Batteries and Supercapacitors



Silicon-multi-walled carbon nanotubes-carbon microspherical composite as high-performance anode for lithium-ion batteries

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ABSTRACT

Silicon-multi-walled carbon nanotubes-carbon (Si-MWNTS-C) microspheres have been fabricated through the ball milling and spray drying method followed by the carbonization process. The as-prepared composite microspheres are confirmed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). The specific capacity of the asprepared microspherical composite as anode in lithium-ion batteries (LIBs) is about 1100 mAh g^{-1} at the current density of 0.2 A g^{-1} (based on the total weight of the composite). At the high current density of 6 A g^{-1} , the Si-MWNTS-C microspheres exhibit reversible capacity of 415 mAh g^{-1} . Through the ex situ SEM, we observed that the Si-MWNTS-C microspherical composite particles have no extinct change on the electrode surface except for the growth of the spherical particles after 100 cycles. The excellent electrochemical performance is ascribed to the synergistic effect between Si nanoparticles (Si NPs) and MWNTS-C microspheres. The as-prepared Si-MWNTS-C microspheres can effectively accommodate large volume changes and provide a 3D conductive network during the lithiation-delithiation processes.

Introduction

With the development of new energy and the deterioration of environment, advanced energy conversion and storage devices have continuously become the focus of researches [1–3]. Under such circumstance, it is urgent to find higher capacity electrode materials to improve the energy density of LIBs [4–7]. On the aspect of anode, alloy anodes have shown to be the most promising candidate materials [8–13], among which Si has caused wide attention mainly for the higher theoretical gravimetric capacity (3579 mAh g⁻¹) [14], larger volumetric capacity

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 $(\approx 2200 \text{ mAh cm}^{-3})$, and relatively low average delithiation plateau (~0.4 V). However, Si anode material suffers from poor cycle life due to its extraordinarily large volume change of up to 300 % during charge and discharge processes. The huge volume change over repeated cycles will cause pulverization and thus, resulting in electrical disconnection among the Si particles and conducting agents as well as current collector. Moreover, pulverization also causes continuous growth of solid electrolyte interphase (SEI) during cycling processes [15]. All of these problems would bring about fast capacity fading of the Si anode.

Obrovac et al. [14] proved that crystalline Si transformed into amorphous Si during the lithiation process and the amorphous Li-Si phase suffered an abrupt crystallization to Li₁₅Si₄ near the end of discharge. Thus, the authors evolved that abrupt transformation from amorphous to crystalline SiLix during the lithiation process could lead to the poor cyclability of Si [16]. In a relevant article, Hatchard et al. [17] discovered that the Si electrodes did not undergo phase transition to crystalline Li₁₅Si₄ when the thickness of Si electrodes was less than 2 µm. Liu et al. [18] discovered that there is a critical particle size of \sim 150 nm below which cracking did not occur, and above which surface cracking and particle fracture took place upon lithiation. These results implied that the cyclability of nanometer-sized Si particles is better than micrometer-sized Si particles.

Si NPs with small enough diameters are able to undergo large volumetric strains without pulverization [19-27]. The challenge for Si NPs is how to electrically connect them within themself and with the current collector. Moreover, how to keep up such a connection after repetitive lithiation and delithiation is also very challenging. In recent years, there are many novel methods developed by researchers against this challenge. For example, Cui et al. [28] developed a method to prepare Si NPs anode, amorphous Si was deposited onto electrode structures and acted as an inorganic binder to connect all the particles together and fix them onto the current collector. This method can help to solve the problem of the electrical disconnection of the Si particle anodes prepared by conventional slurry methods. They prepared 200 nm Si NPs anode with the limited charge capacity of 1200 mAh g^{-1} which showed stable charging-discharging up to 130 cycles in a half-cell test.

In this paper, we designed and prepared Si-MWNTS-C microspheres by the ball milling method or the spray drying method followed by the carbonization process. This kind of microsphere used MWNTS to fabricate spherical conductive frame, Si NPs were packaged into the spherical frame, and C particles were used to increase the conductive connection between the Si NPs and MWNTS. It turned out that the Si-MWNTS-C microspheres solved the problem of pulverization caused by the huge volume changes over repeated cycles, and thus got over the trouble of electrical disconnection among the Si NPs and conducting agents as well as current collector. For the former method, we applied the ball milling to prepare the Si-MWNTS sphere-structural composite. In order to increase the connection between the Si NPs and MWNTS, the Si-MWNTS composite was mixed with the carbon precursor, polyethylene glycol (PEG(20000)), to generate the Si-MWNTS@PEG microspherical precursor. Subsequent thermal treatment of the precursor produced the Si-MWNTS-C microspheres. For spray drying method followed by a carbonization process, we applied spray drying to form the Si-MWNTS@glucose microspherical precursor. Subsequent thermal treatment of the precursor produced the Si-MWNTS-C microspheres. We believe that the Si-MWNTS-C microsphere should be a promising anode material for application in high-performance LIBs due to the fact that it can effectively accommodate large volume changes and supply a 3D conductive network during the charge-discharge processes.

Experiments methods

Materials

The Si NPs with an average diameter of 100 nm was purchased from Huierna Company (China) and used after further processing. Multi-walled carbon nanotubes (MWNTS) were purchased from Chinese Academy of Sciences, Chengdu Organic Chemistry Co., Ltd. and used as received. The MWNTS were dispersed in N-methylpyrrolidone (NMP)and deionized water, and the mass fraction of MWNTS was 8 and 10 %, respectively. Carbon source, polyethylene glycol (PEG20000), and glucose were analytically pure and used as received.









In order to get uniformly dispersed Si NPs, the original Si are treated by wet ball milling for 24 h, followed by the treatment with 5 % HF acid and finally vacuum drying at 60 °C.

Fabrication of the Si-MWNTS-C microspherical composites

The schematic synthetic procedures for fabrication of Si-MWNTS-C sphere-structural composites are summarized in Fig. 1. For the ball milling method, the Si-MWNTS-C sphere-structural composites were prepared by two steps. Firstly, the Si-MWNTS composites were prepared by a wet-type ball milling method. The mixture of Si nanopowder and MWNTS (dispersed in NMP) with the weight ratio of 2:1 was treated by ball milling, and the fine slurry was obtained under the condition of 400 r min⁻¹ for 18 h using 1-mm-sized zircornia beads, 30 min ball milling with 15-min interval was set for each times. Then, Si-MWNTS composites were obtained by drying at 60 °C in vacuum oven overnight. Secondly, the Si-MWNTS composites and PEG(20000)were mixed sufficiently by grinding in a mortar with the mass ratio of 1:1 and calcined in tubular furnace under the protection of argon atmosphere to obtain the Si-MWNTS-C sphere-structural composites. For the spray drying method, first, the prepared Si NPs of 1 g and water dispersing MWNTS of 5 g (namely mixed with the mass ratio of 2:1) were evenly dispersed into 100 mL deionized water by ultrasonication. Then 1.5 g glucose (the total mass ratio of carbon source and Si-MWNTS is 1:1) was added into the solution. Spray drying was carried out with continuous

magnetic stirring. The conditions of spray drying were 200 °C for inlet temperature and 140 °C for outlet temperature. The obtained Si-MWNTS-glucose spherical precursor was calcined under argon atmosphere. The calcination conditions are shown in Fig. S1. Finally, the spherical particle composites of Si-MWNTS-C were obtained. Fig. S1 shows the carbonization process used in this study which consists of stabilization, heating, holding, and natural cooling.

Characterizations

The morphology of materials was observed using field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (TEM, JEOL-2100). The XRD data were tested on Rigaku miniflex 600 equipped with Cu K α radiation operated at 15 mA, 40 kV, and scanned from 10° to 90° at 10° min⁻¹ with the step size of 0.02°.

Electrochemical measurements

The uniform slurry was obtained using deionized water as the solvent and contained 60 wt% Si-MWNTS-C active material, 30 wt% acetylene black (AB), 5 wt% carboxyl methyl cellulose (CMC), and 5 wt% styrene-butadiene resin (SBR). Then, the slurry was coated onto the copper foil current collector to obtain the working electrode. Using the high-purity lithium metal as a counter electrode and the Celgard 2400 polyethylene as a separator, the CR2016 cointype cell was assembled in the argon-filled glove box. The electrolyte was made of 5 wt% fluoroethylene



Figure 2 Si-MWNTS-C microspheres fabricated by the ball milling: a SEM image (inset for Si-MWNTS), b TEM image, c-f element mappings.

carbonate (FEC) additives and 1 M LiPF₆ which was dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) (1:1:1 in volume ratio). Using a battery test system (NEWARE BTS type battery charger, Shenzhen, China), the cells were galvanostatically charged and discharged between 0.02 and 1.5 V (vs. Li⁺/Li) at 25 °C. The current density and specific capacity were calculated based on the weight of composite included in anode. In the voltage range between 0.01 and 1.5 V (vs. Li⁺/Li), at the scan rate of 0.1 mV s⁻¹, the cyclic voltammogram (CV) was tested on a CHI660D potentiostat. Electrochemical impedance spectra (EIS)

were measured with the frequency ranging from 0.01 to 10^5 Hz (Solartron SI 1287). In the same way, Si NPs were used to prepare the comparative electrode and then packaged into half cell.

Results and discussion

The fabrication of the Si-MWNTS-C microspheres is illustrated in Fig. 1 (experimental details are shown in the "Experimental" section). This kind of Si-MWNTS-C microspheres use MWNTS to fabricate spherical conductive frame, Si NPs are packaged into





Figure 3 XRD pattern of Si-MWNTS-C composites fabricated by the ball milling.

the spherical frame and C particles are used to increase the conductive connection between the Si NPs and MWNTS. Therefore, the Si-MWNTS-C microspheres can provide a 3D conductive network and accommodate the huge volume expansion and constriction during charge and discharge so as to solve the problem of pulverization caused by the huge volume changes over repeated cycles. In addition, this structure gets over the trouble of electrical disconnection among the Si NPs and conducting agents as well as current collector.

Fig. S2a displays the SEM image of the original Si. It is obvious that the original Si particles agglomerated to a certain degree. In order to get uniformly dispersed Si NPs, the original Si are further treated by wet ball milling. The Si NPs prepared by the ball milling method possess rough surfaces (Fig. S2b) and irregular morphology with an average diameter of 100 nm.

Figure 2 presents the morphology and element mapping of the Si-MWNTS-C microspheres fabricated by bead mill. Figure 2a displays the SEM image of Si-MWNTS-C microspheres with diameter of several micrometers. Si NPs are wrapped in the



Figure 4 Electrochemical performance of the Si-MWNTS-C microsphere fabricated by ball milling. a Cyclic voltammograms curve, b charge–discharge curve, c charge and discharge cycle diagram, d rating performance diagram.

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microspheres formed by MWNTS and C particles. The TEM image of Si-MWNTS-C microspheres in Fig. 2b further reveals that Si NPs and C particles distribute uniformly in the MWNTS formed microspheres. They establish a good electrical connection among the Si NPs, the MWNTS, and the C particles which can supply a 3D conducting network. And the Si-MWNTS-C microspheres are porous which can effectively accommodate large volume changes during charge and discharge processes. The SEM and TEM images of Si-MWNTS-C microspheres in Fig. S3a, b show that the Si-MWNTS-C composites with the same structure can also be fabricated by spray drying. The element mappings of Si-MWNTS-C microspheres (Fig. 2c-f and Fig. S3c-f) further reveal that Si NPs, C particles, and MWNTS are evenly distributed in the Si-MWNTS-C microspheres.

XRD patterns of samples (Fig. 3 and Fig. S4a) also confirm their structural and compositional differences. The raw Si, Si NPs, and the Si-MWNTS-C microspheres fabricated by ball milling have same peaks of crystalline Si (JCPDS 00-027-1402), which reveals that the Si crystal structure has not been changed in the preparation process. The MWNTS peak is observed significantly in the Si-MWNTS-C microspheres. However, no crystal C peaks are observed which indicate that C particles are amorphous structure. The XRD pattern of the Si-MWNTS-C composites fabricated by spray drying (Fig. S4b) shows the same result.

The voltage curve of the Si-MWNTS-C electrode during charging-discharging at the current density of 0.2 A g^{-1} is shown in Fig. 4b. The curve shows a sloping plateau at about 1.5-0.02 V in the first discharge process. This plateau is absent in the following cycles which is associated with the formation of SEI film and the electrochemical deposition of electrolyte on the surfaces of active particles. And there is a relatively flat plateau up to the cut-off voltage of 0.02 V, which is mainly attributed to the lithiation of crystal Si [29, 30]. Additionally, compared with that of the first cycle, the charge capacity increases slightly in the first few loops. This is corresponding to gradual activation process as explained in other cases [31]. The first charge and discharge capacities of the Si-MWNTS-C electrodes are 1848.4 and 1228.0 mAh g^{-1} , respectively. Accordingly, the initial coulombic efficiency is 66.4 %. Figure 4a illustrates the CV curves of the Si-MWNTS-C electrode at the scanning rate of 0.1 mV s^{-1} with the voltage range of 0.02–1.5 V (vs.

 Li^+/Li) for the first three cycles. There is a noteworthy broad cathodic peak at about 0.7-1.4 V in the first cycle, which could be triggered by the formation of SEI layer on the electrode and the decomposition of the electrolyte. It will disappear after the cycles, indicating the irreversible feature, which gives rise to the loss of irreversible capacity and the lower initial coulombic efficiency. The cathodic peak at 0.1 V is attributed to the lithiation of crystalline Si, which gradually shifts to 0.2 V as a result of phase transformation of crystalline Si to amorphous Si [32, 33]. It is worth noting that there are two anodic peaks in the first cycle which may be triggered by delithiation of Si. The gradual increase of the two anodic peaks intensity is in good agreement with the increase of charge capacity in the first few cycles as Fig. 4b exemplified.

Figure 4c displays the cycling performance of the electrodes at a current density of 0.2 A g^{-1} in the voltage range of 0.02-1.5 V. Although the initial capacity of the Si NPs electrode can reach as high as 2347.3 mAh g^{-1} , it dramatically fades to 23.8 mAh g^{-1} after 50 cycles. Such phenomenon is in accordance with other case [34]. This is attributed to the poor electronic conductivity and the pulverization caused by huge volume changes over repeated cycles which lead to electrical disconnection among the Si NPs and conducting agents as well as current collector. When the Si NPs are coated with the MWNTS-C microsphere, the resulted Si-MWNTS-C microsphere electrode shows excellent cycle performance, namely, it possesses excellent cycling stability and keeps the capacity of 1050 mAh g^{-1} after 60 cycles. Moreover, the coulombic efficiency of the Si-MWNTS-C microsphere electrode is about 98 % and keeps steady in the following cycles. The Si-MWNTS-C microsphere fabricated by spray drying also shows excellent cycle performance (Fig. S5).

The results mentioned above signify that the existence of MWNTS and C particles decrease the capacity of electrode for the electrochemical inactive materials. However, the microsphere coating layer fabricated by C particles and MWNTS improves the coulombic efficiency and cycling stability. This is because the huge volume changes over repeated cycles are suppressed by MWNTS-C microsphere structure, thus the electrical connection among the Si NPs and conducting agents as well as current collector can be preserved. Hence, we can draw a conclusion that the Si-MWNTS-C microsphere structure



Figure 5 Electrochemical impedance spectroscopy of Si-MWNTS-C microsphere fabricated by ball milling. a Nyquist plots for Si NPs and Si-MWNTS-C microsphere electrodes before

charge and discharge, **b** Nyquist plots for Si-MWNTS-C microsphere electrode after a few cycles, **c** equivalent circuit diagram.

may debase the initial coulombic efficiency and capacity of the electrode, while it is of great importance to improve the cycling performance of the composite.

Figure 4d illustrates the rate performance of the Si-MWNTS-C microsphere electrode at the current densities ranging from 0.1 A to 6.0 A g^{-1} and returning to 0.1 A g^{-1} in the end. The Si-MWNTS-C microsphere electrode has the average capacity of 1100, 1025, 885, 730, 595, 450, 425 and 415 mAh g^{-1} at the current densities of 0.1, 0.2, 0.5, 1.0, 2.0, 4.0, 5.0 and 6.0 A g^{-1} , respectively. The capacity of 1047 mAh g^{-1} can be retrieved when the current density goes back to 0.1 A g^{-1} , which signifies a favorable rate performance and reversibility. We can draw a conclusion that the Si-MWNTS-C microsphere structure has not only the excellent cycle performance, but also the excellent rate performance.

To demonstrate the enhanced electrical conductivity, the electrochemical impedance spectroscopy

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(EIS) measurements are performed in the open-circuit voltage. Figure 5a shows that the Nyquist plots for both the Si NPs and Si-MWNTS-C microsphere consist of an inclined line in low frequency and a compressed semicircle in high frequency. The semicircle in the high frequency can be attributed to the charge transfer impedance (Rct) in the interface of electrolyte and electrode. It is clear that the diameter of the semicircle of Si NPs electrode is larger while that of the Si-MWNTS-C microsphere is much lower. Thus, we can get the conclusion that the Si-MWNTS-C microsphere structure is of great help in improving electrical conductivity of the composite, it is very advantageous to optimize rate performance and reversibility. In order to get a better understanding of the superior electrochemical performance of the Si-MWNTS-C microsphere electrode, the EIS are tested after 2 and 5 cycles (in Fig. 5b). The Nyquist plots consist of a sloping line in the low-frequency region and two semicircles in the high-to-medium frequency region. The plots are fitted by the equivalent circuit as shown in Fig. 5c [35, 36]. The sloping line corresponds to the lithium diffusion process, the highfrequency semicircle region is related to dielectric relaxation capacitance (CPE1) and SEI layer resistance (R_f) , and the semicircle in medium-frequency region is related to the charge-transfer resistance (R_{ct}) and electrode/electrolyte interface (CPE2). After 5 cycles, the R_f and R_{ct} values of the Si-MWNTS-C microsphere are almost stable. The R_f and R_{ct} are 130.5 and 41.2 Ω , respectively. The R_f and R_{ct} of the Si-MWNTS-C microsphere are little. This suggests that the Si-MWNTS-C composites build a spherical three-dimensional conductive network to improve the electrical conductivity of the composites. The result confirms that the Si-MWNTS-C microsphere structure can not only dramatically improve rapid electron transfer during the lithiation/delithiation but also preserve the high conductivity of the composites electrode. Therefore, Si-MWNTS-C microsphere composites electrode exhibits excellent cyclic stability and high-rate capability.

Using the Si-MWNTS-C microsphere electrode as the negative electrode and LiCoO₂ electrode as the positive electrode, we assemble the full cell and test performance of the battery, the result is shown in Fig. 6. It shows that when charge–discharged at the current density of 0.2A g⁻¹, the first coulombic efficiency is around 60 %. Specific capacity is around 900 mAh g⁻¹ (at the mass of Si-MWNTS-C microsphere electrode). The cycle stability is excellent, but at the beginning, it will rise to a certain extent, and the reason may be that the battery was not fully activated. The voltage plateau at around 3.7 V can be Figure 7 The ex situ SEM images: **a**, **b** Si NPs electrode before ► charge and discharge, **c**, **d** after charging–discharging 50 cycles, **e**, **f** Si-MWNTS-C electrode before charge and discharge, **f**, **g** after charging–discharging 50 cycles. (Si-MWNTS-C fabricated by ball milling).

seen from the curve of charging and discharging. The voltage curves at the 1st, 2nd, 5th, and 10th cycle coincide with each other well, which means superior cycle stability.

The changes of morphology of the Si NPs and Si-MWNTS-C composite electrode going through lithiation-delithiation process are characterized by ex situ SEM and the results are shown in Fig. 7. The morphological features of the electrodes are collected via the scanning electron microscopy after 100 cycles by disassembling the cell. The morphology of the electrode with the ball-milled Si NPs as the active material is shown in Fig. 7a and b. The electrode shows visible changes in morphology. Namely, the surface is relatively smooth and large particles cannot be observed any more. However, some cracks are left because of the high surface tension which affects the conductivity. We also observe the morphology of the Si NPs electrode after 100 cycles. As can be seen from Fig. 7c and d, the overall electrode surface has no obvious change. But the cracks become deeper due to the Si NPs and conducting volume expansion and contraction during charge and discharge processes. These indicate that the Si NPs make the electrode almost electrical disconnection among the agents as well as current collector resulting in poor battery performance. Figure 7e-h shows that the Si-MWNTS-C spherical composite particles have a close packing



Figure 6 LiCoO₂/Si-MWNTS-C full cell: a cycling performance, b charging–discharging voltage curve. The specific capacity values are calculated based on the mass of Si-MWNTS-C composite. The current density is 200 mA g^{-1} and the voltage range is 2.5–4.0 V.





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and distribute uniformly on the current collector, indicating that the electrode surface is flat and smooth. And we have not observed fracture or cracking despite the high strain. Even after 100 cycles, there is no change in the electrode surface except the growth of the spherical particles. The Si-MWNTS-C spherical composite have an excellent battery performance, which may attribute to the following three reasons: (1) a three-dimensional (3D) conductive network is built by the MWNTS and C particles which can not only enhance electrical connection among the Si NPs and conducting agents as well as current collector but also suppress the volume effect during charge and discharge; (2) the carbon particles formed by carbonization not only play a role as a bridge to connect the Si NPs and MWCNT but also restrain the agglomeration of the Si NPs successfully; and (3) the limited volume effect because of the small size of Si NPs (below 100 nm). All in all, the superior electrochemical properties of anode are attributed to the Si-MWNTS-C spherical structure. Such interesting structure can bridge between the Si NPs and MWNTS and suppress the volume effect, implying that the battery performance can be improved.

Conclusions

In summary, the Si-MWNTS-C microsphere composite material can be obtained using the ball milling method and the spray drying method. The diameter of the Si-MWNTS-C microsphere is about several micrometers. The cycle performance, capacity retention ratio, and rate performance of the Si-MWNTS-C microsphere electrode have been greatly improved. When charge-discharged at the current density of 0.2 A g^{-1} , the specific capacity was about 1100 mAh g^{-1} , and after 50 cycles, the capacity retention was 90 %approximately. Moreover, at the high current density of 6 A g^{-1} , the Si-MWNTS-C microsphere showed the reversible capacity of 415 mAh g^{-1} . The excellent lithium storage performance of the Si-MWNTS-C microspheres is mainly attributed to two aspects: (1) The construction of the Si-MWNTS-C microspheres can greatly improve conductivity of the Si-MWNTS-C anode, in which both the MWNTS as one-dimensional conductive material and the C particles as zero-dimensional conductive material build an excellent three-dimensional conductive network; (2) Si NPs are wrapped into the Si-MWNTS-C microspheres, thus the structure can protect Si NPs from pulverization and falling off when the volume of the Si NPs expand and contract during charge– discharge. Therefore, with the synergy effects of the above two advantages, the Si-MWNTS-C microspheres composite materials have the excellent electrochemical performance.

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