Grass-like Co$_3$O$_4$ nanowire arrays anode with high rate capability and excellent cycling stability for lithium-ion batteries

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A R T I C L E   I N F O

Article history:
Received 1 April 2014
Received in revised form 23 April 2014
Accepted 24 April 2014
Available online 2 May 2014

Keywords:
Lithium-ion batteries
Nanowire arrays
Co$_3$O$_4$
Anode

A B S T R A C T

Grass-like Co$_3$O$_4$ nanowire arrays (NWAs) directly grown on Ti foil were synthesized via a facile hydrothermal process and subsequent thermal treatment. The as-prepared Co$_3$O$_4$ NWAs are constructed by numerous randomly oriented nanowires. The diameters of the nanowires are in the range of 70 to 100 nm, with lengths of several micrometers. Notably, as an anode material for lithium-ion batteries (LIBs), the grass-like Co$_3$O$_4$ NWAs exhibit excellent electrochemical performance including outstanding rate capability and long cycle life. A remarkable capacity of 662 mAh g$^{-1}$ is achieved even at a high current density of 5000 mA g$^{-1}$. The specific capacity of grass-like Co$_3$O$_4$ NWAs could also maintain 1031 mAh g$^{-1}$ at a current density of 500 mA g$^{-1}$ after 100 cycles without capacity decay. The excellent performance is attributed to efficient electron transport from the Co$_3$O$_4$ nanowires to the current collector, good solid contact with the substrate and stable cross-linked structure formed after repeated charge-discharge cycles.

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1. Introduction

In the past decades, lithium ion batteries (LIBs) have attracted much interest due to their high energy density, long cycle life and excellent safety [1,2]. However, the commercially used graphite anode with limited specific capacity (372 mAh g$^{-1}$) and low power density can not meet the demand of applications in high energy and high power devices. Driven by the increasing demand in electric vehicle and hybrid electric vehicle, great efforts have been devoted to explore novel anode materials instead of conventional graphite for LIBs with high performances. Among various anode materials, Co$_3$O$_4$ is one of the most promising anode materials owing to its high theoretical capacity (890 mAh g$^{-1}$) [3]. But, the practical application of Co$_3$O$_4$ is largely restrained by unsatisfactory rate capability due to the slow kinetics of lithium ion and electron transport, as well as the poor capacity retention resulting from the large volume changes over extended cycling [4–6]. One generally accepted strategy to alleviate these problems is to prepare the materials with nanostructures, such as nanoparticles [7], nanorods [8], nanotubes [9], nanosheets [10], and nanocages [11], to shorten the lithium ion diffusion paths and offer more active reaction sites. It was demonstrated that the tailored nanostructured Co$_3$O$_4$ electrodes can significantly improve the electrochemical performance[7–13]. Among the reported nanostructures, self-supported arrays of 1D nanostructure (nanowire [14], nanorod [15], nanotube [16] and nanosheet [17]) grown directly on the conducting substrates represent an attractive architecture. Each 1D nanostructure was directly connected to the current-collector, which eliminates the need for binders and conducting additive, and then increases the mass energy density of the batteries. Moreover, the self-supported 1D nanostructure arrays provide numerous conducting channels for electron transport to the current collector, which improves the rate capability. For instance, Wu et al. prepared Co$_3$O$_4$ nanowire arrays on Ti foil by an ammonia-evaporation-induced method, the diameter of the Co$_3$O$_4$ nanowire is about 500 nm. The as-prepared Co$_3$O$_4$ NWAs exhibit a stable capacity of 700 mAh g$^{-1}$ after 20 cycles at 111 mA g$^{-1}$, and still maintain a capacity 240 mAh g$^{-1}$ at 5550 mA g$^{-1}$ [18]. Xue et al. prepared porous Co$_3$O$_4$ nanoneedle arrays on Cu foil, their reversible capacity is 1167 mAh g$^{-1}$ at 0.5 C rate (≈445 mAh g$^{-1}$) and 925 mAh g$^{-1}$ at 4 C (≈3560 mAh g$^{-1}$) [19]. Mei et al. synthesized porous rhombus-shaped Co$_3$O$_4$ nanorod arrays which deliver more than 1000 mAh g$^{-1}$ at the current density of 111 mA g$^{-1}$ after 20 cycles [20]. The high specific capacity and good rate capability can be attributed to the high surface-to-volume ratio and good electron conduction. Nevertheless, the cycling performance of the self-supported 1D Co$_3$O$_4$ nanostructure arrays was unsatisfactory...
in previous reports [19–24]. The poor long cycle stability is possible due to pulverization and degradation of the mechanical stability of the electrode. The large volume variation during cycling might decrease electrical contact of nanostructures and the current collector and then increase the impedance of the battery. The reversible capacity of porous Co3O4 nanoneedle arrays after 20 cycles was maintained at 813 (0.5 C), and 583 mAh g−1 (4 C), fading to 70% and 63% of the 2nd cycle, showed significant capacity decay [19]. The capacity of nanorod-assembled Co3O4 hexapods decreased from 1100 mAh g−1 (2nd cycle) to 440 mAh g−1 after 40 cycles [23]. Co3O4 nanoneedle arrays on Ni foam delivered a capacity from 870 mAh g−1 (2nd cycle) to less than 600 mAh g−1 after 100 cycles at a current density of 120 mAg−1 [24]. Therefore, it is highly desirable to synthesize Co3O4 nanostructure arrays electrode with highly stable structure during cycling.

In this work, grass-like Co3O4 NWAs with superior structure stability grown directly on Ti foil are synthesized via a simple hydrothermal route and subsequent calcination. In this design, one-dimensional (1D) Co3O4 nanowire facilitates the electron transport along the long dimension and the two short dimensions ensure fast Li+ insertion/extraction which is obviously able to improve the rate capability. Besides, the small NW diameter allows for better accommodation of the large volume changes. Each NW is electrically connected to the current collector makes it possible that every individual nanowire participates in electrochemical reactions. More importantly, the using of NH4F in the hydrothermal synthesis process of Co3O4 NWAs can lead to a robust mechanical adhesion between the final arrays and substrate [25], and the volume of the nanowires expands after several cycles, the nanowires with increased diameter are easily cross linked to each other. The good contact between Co3O4 NWAs and the current collector and cross-linked network sustain a highly stable structure, ensuring a good cycle life. Due to the above-mentioned advantages, the as-prepared grass-like Co3O4 NWAs exhibits high reversible capacity, excellent rate capability and long cycle life.

2. Experimental details

2.1. Preparation of Co3O4 NWAs on Ti substrates

The experiment details were as follows: 1 mmol cobalt nitrate (Co(NO3)2·6H2O), 2 mmol ammonium fluoride (NH4F), and 5 mmol urea (CO(NH2)2) were dissolved in 70 mL deionized water under stirring for 30 min at room temperature. Then the mixed solution was transferred into a 100 mL Teflon-lined stainless autoclave. Afterwards, a piece of Ti foil (1 × 1 cm2) was immersed into the mixed solution and perpendicular to the bottom of the autoclave. The autoclave was heated to 110 °C for 5 h. After it was cooled to room temperature, the Ti foil was taken out and washed with deionized water for several times. Then it was annealed at 350 °C in the flowing argon for 2 h. The mass density of Co3O4 nanowire arrays on Ti foil is about 0.5 mg cm−2.

2.2. Materials characterization

The structure and morphology were characterized by X-ray diffraction (XRD) (Bruker D8 Advance), scanning electron microscopy (SEM) (Quanta 200F) and transmission electron microscopy (TEM) (FEI, Tecnai G2 F30 S-Twin). The X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer. All XPS spectra were corrected using the C 1s line at 284.6 eV. Curve fitting and background subtraction were accomplished.

2.3. Electrochemical measurements

The electrochemical performances of Co3O4 NWAs were investigated using coin cells (CR2025). The celgard 2325 micro porous membrane was used as the separator. The electrolyte consisted of a solution of 1 molL−1 LiPF6 in ethylene carbonate (EC)/diethylcarbonate (DEC) (1:1 by volume). High-pure lithium foil was used as the counter electrode and grass-like Co3O4 NWAs were used as the working electrodes. The coin cells were assembled in an argon-filled glove box (Mikrouna, super 1220) where the oxygen and moisture contents are less than 1 ppm. The cells were galvanostatically discharged and charged using a Battery Testing System (Neware Electronic Co., China) between 0.01–3.0 V. Cylcic voltammetry (CV) measurements were carried out on an electrochemical workstation (Zahner IM6ex) over the potential range of 0.01–3.0 V vs. Li/Li+ at a scanning rate of 0.2 mV s−1. The impedances of the batteries were measured on the Zahner IM6ex electrochemical workstation. The frequency range was set from 0.01 Hz to 1 MHz with the potential amplitude of 5 mV.

3. Results and discussions

The phase composition and structure of the grass-like Co3O4 NWAs were investigated by X-ray diffraction (XRD), as shown in Fig. 1. The diffraction peaks at 38.4°, 40.1°, 53.0°, 62.9°, 70.7°, 76.2° can be indexed to the Ti foil substrate. Besides the peaks from the Ti substrate, the other diffraction peaks at 31.3°, 36.8°, 44.8°, 55.7°, 59.4°, 65.2° can be indexed to (220), (311), (400), (422), (511), (440) planes of the cubic Co3O4, respectively, indicating that the crystalline Co3O4 phase has been formed without any impurities after calcination. Moreover, XPS measurement was carried out to further confirm the formation of NWAs after calcination. Fig. 2 shows the XPS spectra of Co 2p and O 1s of Co3O4 nanowires. As indicated in Fig. 2a, the two strong peaks located at 780.3 eV and 795.6 eV are assigned to Co 2p3/2 and Co 2p1/2 respectively [26,27]. After deconvolution of Co 2p3/2 branch it can be seen that the peak of Co3+ locates at 780.1 eV and that of Co2+ locates at 782.0 eV, which are in agreement with the binding energies of Co3+, Co2+, respectively [28,29]. The two peaks of Co 2p1/2 branch located at 795.2 and 796.9 eV have the similar assignments with Co 2p3/2 branch. The O 1s spectra in Fig. 2b can be deconvoluted into two peaks at 530 eV and 531.5 eV, generally attributed to the lattice oxygen
in the Co$_3$O$_4$ and the oxygen in hydroxide ions [30], respectively, which further indicates the formation of Co$_3$O$_4$ after calcination.

The SEM images of Co$_3$O$_4$ NWAs before and after calcination are shown in Fig. 3a and b. It can be clearly observed that the Ti foil is fully covered with nanowires. The thermal treatment does not change the morphology of the NWAs. The nanowires like grasses with lengths of several micrometers grow on the Ti foil in a random orientation. Fig. 3c shows the representative SEM image of the nanowires, each nanowire has a sharp tip and the diameter of the nanowire is in the range of 70–100 nm. The cross-sectional SEM image of the NWAs is shown in Fig. 2d, the Co$_3$O$_4$ NWs with the length of about 9 μm are uniformly distributed on the Ti foil. Each nanowire has a good solid contact with the substrate which means that the nanowire would not easily fall off from the substrate when used as an electrode during charge-discharge cycling.

The typical TEM image for a single nanowire shown in Fig. 4a, demonstrates that the Co$_3$O$_4$ NW is composed of numerous interconnected nanoparticles. The interplanar distances between adjacent lattice planes are 0.28 nm, 0.24 nm, corresponding to the (220), (311) plane of Co$_3$O$_4$ crystals, respectively. The selected area electron diffraction (SAED) pattern is shown inset in Fig. 4a. The distinct diffraction spots indicate the crystalline of the Co$_3$O$_4$ nanowires. The high-resolution TEM (HRTEM) image shown in Fig. 4b further reveals that the Co$_3$O$_4$ nanowire was composed of lots of crystalline Co$_3$O$_4$ particles with a size of ca. 10 nm. Besides, irregular pores with an average size of 4 nm are numerously disturbed in the Co$_3$O$_4$ NWs, forming bicontinuous mesoporous structure. The existence of pores in nanowire could buffer the strain induced by the volume change, and enhance the electrochemical performance of the electrode. Meanwhile, the porous nature allows a fast Li-ion diffusion and provides larger contact areas with electrolyte, leading to an increased number of electrochemically active surface sites.

Inspired by the attractive nanostructure arrays, grass-like Co$_3$O$_4$ NWAs were tested as an anode electrode for LIBs. The electrochemical performances of the Co$_3$O$_4$ NWAs were evaluated using a standard coin cell. The cyclic voltammetry (CV) profile is recorded for the initial three cycles in the voltage range of 0.01–3.0 V at a scan rate of 0.2 mV s$^{-1}$. As shown in Fig. 5a, in the first cycle, there is an intense cathodic peak observed at 0.75 V corresponding to the initial reduction of Co$_3$O$_4$ to Co and the formation of the solid electrolyte interphase (SEI) film, which is in accordance with the previous reports [31,32]. One anodic peak is recorded at around 2 V, which is ascribed to the complex phase transformation of Co$^0$ – Co$^{2+}$ [20]. In the subsequent cycles, the reduction peak shifts to 0.98 V, while the oxidation peak is almost unchanged. It is found that the CV curves are well overlapped after the first cycle, indicating the good electrochemical reversibility of the grass-like Co$_3$O$_4$ NWAs electrode. Fig. 5b shows the charge-discharge curves of the grass-like Co$_3$O$_4$ NWAs electrode for the first, second and third cycles at the current density of 100 mA g$^{-1}$. In the first discharge curve, there are two voltage plateaus at about 1.2 V and 1.0 V, followed by a sloping curve down to the cutoff voltage of 0.01 V, which are ascribed to the reduction of Co$_3$O$_4$ to Co$^0$ [33]. In addition, the discharge plateau shifted to higher potential in the subsequent cycles, which is consistent with the CV results. The initial discharge and charge capacities are 1058 mAh g$^{-1}$ and 804 mAh g$^{-1}$, respectively. The corresponding coulombic efficiency is 76.0%. The first cycle capacity loss can be normally attributed to the possible irreversible process such as electrolyte decomposition and inevitable formation of a SEI layer [34]. Despite of the irreversible loss in the first cycle, the Co$_3$O$_4$ NWAs electrode still maintains a high charge capacity. The reversible specific capacities of the second and third cycles are slightly increased to 842 and 845 mAh g$^{-1}$, respectively, which shows a good reversibility.

The high rate capability is a very beneficial feature for high power applications such as electric vehicles. Fig. 5c shows the rate capability of the grass-like Co$_3$O$_4$ NWAs. It exhibits 964 mAh g$^{-1}$ at a current density of 200 mA g$^{-1}$, and then slightly reduces to 960 mAh g$^{-1}$, 905 mAh g$^{-1}$ and 823 mAh g$^{-1}$ at 500, 1000 and 2000 mAh g$^{-1}$, respectively. Even at a high rate of 5000 mA g$^{-1}$, the specific capacity still maintains higher than 662 mAh g$^{-1}$. To the best of our knowledge, the rate capability of the as-prepared Co$_3$O$_4$ NWAs is much better than that reported in previous literatures [22,24,35]. Importantly, after the high rate measurements, the specific capacity of the grass-like Co$_3$O$_4$ electrode cycled under 200 mA g$^{-1}$ can be recovered to its original capacity or even a little higher (1059 mAh g$^{-1}$), implying good reversibility. The good rate capability is attributed to the following reasons: (1) the direct attachment and close solid contact of Co$_3$O$_4$ NWs on the Ti current collector can enable fast charge transfer pathways; (2) the open space between Co$_3$O$_4$ NWs can expand the electrochemically active area, provide effective electrolyte-accessible channels for ion transportation, and shorten the distance for lithium ion diffusion.

Fig. 5d displays the cycling performance and coulombic efficiency of Co$_3$O$_4$ NWAs at a current rate of 500 mA g$^{-1}$. The initial three cycles were operated at 100 mA h g$^{-1}$ to activate the cell, and a discharge capacity of 1058 mAh g$^{-1}$ was achieved in the
Fig. 3. SEM images of as-prepared NWAs before (a) and after (b) heat treatment. (c) high magnitude SEM image of Co$_3$O$_4$ nanowires. (d) SEM images of Co$_3$O$_4$ NWAs from the side view.

Fig. 4. (a) TEM image of the single Co$_3$O$_4$ nanowire (inset is the SAED pattern), (b) HRTEM image of the Co$_3$O$_4$. 
first cycle. The electrode materials are gradually activated in the first few cycles. Accompanied with the cycle number increasing, the discharge capacity experiences a gradual increase in the initial 40 cycles and stabilizes at 1031 mAh g⁻¹ after 100 cycles. Similar phenomenon has been observed in the previously reported results for micro-/mesoporous anode materials [10,36–38]. The capacity increment can be ascribed to the reversible growth of a polymeric gel-like film, which is caused by the decomposition of electrolytes [39]. In addition, the coulombic efficiency has been maintained above 97% after the first cycle, indicating the high lithium storage capability and the excellent cycling stability. Notably, compared to commercially used graphite anode, the reversible capacity per unit mass of the grass-like Co₃O₄ NWAs (1031 mAh g⁻¹) is nearly triple that of graphite (372 mAh g⁻¹), and the volumetric capacity of Co₃O₄ nanowire arrays based on electrode volume is 572 mAh cm⁻³, which is close to that of graphite (600 mAh cm⁻³) [40]. The results show that the as-prepared grass-like Co₃O₄ NWAs is a promising anode with high energy density.

In order to investigate the electrical contact of Co₃O₄ nanowires and the substrate during cycling, the impedance spectra of the battery after different cycles were performed, as shown in Fig. 6. The resulting Nyquist plots exhibit two distinct parts, including two semicircles in the high frequency region and a sloped line in the low frequency region. In the case of oxides materials, the semicircle part is mostly related to the SEI film resistance and charge-transfer resistance [5,37,41]. It is worth noting that the diameter of the semicircle is decreased during cycling, which indicates that the contact and charge-transfer resistances of the electrode decrease with increasing the cycle numbers. The decreased impedance also demonstrates that the nanowires still have a good solid contact with the current collector during cycling, attributing to the excellent cycling stability. The decreased impedance is mostly related to the cross-linked structure formed after cycling (shown in Fig. 7). Co₃O₄ nanowires cross link together due to the volume expansion during cycling. The connection of the nanowires not only increases the structure stability but also benefits the electronic diffusion, and then decreases the impedance of the battery.

In order to prove the relationship of excellent cycling performance and the stable structure, the morphological analysis of electrochemical tested grass-like Co₃O₄ NWAs after 100 cycles at 500 mA g⁻¹ is investigated. Fig. 7 shows the typical SEM observations of samples before (Fig. 7a) and after (Fig. 7b) cycling test, the diameter of the nanowires increased to 300 nm from 100 nm after 100 cycles because of the large volume variation during charge-discharge process [3–6]. Figure 7c schematically illustrates the possible transformation process for novel interconnected structure of Co₃O₄ nanowires. After repeated charge-discharge cycles, the diameter of the nanowires increases, and then the randomly orientation nanowires cross linked to each other and maintain a stable reticular structure. The highly stable architecture contributes to the long cycle life of the Co₃O₄ NWAs. On the other way, the cross-linked structure effectively improves the connection of nanowires and thus facilitates the electron transportation. This might be the

**Fig. 5.** (a) Cyclic voltammograms of the Co₃O₄ NWAs electrode, (b) typical charge and discharge curves of first three cycles at a current density of 200 mA g⁻¹, (c) rate capability under various current densities ranging from 200 to 5000 mA g⁻¹, (d) long term cycling performance at a current density of 500 mA g⁻¹.
other reason for the increased capacity in the early cycles shown in Fig. 5d and the decreased impedance after several cycles shown in Fig. 6.

4. Conclusions

The grass-like Co$_3$O$_4$ NWAs electrode is prepared by a simple hydrothermal method and subsequent calcination. The as-synthesized Co$_3$O$_4$ electrode is composed of Co$_3$O$_4$ nanowires grown on Ti foil in a random orientation with the diameter from 70 nm to 100 nm. As an anode material for LIB, the electrode shows excellent rate capability (662 mAh g$^{-1}$ at 5000 mA g$^{-1}$). Furthermore, the grass-like Co$_3$O$_4$ NWAs electrode Exhibits 1031 mAh g$^{-1}$ after 100 cycles at 500 mAh g$^{-1}$ without capacity decay, which shows high cycling stability. The excellent electrochemical performance can be contributed to the following reasons: (1) fast electron transfer ability of nanowires; (2) good solid contact of nanowires with the substrate; (3) stable reticulated structure constructed by the cross-linked nanowires after several cycles. Because hydrothermal method is a facile, low cost and repeatable synthetic method, there is a great possibility to extend the production of the as-prepared Co$_3$O$_4$ NWAs to meet current needed in industry. And as a novel anode material, the as-prepared Co$_3$O$_4$ arrays electrode has high capacity, superior rate capability, long cycle life and excellent mechanical stability, which accords with the demand for high performance lithium-ion batteries used in electric cars.

Acknowledgements

The authors greatly acknowledge the financial support by National Science Fund for Distinguished Young Scholars of China (No. 21225625), Natural Science Foundation of China (No. 21306057), Natural Science Foundation of Guangdong Province (S2012010007495) and The Pearl River Scholar Program of Guangdong Province.

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