Porous CoFe₂O₄ nanowire arrays on carbon cloth as binder-free anodes for flexible lithium-ion batteries

Saihua Zhao, Jinxin Guo, Fei Jiang, Qingmei Su, Gaohui Du*

Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China.

* Corresponding author. Fax: 86-579-82282595; Tel: 86-579-82283897

E-mail address: gaohuidu@zjnu.edu.cn

Abstract: A three-dimensional CoFe₂O₄ nanowire array on carbon cloth was fabricated with a hydrothermal method together with a post-annealing treatment. As a binder-free and flexible anode material for LIBs, it showed an improved electrochemical performance with high cycling stability and excellent rate capability. It exhibited an initial discharge capacity of 1615 mAh g⁻¹ and retained a reversible capacity of about 1204 mAh g⁻¹ after 200 cycles at a specific current of 500 mA g⁻¹. The high capacity, outstanding rate performance and cycling stability can be attributed to the special configuration of hierarchal porous CoFe₂O₄ nanowires on carbon cloth, which possess many advantages like short diffusion length, easy strain relaxation and fast electron transport. Moreover, the integrated CoFe₂O₄ nanowires/carbon cloth electrode shows high flexibility and high areal capacity (2.41 mAh cm⁻²), which makes it suitable for use as a binder-free anode to build flexible LIBs.

Keywords: A. nanostructures; A. oxides; B. chemical synthesis; C. electron microscopy;
D. energy storage

1. Introduction

Flexible electronics is an emerging and promising technology for the next-generation optoelectronic devices, like rollup displays, smart electronics and wearable devices [1-4]. These devices demand batteries with high energy and power densities, which make flexible lithium-ion batteries (LIBs) suitable for utilization [5-7]. Flexible electrodes in LIBs are usually made from various functional organic and/or inorganic materials built on flexible conductive membrane substrates without conductive additives and binders. Recently, a lot of attention has been focused on the assembly of flexible LIBs and promising results have been reported [8-12]. The key challenge to realize flexible batteries is to design and fabricate reliable materials with high rate capability, cycling stability, and robust flexibility.

In order to meet the flexible performance of devices, various flexible electrode materials for LIBs have been prepared from carbonaceous and other membrane materials. For example, electrode materials based on CNTs [13-15], graphene [16, 17], carbon cloth [18-20], conductive paper (cellulose) [21], textiles [1], and low-dimensional nanostructured materials [22] have been reported. Carbon cloth, as a new kind of substrate, possesses some advantageous properties over other materials, including low cost, high conductivity, high strength, excellent structural stability and good corrosion resistance, which make it commercially available and can be used as a lightweight, flexible current collector without any ancillary binders and conductive additives. These characteristics allow it to serve as a platform for the construction of flexible LIBs with improved properties and functionalities.

Recently, cobalt ferrite (CoFe_2O_4) has attracted great attention due to its high gravimetric specific capacity (916 mAh g^{-1}), safety, low cost, and environmental friendliness. However, like other transition metal oxides, CoFe_2O_4 suffers from the problems of poor electrical conductivity and electrode pulverization induced by huge volume changes during the charge–discharge processes, leading to poor

cycling stability and rate capability. Thus, three-dimensional (3D) hierarchical architectures with large surface area, better permeability, and more active sites have been reported to solve the problems.

In this work, we report the fabrication of 3D CoFe_2O_4 nanowires on flexible carbon cloth via a simple hydrothermal method and subsequent annealing treatment. In this novel electrode design, CoFe_2O_4 nanowires of highly crystalline quality were directly grown on conductive carbon cloth to ensure quick electron transport. The 3D hierarchical architectures offer many advantages for flexible LIBs, such as large surface area and short Li-ion diffusion length. By using the hierarchical CoFe_2O_4 nanowires/carbon cloth as both a new class of binder-free anode and the current collector, the highly flexible LIBs demonstrate an improved electrochemical performance. To the best of our knowledge, the porous 3D CoFe_2O_4 nanowires/carbon cloth flexible electrodes for LIBs have not yet been reported.

2. Experiment

2.1. Synthesis of materials

All chemicals (purchased from Sinopharm Chemical Reagent Co., Ltd) were of analytical grade and used as starting materials without further purification. The carbon cloth (WOS1002, CeTech Co., Ltd.) was cleaned by sonication sequentially in acetone, deionized water and ethanol for 2 h each. Subsequently, the nitric acid was used to active the well-cleaned carbon cloth for 4 h. The CoFe_2O_4 nanowires/carbon cloth was synthesized via a two-step process. In a typical synthesis, 1 mmol cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2 mmol ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), 2 mmol ammonium fluoride (NH_4F) and 5 mmol urea ($\text{CO}(\text{NH}_2)_2$) were added to 35 mL of distilled water and stirred for 30 min. The mixed solution was transferred into a Teflon-lined autoclave with a piece of round carbon cloth with a diameter of 14 mm and then heated to 120 °C for 12 h. After being cooled to room temperature, the carbon cloth was collected, washed, and then calcined at 450 °C in Ar atmosphere for 2 h.

2.2. Characterization

The products were characterized using X-ray powder diffraction (XRD) on a philips PW3040/60 X-ray diffractometer with Cu K α ($\lambda=1.5418$ Å) radiation for phase identification. The morphologies were examined using scanning electron microscopy (SEM) on a Hitachi S4800 microscope, and the microstructures were investigated using transmission electron microscopy (TEM) and selected area electron diffraction (SAED) performed on a JEOL 2100F instrument.

2.3. Electrochemical test

The CoFe₂O₄ nanowires/carbon cloth composite was directly used as working electrode in coin-type half cells (CR2025), which were assembled in an argon-filled glove box with metallic lithium foil (China Energy Lithium Co., Ltd) as the counter electrode and Celgard 2400 membranes as separator. The electrolyte was 1 M LiPF₆ in ethylene carbonate and diethyl carbonate (1:1 by volume) (China Energy Lithium Co., Ltd). Coin-type half-cells were cycled at various specific current in the voltage range of 0.005–3.0 V (vs. Li/Li⁺) at room temperature with a multichannel battery measurement system (Neware, China). Cyclic voltammetry (CV) was conducted on an Autolab work station. The CV was carried out in the range of 0.02–3.00 V (vs. Li/Li⁺) at a scan rate of 0.1 mV s⁻¹.

3. Results and discussion

Fig.1 shows the XRD pattern of the resultant CoFe₂O₄ nanowires on carbon cloth. All the diffraction peaks in this pattern can be readily indexed as spinel CoFe₂O₄ (JCPDS Card NO. 22-1086). The peaks around 26° and 43° are also observed and can be assigned to the carbon cloth substrate. Furthermore, the diffraction peaks are sharp and intense, implying the successful synthesis of highly crystalline CoFe₂O₄.

The structure of CoFe₂O₄ nanowires/carbon cloth was characterized using SEM technique as shown in Fig. 2. The SEM image of the pure carbon cloth is shown in Fig. 2(a), which exhibits ordered texture

structure, and each carbon fiber has a smooth surface and a uniform diameter of around 9 μm . Fig. 2(b) clearly reveals that the final product still remains the ordered woven structure of the carbon cloth substrate. High-magnification SEM images shown in Fig. 2(c-e) provide clear information about the CoFe_2O_4 nanowires. Obviously, the nanowires are densely grown on the whole surface of carbon fibers, and the nanowires are well aligned, forming an array with a highly open structure on large scale. Fig. 2(f) shows a photo of the integrated CoFe_2O_4 nanowires/carbon cloth electrode, which can be readily rolled up with tweezers (Fig. 2g). It can be clearly observed that the electrodes exhibit excellent flexibility, which makes them possible for application in flexible devices. The CoFe_2O_4 nanowires with high density have been successfully grown on the carbon cloth by using a facile hydrothermal method. The exact mass of the nanowires was determined by weighing the carbon cloth before/after the nanowire growth. The loading density of the CoFe_2O_4 active material is calculated to be 1.7-2.0 mg cm^{-2} .

The microstructure of the CoFe_2O_4 nanowires was analyzed by means of TEM and SAED. Fig. 3(a) reveals that the diameters of CoFe_2O_4 nanowires are about 50-100 nm. These CoFe_2O_4 nanowires are found to be porous (Fig. 3b), which was induced by dehydration and pyrolysis during the calcination process. The porous feature of the nanowires is beneficial for electrode materials due to the large surface area and the short Li ion diffusion pathways. The HRTEM image shown in Fig. 3(c) reveals two sets of lattice fringes with spacing of 0.25 nm and 0.19 nm, respectively, corresponding to the (311) and (331) planes of spinel CoFe_2O_4 phase. The corresponding SAED pattern shown in Fig. 3(d) indicates the polycrystalline nature of CoFe_2O_4 nanowires. The dominating diffraction rings are assigned to (111), (220), (311), (331), (511), (444) and (642) planes, which are in good agreement with the above XRD results.

The obtained CoFe_2O_4 nanowires/carbon cloth was directly applied as a flexible anode for LIBs to evaluate its electrochemical lithium-storage performance. To elucidate the electrochemical reactions, CV

was carried out at a scan rate of 0.1 mV s^{-1} for four cycles. As shown in Fig. 4(a), the cathodic peak at 0.01 V and the anodic peak at 0.24 V are ascribed to the Li^+ ion insertion into and extraction from the carbon cloth, which provides some capacity contribution for the anode materials [23]. In the first cycle, the main discharge peaks at 0.67 V and 0.89 V could be attributed to the reduction of Fe^{3+} and Co^{2+} to their metallic states together with the formation of Li_2O and solid electrolyte interphase (SEI) layer [24-26]. The broad anodic peaks at 1.60 V and 2.05 V are probably related to the multistep oxidation of metallic Fe and Co to their oxide states. In the following three cycles, the intense cathodic peaks shift to 0.76 V and 1.20 V; the difference of the subsequent cycles from the first one is mainly due to the irreversible structural rearrangement during lithium insertion and extraction in the first cycle. The conversion reaction is similar with the mechanism reported for NiFe_2O_4 [27] and described as follows [28]:

Fig. 4(b) is the charge/discharge curves of CoFe_2O_4 nanowires/carbon cloth for the 1st, 2nd, 10th, 100th, and 200th cycle at the specific current of 500 mA g^{-1} . In the first cycle, the electrode delivers a discharge capacity of 1615 mAh g^{-1} (areal capacity: 3.23 mAh cm^{-2}) and a charge capacity of 1392 mAh g^{-1} (2.78 mAh cm^{-2}). The voltage plateau at 0.89 V corresponds to the reduction reaction, which matches well with the CV measurement. The initial irreversible capacity may result from the formation of SEI film and irreversible phase conversion, which is commonly observed for a variety of metal oxide electrode materials [29-31]. From the 2nd to 10th cycle, the capacity gradually decreased from 1287 mAh g^{-1} (2.57 mAh cm^{-2}) to 1151 mAh g^{-1} (2.30 mAh cm^{-2}). It is worth noting that the discharge and charge capacities increase dramatically from the 10th to 100th cycle, which could be related to the partially reversible formation of the SEI layer during the repetitive lithiation and delithiation.

Fig. 4(c) shows the rate capability of CoFe₂O₄ nanowires. It delivers a capacity of ~1600, 800, 600, 300 mAh g⁻¹ at the specific current of 0.1, 1, 2, 5 A g⁻¹, respectively. When the specific current is switched to 0.1 A g⁻¹ again, the reversible capacity of 1580 mAh g⁻¹ is recovered, suggesting the structure-preservation ability of the electrode material during high-rate lithium uptake and release processes even after cycling at a high rate of 5 A g⁻¹.

The cycling performance of the sample at the specific current of 500 mA g⁻¹ for 200 cycles is presented in Fig. 4(d). After a rapid initial drop, the capacity of the CoFe₂O₄ nanowires decreases gradually until the 50th cycle, and then starts to increase and reaches 1400 mAh g⁻¹. A similar tendency of capacity variation upon cycling has also been observed for CoFe₂O₄ mesoporous platelets [24]. The rapid capacity drop in the initial cycles is considered to be due to the pulverization of electrode, irreversible structural rearrangement [30, 31] and irreversible formation of SEI layers. The Coulombic efficiency of the samples increases from the initial 86.0% to 99.6% at the 10th cycle, and then remains about 99.1% after 50 cycles. In the subsequent cycles, the electrolyte penetrates through the nanowires, and gradually activates the inner active materials [32-35], leading to a gradual capacity increase from the 50th to 75th cycle. At the 200th cycle, it shows a capacity of 1204 mAh g⁻¹, which is higher than the theoretical value (916 mAh g⁻¹) of CoFe₂O₄. For an anode comprising metal oxides or their composites with graphene, a specific capacity higher than the theoretical value has been usually observed, and different mechanisms have been proposed for this deviation, like better conductivity and synergistic effect between oxide and graphene [24, 36-38]. In our case, the excess capacity is mainly associated with the continuous formation of a reversible polymeric gel-like film due to the Co and Fe catalyzed electrolyte degradation, as suggested for the Co₃O₄ and Fe₃O₄ anodes [39-41]. At the same time, the carbon cloth substrate can not only allow rapid access of Li⁺ to the CoFe₂O₄ but also offer a buffer matrix to alleviate the mechanical stress resulting from the huge volume

expansion during cycling [42], and the carbon cloth has some capacity contribution owing to the lithium insertion and extraction (Fig. S1(a)). To evaluate the contribution of carbon cloth to the capacity, the electrochemical performance of pristine carbon cloth was tested. The pure carbon cloth delivers a reversible specific capacity of 67 mAh g^{-1} (0.61 mAh cm^{-2}) after 100 cycles at a specific current of 50 mA g^{-1} (Fig. S1(b)), which is much lower than the theoretical capacity of graphite (372 mAh g^{-1}). If the mass of carbon cloth was included, the reversible gravimetric capacity of the integrated CoFe_2O_4 nanowires/carbon cloth electrode is only 210 mAh g^{-1} due to low reversible capacity of carbon cloth. Considering that the binder, metal current collectors and conducting agents (e.g. acetylene carbon black) are required in general electrode preparation and their masses are excluded for the capacity calculation, all of the specific capacities were calculated on the basis of the mass of CoFe_2O_4 nanowires in the experiments. Moreover, areal capacity is an important parameter for flexible electrode. The reversible areal capacity of CoFe_2O_4 nanowires/carbon cloth is 2.41 mAh cm^{-2} after 200 cycles at 0.5 A g^{-1} , which is higher than that of most reported materials, such as $\text{SnO}_2@\text{Si}$ nanowire/carbon cloth ($1.386 \text{ mAh cm}^{-2}$ after 50 cycles) [43], Cu-Sn nanowires (0.07 mAh cm^{-2} after 100 cycles) [44], Si-CNT nanocomposites (1 mAh cm^{-2}) [45], and $\text{SnO}_2/\text{Fe}_2\text{O}_3$ nanotubes ($1.298 \text{ mAh cm}^{-2}$) [46].

The cycling performance of the sample was also evaluated at a rate of 1 A g^{-1} and 2 A g^{-1} as shown in Fig. 4(e, f). Similar to the tests performed at 0.5 A g^{-1} , the capacity first experiences a reduction, and then starts to increase. The capacity reaches a saturation value of $\sim 612 \text{ mAh g}^{-1}$ (1.22 mAh cm^{-2}) at the 100th cycle in Fig. 4(e); after 250 cycles, the capacity remains 537 mAh g^{-1} (1.07 mAh cm^{-2}) for the current of 1 A g^{-1} . In contrast to the test at 0.5 A g^{-1} and 1 A g^{-1} , the inflection is delayed to the 75th cycle when the density is 2 A g^{-1} as shown in Fig. 4(d); it delivers an initial capacity of 896 mAh g^{-1} (1.79 mAh cm^{-2}), and reaches a saturation value of 440 mAh g^{-1} (0.88 mAh cm^{-2}) at the 150th cycle. Subsequently, the capacity

gradually decreases to 341 mAh g⁻¹ (0.68 mAh cm⁻²) at the 250th cycle.

The excellent electrochemical performance of the designed electrode can be ascribed to the following advantages. First, the highly crystalline CoFe₂O₄ nanowire arrays were directly grown on conductive carbon cloth, which can ensure quick electron/ion transport. Second, the integrated nanowires/carbon cloth is used directly as working electrode, avoiding the use of polymer binders and conductive additives, which significantly reduced the inactive interface. Third, the porous nanowires provide large surface area and short Li-ions diffusion pathways in LIBs.

4. Conclusions

In summary, smartly designed CoFe₂O₄ nanowires have been successfully grown on highly flexible carbon cloth by a facile hydrothermal method along with a post-annealing treatment. The CoFe₂O₄ nanowires are porous with a diameter of around 50-100 nm. The porous feature and the presence of conductive substrate in the composite are favorable for the improved specific capacity, rate capability, and cycling stability as anodes in flexible LIBs. The integrated CoFe₂O₄ nanowires/carbon cloth electrode delivers a high reversible capacity of 1204 mAh g⁻¹ (areal capacity: 2.41 mAh cm⁻²) after 200 cycles at 0.5 A g⁻¹ and a capacity of 612 mAh g⁻¹ at 1 A g⁻¹. The excellent lithium-storage performance makes it a promising candidate for a binder-free anode material in flexible LIBs.

Acknowledgments

This work was supported by the National Science Foundation of China (No. 11574273, and 11504330) and the Natural Science Foundation of Zhejiang Province (No. LQ15B010001, and LY16B030003).

References

- [1] X. Pu, L. Li, H. Song, C. Du, Z. Zhao, C. Jiang, G. Cao, W. Hu, Z.L. Wang, A self-charging power unit by integration of a textile triboelectric nanogenerator and a flexible lithium-ion battery for wearable electronics, *Adv. Mater.* 27 (2015) 2472-2478.
- [2] Y. Zhang, W. Bai, X. Cheng, J. Ren, W. Weng, P. Chen, X. Fang, Z. Zhang, H. Peng, Flexible and stretchable lithium-ion batteries and supercapacitors based on electrically conducting carbon nanotube fiber springs, *Angew. Chem.* 126 (2014) 14792-14796.
- [3] A.M. Gaikwad, A.C. Arias, D.A. Steingart, Recent progress on printed flexible batteries: Mechanical challenges, printing technologies, and future prospects, *Energy Technology* 3 (2015) 305-328.
- [4] X. Pu, L. Li, H. Song, C. Du, Z. Zhao, C. Jiang, G. Cao, W. Hu, Z.L. Wang, A self-charging power unit by integration of a textile triboelectric nanogenerator and a flexible lithium-ion battery for wearable electronics, *Adv. Mater.* (2015) 2472-2478.
- [5] J.J. Shi, X.Y. Zhou, Y. Liu, Q.M. Su, J. Zhang, G.H. Du, One-pot solvothermal synthesis of ZnFe_2O_4 nanospheres/graphene composites with improved lithium-storage performance, *Mater. Res. Bull.* 65 (2015) 204-209.
- [6] D.S. Jung, Y.N. Ko, Y.C. Kang, S.B. Park, Recent progress in electrode materials produced by spray pyrolysis for next-generation lithium ion batteries, *Adv. Powder Technol.* 25 (2014) 18-31.
- [7] W. Li, L. Yang, J. Wang, B. Xiang, Y. Yu, Three-dimensionally interconnected TaS_3 nanowire network as anode for high-performance flexible li-ion battery, *ACS Appl. Mater. Interfaces* 7 (2015) 5629-5633.
- [8] G. Zeng, N. Shi, M. Hess, X. Chen, W. Cheng, T. Fan, M. Niederberger, A general method of fabricating flexible spinel-type oxide/reduced graphene oxide nanocomposite aerogels as advanced anodes for lithium-ion batteries, *ACS Nano* 9 (2015) 4227-4235.

- [9] S. Cao, X. Feng, Y. Song, X. Xue, H. Liu, M. Miao, J. Fang, L. Shi, Integrated fast assembly of free-standing lithium titanate/carbon nanotube/cellulose nanofiber hybrid network film as flexible paper-electrode for lithium-ion batteries, *ACS Appl. Mater. Interfaces* 7 (2015) 10695-10701.
- [10] M.-H. Park, M. Noh, S. Lee, M. Ko, S. Chae, S. Sim, S. Choi, H. Kim, H. Nam, S. Park, J. Cho, Flexible high-energy li-ion batteries with fast-charging capability, *Nano Lett.* 14 (2014) 4083-4089.
- [11] Y. Liu, W. Wang, L. Gu, Y. Wang, Y. Ying, Y. Mao, L. Sun, X. Peng, Flexible CuO nanosheets/reduced-graphene oxide composite paper: Binder-free anode for high-performance lithium-ion batteries, *ACS Appl. Mater. Interfaces* 5 (2013) 9850-9855.
- [12] B. Liu, J. Zhang, X. Wang, G. Chen, D. Chen, C. Zhou, G. Shen, Hierarchical three-dimensional ZnCo_2O_4 nanowire arrays/carbon cloth anodes for a novel class of high-performance flexible lithium-ion batteries, *Nano Lett.* 12 (2012) 3005-3011.
- [13] C. Kang, R. Baskaran, J. Hwang, B.-C. Ku, W. Choi, Large scale patternable 3-dimensional carbon nanotube-graphene structure for flexible Li-ion battery, *Carbon* 68 (2014) 493-500.
- [14] X. Fang, C. Shen, M. Ge, J. Rong, Y. Liu, A. Zhang, F. Wei, C. Zhou, High-power lithium ion batteries based on flexible and light-weight cathode of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /carbon nanotube film, *Nano Energy* 12 (2015) 43-51.
- [15] H. Lin, W. Weng, J. Ren, L. Qiu, Z. Zhang, P. Chen, X. Chen, J. Deng, Y. Wang, H. Peng, Twisted aligned carbon nanotube/silicon composite fiber anode for flexible wire-shaped lithium-ion battery, *Adv. Mater.* 26 (2014) 1217-1222.
- [16] P. Kumar, F.-Y. Wu, L.-H. Hu, S. Ali Abbas, J. Ming, C.-N. Lin, J. Fang, C.-W. Chu, L.-J. Li, High-performance graphene/sulphur electrodes for flexible li-ion batteries using the low-temperature spraying method, *Nanoscale* 7 (2015) 8093-8100.

- [17] H. Tang, Y.J. Zhang, Q.Q. Xiong, J.D. Cheng, Q. Zhang, X.L. Wang, C.D. Gu, J.P. Tu, Self-assembly silicon/porous reduced graphene oxide composite film as a binder-free and flexible anode for lithium-ion batteries, *Electrochim. Acta* 156 (2015) 86-93.
- [18] G. Zhang, S. Hou, H. Zhang, W. Zeng, F. Yan, C.C. Li, H. Duan, High-performance and ultra-stable lithium-ion batteries based on mof-derived ZnO@ZnO quantum dots/c core-shell nanorod arrays on a carbon cloth anode, *Adv. Mater.* 27 (2015) 2400-2405.
- [19] M.-S. Balogun, C. Li, Y. Zeng, M. Yu, Q. Wu, M. Wu, X. Lu, Y. Tong, Titanium dioxide@titanium nitride nanowires on carbon cloth with remarkable rate capability for flexible lithium-ion batteries, *J. Power Sources* 272 (2014) 946-953.
- [20] W. Ren, D. Kong, C. Cheng, Three-dimensional Tin nanoparticles embedded in carbon nanotubes on carbon cloth as a flexible anode for lithium-ion batteries, *ChemElectroChem* 1 (2014) 2064-2069.
- [21] K. Zhang, W. Zhao, J.-T. Lee, G. Jang, X. Shi, J.H. Park, A magnetic field assisted self-assembly strategy towards strongly coupled Fe₃O₄ nanocrystal/rGO paper for high-performance lithium ion batteries, *J. Mater. Chem. A* 2 (2014) 9636-9644.
- [22] J. Lee, C. Jo, B. Park, W. Hwang, H.I. Lee, S. Yoon, J. Lee, Simple fabrication of flexible electrodes with high metal-oxide content: electrospun reduced tungsten oxide/carbon nanofibers for lithium ion battery applications, *Nanoscale* 6 (2014) 10147-10155.
- [23] Q.Q. Xiong, J.P. Tu, X.H. Xia, X.Y. Zhao, C.D. Gu, X.L. Wang, A three-dimensional hierarchical Fe₂O₃@NiO core/shell nanorod array on carbon cloth: A new class of anode for high-performance lithium-ion batteries, *Nanoscale* 5 (2013) 7906-7912.
- [24] Z. Zhang, W. Li, R. Zou, W. Kang, Y. San Chui, M.F. Yuen, C.-S. Lee, W. Zhang, Layer-stacked cobalt ferrite (CoFe₂O₄) mesoporous platelets for high-performance lithium ion battery anodes, *J. Mater.*

Chem. A 3 (2015) 6990-6997.

[25] H. Guo, T. Li, W. Chen, L. Liu, X. Yang, Y. Wang, Y. Guo, General design of hollow porous CoFe_2O_4 nanocubes from metal-organic frameworks with extraordinary lithium storage, *Nanoscale* 6 (2014) 15168-15174.

[26] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries, *Nature* 407 (2000) 496-499.

[27] R. Alcántara, M. Jaraba, P. Lavela, J.L. Tirado, J.C. Jumas, J. Olivier-Fourcade, Changes in oxidation state and magnetic order of iron atoms during the electrochemical reaction of lithium with NiFe_2O_4 , *Electrochem. Commun.* 5 (2003) 16-21.

[28] Y. Xiao, X. Li, J. Zai, K. Wang, Y. Gong, B. Li, Q. Han, X. Qian, CoFe_2O_4 -graphene nanocomposites synthesized through an ultrasonic method with enhanced performances as anode materials for li-ion batteries, *Nano-Micro Lett.* 6 (2014) 307-315.

[29] Q. Xiong, X. Xia, J. Tu, J. Chen, Y. Zhang, D. Zhou, C. Gu, X. Wang, Hierarchical $\text{Fe}_2\text{O}_3@\text{Co}_3\text{O}_4$ nanowire array anode for high-performance lithium-ion batteries, *J. Power Sources* 240 (2013) 344-350.

[30] Q.M. Su, D. Xie, J. Zhang, G.H. Du, B.S. Xu, In situ transmission electron microscopy observation of the conversion mechanism of Fe_2O_3 /graphene anode during lithiation-delithiation processes, *ACS Nano* 7 (2013) 9115-9121.

[31] Q.M. Su, J. Zhang, Y.S. Wu, G.H. Du, Revealing the electrochemical conversion mechanism of porous Co_3O_4 nanoplates in lithium ion battery by in situ transmission electron microscopy, *Nano Energy* 9 (2014) 264-272.

[32] M. Zhen, S. Guo, G. Gao, Z. Zhou, L. Liu, TiO_2 -B nanorods on reduced graphene oxide as anode materials for Li ion batteries, *Chem. Commun.* 51 (2015) 507-510.

- [33] X. Huang, M.G. Willinger, H. Fan, Z.L. Xie, L. Wang, A. Klein-Hoffmann, F. Girgsdies, C.-S. Lee, X.-M. Meng, Single crystalline wurtzite ZnO/Zinc blende ZnS coaxial heterojunctions and hollow zinc blende ZnS nanotubes: Synthesis, structural characterization and optical properties, *Nanoscale* 6 (2014) 8787-8795.
- [34] G. Zhang, L. Yu, H.B. Wu, H.E. Hoster, X.W. Lou, Formation of ZnMn_2O_4 ball-in-ball hollow microspheres as a high-performance anode for lithium-ion batteries, *Adv. Mater.* 24 (2012) 4609-4613.
- [35] L. Hu, H. Zhong, X. Zheng, Y. Huang, P. Zhang, Q. Chen, CoMn_2O_4 spinel hierarchical microspheres assembled with porous nanosheets as stable anodes for lithium-ion batteries, *Sci. Rep.* 2 (2012) 986.
- [36] J. Zai, C. Yu, L. Tao, M. Xu, Y. Xiao, B. Li, Q. Han, K. Wang, X. Qian, Synthesis of Ni-doped NiO/RGONS nanocomposites with enhanced rate capabilities as anode materials for Li ion batteries, *CrystEngComm* 15 (2013) 6663-6671.
- [37] Q. Han, J. Zai, Y. Xiao, B. Li, M. Xu, X. Qian, Direct growth of SnO_2 nanorods on graphene as high capacity anode materials for lithium ion batteries, *RSC Adv.* 3 (2013) 20573-20578.
- [38] H.F. Xiang, Z.D. Li, K. Xie, J.Z. Jiang, J.J. Chen, P.C. Lian, J.S. Wu, Y. Yu, H.H. Wang, Graphene sheets as anode materials for Li-ion batteries: Preparation, structure, electrochemical properties and mechanism for lithium storage, *RSC Adv.* 2 (2012) 6792-6799.
- [39] K.T. Nam, D.-W. Kim, P.J. Yoo, C.-Y. Chiang, N. Meethong, P.T. Hammond, Y.-M. Chiang, A.M. Belcher, Virus-enabled synthesis and assembly of nanowires for lithium ion battery electrodes, *Science* 312 (2006) 885-888.
- [40] L.W. Su, Zhong, Y.R. Zhong, Z. Zhou, Role of transition metal nanoparticles in the extra lithium storage capacity of transition metal oxides: a case study of hierarchical core-shell $\text{Fe}_3\text{O}_4@\text{C}$ and $\text{Fe}@\text{C}$ microspheres. *J. Mater. Chem. A* 1 (2013) 15158-15166.

- [41] S. Grugeon, S. Laruelle, R. Herrera-Urbina, L. Dupont, P. Poizot, J-M. Tarascon, Particle Size Effects on the Electrochemical Performance of Copper Oxides toward Lithium, *J. Electrochem. Soc.* 148 (2001) A285-A292.
- [42] W. Li, M. Li, Z. Yang, J. Xu, X. Zhong, J. Wang, L. Zeng, X. Liu, Y. Jiang, X. Wei, L. Gu, Y. Yu, Carbon-coated germanium nanowires on carbon nanofibers as self-supported electrodes for flexible lithium-ion batteries, *Small* 11 (2015) 2762-2767.
- [43] W. Ren, C. Wang, L. Lu, D. Li, C. Cheng, J. Liu, SnO₂@Si core-shell nanowire arrays on carbon cloth as a flexible anode for Li ion batteries, *J. Mater. Chem. A* 1 (2013) 13433-13438.
- [44] G.F. Ortiz, M.C. López, R. Alcántara, J.L. Tirado, Electrodeposition of copper-tin nanowires on Ti foils for rechargeable lithium micro-batteries with high energy density, *J. Alloys Compd.* 585 (2014) 331-336.
- [45] Q. Xiao, Y. Fan, X. Wang, R.A. Susantyoko, Q. Zhang, A multilayer Si/CNT coaxial nanofiber LIB anode with a high areal capacity, *Energ. Environ. Sci.* 7 (2014) 655-661.
- [46] W. Zeng, F. Zheng, R. Li, Y. Zhan, Y. Li, J. Liu, Template synthesis of SnO₂/α-Fe₂O₃ nanotube array for 3D lithium ion battery anode with large areal capacity, *Nanoscale* 4 (2012) 2760-2765.

Figures captions

Fig.1 XRD pattern of CoFe₂O₄ nanowires/carbon cloth composite.

Fig. 2 (a) SEM image of pure carbon cloth; (b-e) SEM images of CoFe₂O₄ nanowire arrays/carbon cloth; photos of the prepared electrode (f) and the electrode under bending (g).

Fig. 3 (a, b) TEM image of CoFe₂O₄ nanowires; (c) HRTEM image of CoFe₂O₄ nanowires (Inset: the corresponding FFT pattern); (d) SAED pattern of a CoFe₂O₄ nanowire.

Fig. 4 (a) CV curves, (b) charge/discharge curves, and (c) rate performance curves of CoFe₂O₄ nanowires/carbon cloth electrode. (d) Capacity retention and Coulombic efficiency of CoFe₂O₄ nanowires/carbon cloth electrode at 500 mA g⁻¹. (e, f) Capacity retention of CoFe₂O₄ nanowires/carbon cloth electrode at the specific current of 1 and 2 A g⁻¹.

Fig. 1

Fig. 2

Fig. 3

Fig. 4