N-doped coaxial CNTs@α-Fe₂O₃@C nanofibers as anode material for high performance lithium ion battery

Peng Huang, Wei Tao, Haixia Wu, Xiaogang Li, Ting Yin, Qian Zhang, Wen Qi, Guo Gao, Daxiang Cui

Institute of Nano Biomimicry and Engineering, Shanghai Engineering Research Center for Intelligent Diagnosis and Treatment Instrument, Department of Instrument Science and Engineering, School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

College of Chemistry and Bioengineering, Yichun University, Yichun 336000, Jiangxi, China

Abstract

N-doped coaxial CNTs@α-Fe₂O₃@C nanofibers have been successfully synthesized according to a facile solvothermal/hydrothermal method. The obtained CNTs@α-Fe₂O₃@C nanofibers composites exhibited special three-dimensional (3-D) network structure, which endows them promising candidate for anode materials of lithium ion battery. The coaxial property of CNTs@α-Fe₂O₃@C nanofibers could significantly improve the cycling and rate performance owing to the acceleration of charge/electron transfer, improvement of conductivity, maintaining of structural integrity and inhibiting the aggregation. The α-Fe₂O₃ nanoparticles with small size and high percentage of N-doped amount could further improve the electrochemical performance. As for the CNTs@α-Fe₂O₃@C nanofibers, the capacity presented a high value of 1255.4 mAh/g at 0.1 C, and retained at 1213.4 mAh/g after 60 cycles. Even at high rate of 5 C, the capacity still exhibited as high as 319 mAh/g. The results indicated that the synthesized N-doped coaxial CNTs@α-Fe₂O₃@C nanofibers exhibited high cycling and rate performance.

© 2017 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. and Science Press. All rights reserved.

1. Introduction

In the recent few years, tremendous efforts have been focusing on resolving the excessive energy consumption of fossil fuels due to the rapid economic development. Clean energy is becoming one of the promising candidates to satisfy the energy demand of human beings and reduce the fossil fuels consumption, greenhouse gas emission [1,2]. Rechargeable lithium ion batteries (LIBs) are increasingly developed as an energy storage device for portable electronics and electric vehicles owing to its promising potential as clean energy source, which attract great attention in the area of the electrode materials. As the key part of LIBs, anode materials, which are cheap, nontoxic, high capacity and stable, are the main requirements in the latest study [3–5]. However, the commercial anode material of LIBs, graphite, possesses a low practical capacity about 320 mAh/g [6]. Therefore, it is urgent to seek higher capacity anode materials to replace graphite. Recently, many various high capacity anode materials were developed, such as Co₃O₄ [7], Mn₃O₄ [8] and Si [9]. Among these materials, iron oxide, α-Fe₂O₃ [10,11], γ-Fe₂O₃ [5,12], and Fe₃O₄ [13], attracted great attention in the application as anode materials owing to their abundance, safety, high power density and high theoretic capacity. Specially, α-Fe₂O₃ becomes a prior selection among these promising candidates for its easy synthesis compared with γ-Fe₂O₃ and a theoretic capacity (1007 mAh/g) even higher than Fe₃O₄ (926 mAh/g).

However, a main problem of α-Fe₂O₃ is that the volume changes is huge (>200%) during the cycling for the insertion/extraction of Li ions, especially at high current density. Besides, low conductivity, which exists in many metal oxide anode materials, is another serious problem of α-Fe₂O₃. The above-mentioned reasons could lead to poor cycle performance, capacity and rate performances [14–16]. One of effective strategies to solve the volume change of α-Fe₂O₃ is to design a special nanostructure material and introduce carbon materials, such as graphene oxide (GO), CNT and amorphous carbon. Great efforts have been done to synthesize special nanostructures, such as cubes [17,18], nanodisk [16,19], hollow structures [14,20,21], nanoflakes [22], spheres, [23] rods [24,25], nanotubes [10], spindles [26], raspberry [27] and foam [28] to improve the performance in a certain degree. Besides, many α-Fe₂O₃ composites, such as α-Fe₂O₃@GO...
2.2. Synthesis of CNTs@α-Fe2O3@C nanofibers

The CNT@α-Fe2O3 products were dissolved in 10 ml water, followed by adding 30 ml DI water with 2 g glucose dissolving in it. Then, 20 ml anhydrous ethanol was added in the former solution to form final solution. The final solution was transferred into a 50 ml Teflon-lined autoclave and heated at 190 °C for 12 h. The products were obtained by centrifugation and repeatedly washed with anhydrous ethanol and DI water.

2.4. Synthesis of CNTs@α-Fe2O3@C nanofibers

The CNT@α-Fe2O3 products were dissolved in 10 ml water, followed by adding 30 ml DI water with 2 g glucose dissolving in it. Then, 20 ml anhydrous ethanol was added in the former solution to form final solution. The final solution was transferred into a 50 ml Teflon-lined autoclave and heated at 190 °C for 12 h. The products were obtained by centrifugation and repeatedly washed with anhydrous ethanol and DI water and were dried in the stove at 80 °C for 12 h. The dried products were heated at 600 °C for 12 h in a tube furnace with N2 atmosphere at 6 °C/min.

2.5. Characterization

The crystal structure was characterized by X-ray powder diffractometer (XRD/D8 ADVANCE Da Vinci). The structure and morphology were analyzed by field emission scanning electron microscope (FESEM/Jeol JSM-7800F Prime) and 120 kV Biology transmission electron microscope (TEM/Tecnai G2 Spirit Biotwin). X-ray photoelectron spectroscopy (XPS/AXIS Ultra DLD) was used to investigate the surface chemical species and states. Thermo Gravimetric Analyzer (TGA/Pyris 1 TGA) was conducted to measure the weight ratio under nitrogen atmosphere at a heating rate of 10 °C/min from 20 to 900 °C.

2.6. Electrochemical characterization

Lithium ion batteries were prepared by CR2032 coin cells. Typically, Fe2O3 nano-composite (80 wt%), acetylene black (10 wt%) and polyvinylidene fluoride (PVDF) (10 wt%) binder in N-methylpyrrolidone (NMP) were mixed to fabricate working electrodes. Then the copper foil current collector coated by slurry was dried at 120 °C for 12 h in vacuum oven. The diameter of the copper foil is about 10 mm. Lithium disc was used as counter electrode. An argon-filled glove box was used to assemble coin cells. 1 M LiPF6 in ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC, 1/1/1 by volume) was used as electrolyte. The amount of electrolyte in each cell is about 0.3–0.35 ml (6–7 drops). Galvanostatic tests by LAND battery testing system were measured between 0.01 and 3.00 V (versus Li+/Li) at different C. To understand the reaction mechanism, cyclic voltammetry (CV) measurement was conducted on electrochemical workstation (Zahner IM6e) between 0.01 and 3.00 V at a scan rate of 0.3 mV/s. Electrochemical impedance spectroscopy (EIS) was carried out before cycle on the same instrument from 0.1 MHz to 0.1 Hz with an AC voltage amplitude of 5 mV.

3. Results and discussion

Fig. 1 shows the illustration of the synthesis process for N-doped CNTs@α-Fe2O3@C nanofibers, which included four steps. Firstly, the CNT was treated by concentrated nitric acid and sulfuric acid (1:3 by volume), which can modify the surface of CNT with many functional oxygen-containing groups, such as –OH or –OOH. Secondly, α-Fe2O3 was prepared according to solvothermal method with the mixture of oxidized CNT, precursor and PVP. Precursor attached on the surface of CNT by the functional groups
Fig. 1. Schematic illustration of the synthesis process for CNTs@α-Fe₂O₃@C nanofibers.

to form numerous crystal nucleus and the crystal nucleus further grow into Fe₂O₃ particles to form CNTs@α-Fe₂O₃ nanofibers. PVP acted as a soft template in the synthesis process to promote the formation of particles with small size by restraining the aggregation of the Fe₂O₃. Besides, CNT also played a role to control the growth of Fe₂O₃ particles by forming 3D net structure and numerous crystal nucleus—and make positive contribution to small size via dispersing precursor in different functional group. Thirdly, CNTs@α-Fe₂O₃@C nanofibers were obtained in hydrothermal system by heating glucose to coat the composites with uniform carbon layer. That the functional groups can trap the glucose molecule easily can be the main cause of uniform carbon layer on the surface. Lastly, the CNTs@α-Fe₂O₃@C nanofibers were further carbonized in tube furnace with nitrogen to remove the redundant oxygen and hydrogen in the carbon layer, which can stabilize the amorphous carbon layer.

As shown in Fig. 2(a), pure CNT@α-Fe₂O₃ composites without carbon layer were prepared. In the composites, it is observed that CNT presented a 3D net structure by the interconnection of CNT with Fe₂O₃ nanoparticles distributing uniformly on the net structure. It is evident that no obvious diameter difference of Fe₂O₃ particles exists, which clearly indicates that the Fe₂O₃ nanoparticles present uniform size and morphology. The diameter of Fe₂O₃ particles is about 40-50 nm. A reasonable explanation is that the 3D net structure forms a steric hindrance to limit the further growth of Fe₂O₃. From the SEM image, it also can be observed that the Fe₂O₃ particles tend to distribute along the CNT, which may result from the junction of ions and the oxidized CNT in the precursor. Fig. 2(b) is the SEM image of CNTs@α-Fe₂O₃@C nanofibers treated by hydrothermal method. That no obvious difference, compared with pure CNT@Fe₂O₃, is observed indicates that CNT@α-Fe₂O₃ composites are coated by glucose uniform molecules to form uniform and thin carbon layer of the coaxial nanofibers. Fig. 2(c) is SEM image of CNTs@α-Fe₂O₃@C nanofibers further heated by tube furnace. The morphology of the composites remains the same as the pure CNT@α-Fe₂O₃ composites, which means the heat process did not destroy the 3D net structure.

TEM characterization was operated to further confirm the microstructure of the CNTs@α-Fe₂O₃@C nanofibers. Based on TEM observation, we can clearly observe how the carbon, carbon nanotube and Fe₂O₃ nanoparticles form in the final composites. Fig. 3(a) is TEM image of co-axial CNTs@α-Fe₂O₃@C nanofibers after hydrothermal treatment, which reveals that the expected nano-composites were successfully synthesized. An amorphous carbon layer was uniformly coated on the surface of CNT@α-Fe₂O₃, and its thickness is about 10 nm. Another interesting phenomenon observed in the TEM images is that the Fe₂O₃ and the CNT are coated together by the carbon layer to reinforce the connection of them. However, the thickness of carbon layer shown in Fig. 3(b) reduces to 4-5 nm after the composites were treated in the tube furnace at 600 °C for 12 h, which is caused by the decomposition of amorphous carbon layer to remove the contained hydrogen and oxygen groups. Fig. 3(c) shows the HRTEM image of the α-Fe₂O₃ particles, in which it can be observed that the lattice-fringe spacing is 0.199 nm corresponding to the (110) plane of α-Fe₂O₃. The HRTEM image of the coaxial CNT@C nanotubes shown in Fig. 3(d) indicates that the coaxial structure was successfully synthesized according to our reported method. The carbon layer with a thickness about 4 nm coated on the CNT uniformly to form coaxial structure and no lattice-fringe of the carbon layer can be observed indicates that the carbon layer is amorphous.

To investigate the composition and structure of the prepared composites, XRD, which was shown in the Fig. 4(a), was carried out to analyze the composites. It is obvious that the composites show sharp peaks, which indicates the composites possessing high crystallinity. The characteristic peaks are matched with the JCPDS no. 1-1053 structure well, suggesting that the composites are highly pure and no impure phase exist in it. Fig. 4(b) shows the nitrogen adsorption/desorption isotherms of CNTs@α-Fe₂O₃@C nanofibers which belongs to type IV and the inset is the BJH adsorption pore distribution. The curves type indicates that the composites possess a relatively large pore and a surface area of 150 m²/g, which can be calculated. The large surface areas increased the contact areas of anode and electrolyte to improve the electrochemistry performance of anode. However, the BJH adsorption total volume of CNTs@α-Fe₂O₃@C nanofibers is 0.57 cm³/g. The high volume values further indicates that the material contains
Fig. 3. TEM images of (a) hydrothermal treatment, (b) tube furnace treatment of CNTs@α-Fe$_2$O$_3$@C nanofibers. HRTEM images of (c) α-Fe$_2$O$_3$ particles embedded in CNTs@α-Fe$_2$O$_3$@C nanofibers and (d) coaxial CNT@C nanotubes.

Fig. 4. (a) XRD pattern, (b) nitrogen adsorption/desorption isotherms, the inset in (b) BJH adsorption pore distribution, (c) Raman spectra, (d) high resolution Raman spectra of the CNTs@α-Fe$_2$O$_3$@C nanofibers.
numerous pores. From the BJH adsorption pore size distribution, it is obvious that the proportion of pores above 20 nm is bigger. The Raman spectra of the composites were shown in Fig. 4(c) and (d). Three obvious shark peaks located at 1346, 1580 and 2688 cm⁻¹, which correspond to D-band, G-band and 2D-band, respectively, can be observed in Fig. 4(c). The previous study indicates that the defects and disorders existing in the hexagonal reticulation structure CNT are the causes of the D-band and the G-band peaks. The G-band peaks have arisen from sp² hybridization of well-ordered carbon atoms in the plane structure hexagonal lattice [33]. The 2D-band is arisen from the boundary point K of Brillouin zone existing in CNT [34]. Furthermore, Fig. 4(d) revealed the high resolution Raman spectra between 150 and 600 cm⁻¹, from which we can observe that the peaks of A₁g and E_g arisen from α-Fe₂O₃. The peaks located at 218 and 479 cm⁻¹ were assigned to the A₁g vibration modes and peaks at 281, 393 and 584 cm⁻¹ were caused by E_g [35]. XRD and Raman proved that the carbon coated CNT@α-Fe₂O₃ was well designed and prepared. The intensity ratio I_D/I_G can be used to describe the order degree of carbon materials, smaller ratio value means higher order degree. The relatively low I_D/I_G about 1.05 indicates that the CNT in this composite is of high order degree.

X-ray photoelectron spectroscopy (XPS) was carried to further identify the elements component and valence structure in detail. As the Fig. 5(a) reveals, the CNTs@α-Fe₂O₃@C nanofibers contain four kind of peaks, including Fe 2p, Fe 3p, O 1s, O 2s, C 1s and N 1s, which indicates the existence of O, C and N. Fe element comes from Fe₂O₃ nanoparticles. O and C mainly come from Fe₂O₃, carbon layer and CNT. Two distinct peaks at 724.8 eV and 711.5 eV are observed in the narrow spectrum of Fig. 5(b), corresponding to Fe 2p₁/₂ and Fe 2p₃/₂ of Fe⁴⁺, respectively [36]. What’s more, a broad satellite peak, which is located about 8 eV higher than Fe 2p₃/₂, further indicates the Fe⁴⁺ belongs to Fe₂O₃ [37]. Specifically, N, which is introduced by the surfactant PVP, is proved to be able to enhance the electrochemical property and offer sites for combination of Li⁺ [37]. The content of N element, which is about 3.9 wt%%, can be calculated by XPS analysis. It is obvious that three types N located at 399.8, 400.4 and 401.1 eV, corresponding to pyridinic, pyrrolic, and graphitic, are displayed in Fig. 5(c) [38]. The curve shown in Fig. 5(d) can be fitted into four peaks, which correspond to four kind of carbon belonging to C₁s. Peak at 284.79 eV is assigned to C==C or C–C bond, and peaks at 285.89 eV, 286.89 eV, 287.99 eV are caused by C-C, C==O and C-O/C==O/O–C==O, respectively [30]. Furthermore, the sharp peak at 284.79 eV suggesting good crystallinity of carbon layer was formed during the heated process [30,39]. Three type of oxygen were obtained by analyzing O 1s in Fig. 5(e). In Fig. 5(e), the peak at 530.39 eV of O illustrates that no Fe⁰ exists in the composites [40]. Peak at 530.39 eV is attributed by the oxygen in α-Fe₂O₃, which indicates high crystallinity of α-Fe₂O₃. While the peak at 530.79 and 533.89 eV are ascribed to the C–O and C==O bonds, which may belong to the oxidized CNTs and surfactant, respectively [2,30]. To analyze the weight ratio of the composites, TGA measurement was carried out between 20 and 900 °C at a rate of 10 °C/min under air atmosphere. As Fig. 5(f) shown, the weight loss between 20 and 100 °C was attributed to the removal of water molecule. A dramatic weight loss between 250 and 650 °C was observed, which can be arisen from the oxidation of CNT and carbon shell. From the TGA curves, it can be calculated that the weight ratio of CNTs, Fe₂O₃ and carbon shell in the N-doped coaxial CNTs@α-Fe₂O₃@C nanofibers are about 21.4%, 23.6% and 55%, respectively.

To assess the electrochemical performances of the composites, the co-axial CNTs@α-Fe₂O₃@C nanofibers were tested as anodes for LIBs. Fig. 6(a) demonstrates the galvanostatic charge/discharge profiles of coaxial CNTs@α-Fe₂O₃@C nanofibers at the voltage range between 0.01 and 3 V. It showed the curves in 1st, 2nd, 3rd and 60th at a low current density (0.1 C = 100.5 mAh/g). A voltage platform about 0.88 V existed during the first discharge cycle of CNTs@α-Fe₂O₃@C nanofibers and then arrived 0 V after a long slope. As the previous study, the formation of the solid electrolyte interphase (SEI) film coated on the surface of active materials and the insertion of lithium into the α-Fe₂O₃ caused the voltage platform [19]. As for coaxial CNTs@α-Fe₂O₃@C nanofibers, the discharge/charge capacity of it in the 1st cycle is 1773.1/1201.4 mAh/g, and the values decline to 1218.8/1179.2 mAh/g after 60 cycles. The high capacity of 1773.1 mAh/g in the first cycle can be as-

Fig. 5. (a) Full XPS spectrum of CNTs@α-Fe₂O₃@C nanofibers. High resolution narrow spectrum of (b) Fe 2p, (c) N 1s, (d) C 1s and (e) O 1s in CNTs@α-Fe₂O₃@C nanofibers. (f) TGA curves of co-axial CNTs@α-Fe₂O₃@C nanofibers under air atmosphere.
Fig. 6. (a) Charge–discharge profiles, (b) rate performance curves, (c) CV curves and (d) electrochemical impedance spectra of the CNTs@α-Fe$_2$O$_3$@C nanofibers.

dscribed to the insertion of about 11 Li into one α-Fe$_2$O$_3$ [19]. Even though about 31% loss of the discharge capacity was observed after 60 cycles, a high capacity of 1218.8 mAh/g can be obtained after 60 cycles. The capacity loss mainly caused by the electrolyte decomposition, solid electrolyte interphase (SEI) film and formation of amorphous Li$_2$O [2]. However, it can be seen that the charge capacity of coaxial CNTs@α-Fe$_2$O$_3$@C nanofibers fade slowly. Only about 1.8% capacity loss was calculated after 60 cycles.

As Fig. 6(b) shows, the rate performance of the composites were tested under different current densities, including 0.1, 0.5, 1, 2, 5 and back to 0.1 C (1 C = 1005 mAh/g). As for the CNTs@α-Fe$_2$O$_3$@C nanofibers, what we can observed is that the charge capacities are about 1255.4, 790.8, 592, 466.5, 319 and 121.4 mAh/g, corresponding to 0.1, 0.5, 1, 2, 5 and 0.1 C, respectively. An obvious phenomenon is that the coaxial CNTs@α-Fe$_2$O$_3$@C nanofibers behave well in rate performance under all current densities. The coaxial CNTs@α-Fe$_2$O$_3$@C nanofibers are about 1.25 times the theoretical capacity of α-Fe$_2$O$_3$ under the current densities of 0.1 C. As for graphene, the value is 3.4 times under the current densities of 0.1 C, which indicates that the capacity of CNTs@α-Fe$_2$O$_3$@C nanofibers is high. A high capacity ~319 mAh/g obtained at 5 C suggests that CNTs@α-Fe$_2$O$_3$@C nanofibers behave well in both stability and rate performance. The distinct performance variation illustrates that the special structure of coaxial CNTs@α-Fe$_2$O$_3$@C nanofibers plays an important role for improving the battery performance. Three causes may be contributed to the improvement of electrochemical performance. (1) Small α-Fe$_2$O$_3$ particles can enhance the reaction efficiency with Li ion. (2) The carbon materials can improve the conductivity by accelerating the charge transfer and can maintain the integrity by the stable net structure. (3) The N-doped behavior can offer extra attached sites for Li ion.

To investigate the redox reaction mechanism, cyclic voltammetry (CV) curves were shown in Fig. 6(c), which was conducted between 0.01 and 3 V at a rate of 0.03 mV/s. It is obvious that one sharp reduction peaks belonging to the first cathodic scan process at 0.45 V was observed, which was ascribed to the reduction process of Fe$^{3+}$ to Feø by Li [23]. Firstly, cubic Li$_2$Fe$_3$O$_5$ formed by the insertion of Li into α-Fe$_2$O$_3$ (Fe$_2$O$_3$ + 3Li$^+$ + 3e$^-$ → Li$_2$Fe$_3$O$_5$). Then, amorphous Li$_2$O appeared by the insertion of more Li (Li$_2$Fe$_3$O$_5$ + 4Li$^+$ + 4e$^-$ → 2Fe ø + 3Li$_2$O), which caused the irreversible loss of capacity during cycle [24]. A broad peak located at 1.88 V, was corresponded to the oxidation of Fe$^0$ to Fe$^{3+}$ in the anodic scan process [41]. Compared to the first cycle, the peaks intensity of the following several cycles decreased, which indicated that capacity decreased. The nearly unchanged peaks position and integrated area during the following several cycles implied the good reversibility. Electrochemical impedance spectroscopy (EIS) was used to investigate the electrochemical process from 100 KHz to 0.1 Hz and Nyquist plots are shown in Fig. 6(d). A quasi-semicolonircle with center under the real axis appeared in the high frequency stage, following by an increased linear line with an angle about 45° in the low frequency stage. According to the former study, resistant of charge transfer and lithium ion diffusion called Warburg impedance are the reasonable causes of the quasi-semicolonircle and linear line, respectively [24]. It is obvious that the diameter of the quasi-semicolonircle of CNTs@α-Fe$_2$O$_3$@C nanofibers is small, which illustrates that the CNTs@α-Fe$_2$O$_3$@C nanofibers pos-
sessed good electrical conductivity originated from the low charge transfer resistance and contact resistance in high frequency stage. The depressed semicircular indicates that a film on the electrode was formed.

The SEM images shown in Fig. 7 reveal the structure and morphology of the active materials before and after 50 cycles, respectively. It is obvious that the active material before cycle demonstrates an integrated and dispersive structure, which is shown in Fig. 7(a). As shown in Fig. 7(b), some distinct aggregation has occurred after 50 cycles, which may be the reason of the small capacity loss. However, the active material remained integrated, which indicated that CNTs@α-Fe₂O₃@C nanofibers possessed a stable structure. This could be the reason why coaxial CNTs@α-Fe₂O₃@C nanofibers behaved well in electrochemical performance, including the cycle performance, rate performance and electrochemical impedance.

As for the mechanism of the coaxial CNTs@α-Fe₂O₃@C nanofibers about how to enhance the electrochemical performance, it can be summarized as follows. (1) The prepared α-Fe₂O₃ particles with small diameter can enhance the capacity efficiency by increasing the specific surface area which reacts with lithium ion. As we all know, the specific surface area of the particles increases as the particle diameter decreases. The particles with a diameter about 40–50 nm possess higher specific surface area than big particles, indicating that it can accelerate the charge transfer and shorten the transmission distance by trapping the Li⁺ quickly. Besides, small particles can accommodate the mechanical stress caused by lithium ion insertion/extraction much better than big particles for its good crystalline. Therefore they are not easily smashed during the cycle process, which can ensure their structural stability and cycling capability. Liu et al. [42] prepared a kind of nanoray with length about 1 μm and width about 300 nm, the capacity of which reduced from 1.37 mAh/cm² to 0.25 mAh/cm² after 100 cycles at a current density of 0.1 mA/cm² and only 0.4 mAh/cm² retained after 66 cycles at different current densities, which suggest that the cycling and rate performance of this material did not behave well. The low specific surface area and stability of the nanoray with big size can be responsible for the poor electrochemical performance. (2) The addition of CNT and amorphous carbon can improve the conductivity of electrode, relieve stress caused by the volume variation and inhibit the aggregation of the particles during cycle. As for Fe₂O₃, low conductivity is desired for improvement. The carbon layer can trap the lithium ions by the surface mesoporous or defect of carbon layer caused by the carbonation process to enhance the conductivity, reversible capacity and kinetic properties. CNTs have the same function to shorten transportation path of Li⁺ within inner holes and defects arose from the oxidation process in the mixed acid solution. During the cycle process, the volume expansion of the electrode materials can cause the stress to destroy the integrity of the particles, which is a major factor of the fading capacity and poor stability. CNT, act as a robust network backbone, can absorb the stress to improve the integrity of the materials and the carbon layer coated on the surface of the particles further restrict the expansion. Another function of the carbon materials is that the aggregation of particles can be inhibited by the dispersion of CNT and isolation of the carbon layer. (3) The nitrogen doped in carbon can enlarge the lattice spacing, afford more active nucleation sites and abundant edges on the surface for trapping Li ion and oxygen reduction reaction, which act as a stimulative role to improve the reversible capacity [43]. Liu et al. [5] prepared γ-Fe₂O₃@C/MWNT composite, the capacity of which rose from 731 to 1139 mAh/g after 60 cycles at 100 mAh/g. The material prepared in this work possessed a high capacity about 1255 mAh/g at the first several cycles and 1213 mAh/g retained even after 60 cycles, which implied that the N-doped behavior improved the capacity by offering additional sites to trap extra Li ion.

4. Conclusions

In summary, we have successfully synthesized N-doped coaxial CNTs@α-Fe₂O₃@C nanofibers according to a facile solvothermal/hydrothermal method. The results illustrate that the designed 3D network structure can effectively improve the electrochemical performance. The synthesized N-doped CNTs@α-Fe₂O₃@C nanofibers presented a high capacity of 1255.4 mAh/g, and retained at 1213.4 mAh/g after 60 cycles. Even at high rate of 5 C, a capacity of 319 mAh/g can be still obtained. It can be concluded that N-doped coaxial CNTs@α-Fe₂O₃@C nanofibers have good cycling and rate performance. The improvement of electrochemical performance can be attributed to the special structure of coaxial N-doped CNTs@α-Fe₂O₃@C nanofibers. Besides, high percentage of N-doping and small size α-Fe₂O₃ particles can also ensure the good electrochemistry performance of coaxial N-doped CNTs@α-Fe₂O₃@C nanofibers.

Conflict of interest

The authors declare no competing financial interest.

Acknowledgments

We thank the National Natural Science Foundation of China (No. 91634108, 21376148 and 61503246), and National Key Program (2017FY10205300).

References
