⁻¹ at 50 th and 100 th, and the capacity retentions are 77.7 % and 72.2 %, respectively, which is higher than those of the reports [29-32]. These results indicate that the combinative effect of graphene and carbon nanofiber can improve the electrochemical performance of silicon nanoparticles effectively. In order to explain the better electrochemical performance of Si@RGO@C NFs compared with Si NPs, EIS measurements were carried out with the working frequency from 10⁻² Hz to 10⁵ Hz and the perturbation amplitude of 5 mV, as shown in Fig.3 (d). These plots are well fitted using the electric equivalent circuit shown in the inset figure of Fig.3 (d). Obviously, the charge-transfer resistances decrease from 153.0 Ω (Si NPs) to 62.8 Ω (Si@RGO@C NFs) under the combinative effect of graphene and carbon nanofiber.

Fig.3 Typical charge/discharge curves of (a) Si NPs and (b) Si@RGO@C NFs, (c) Cycle properties

of Si NPs and Si@RGO@C NFs, (d) impedance spectra of Si NPs and Si@RGO@C NFs, the inset figure shows the equivalent circuit for the plot fitting.

4. Conclusion

In summary, **silicon/graphene/carbon** nanofibers with a novel hierarchical structure have been prepared based on the electrospinning technique. For the composite nanofibers, Si NPs are wrapped in the graphene nanosheets **to obtain** the Si@RGO powders, and then Si@RGO@C NFs are synthesized by encapsulate these as prepared Si@RGO particles into carbon nanofibers. The combinative coating layer of graphene and carbon naofibers **not only** can accommodate the strain associated with volume change, but also suppress the formation of unstable SEI films on the surface of Si NPs. Besides, the combinative coating layer can enhance the conductivity of lithium ions and electrons dramatically, which guarantee the Si@RGO@C NFs **displays better** electrochemical properties compared to Si NPs.

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