Porous Co_3O_4 irregular Micro-cubes with lithium storage performances

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Keywords: Porous, Co_3O_4, irregular, Micro-cubes, Lithium-ion battery

Abstract: Porous Co_3O_4 irregular structure are fabricated by a facile hydrothermal process. The microstructures and morphologies of the porous Co_3O_4 irregular micro-cubes was characterized using powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The discharge capacity of porous Co_3O_4 irregular micro-cubes show a larger initial capacity of 1174 mAh/g and still retains a high capacity of 796 mAh/g, even after 100 cycles. More importantly, when the current density increased to 4000 mA/g, it can render reversible capacity of 434 mAh/g, indicating its potential applications for high power lithium ion batteries (LIBs).

Introduction

Over the past few years, with the increase in portable electronics and electrical vehicles, the demand for rechargeable lithium-ion batteries (LIBs) has significantly increased [1]. Transition metal oxides have been demonstrated to have high reversible capacities at a relatively low potential, which have been intensively investigated as possible substitutes for the graphite anode in order to meet the higher requirements of electrochemical energy storage[2]. Co_3O_4 is a transition metal oxide with high theoretical capacity (890 mAh/g), which can be conveniently produced and storage, and it has demonstrated great potentials in the applications of LIBs [3]. Great efforts have been made to address the above issues and improve the electrochemical performances of Co_3O_4. One method for enhancing electrochemical properties of Co_3O_4 is to synthesize nanostructured Co_3O_4 with different morphology, such as nanowires, nanorods, nanosheets [4]. These nanostructured Co_3O_4 with various pores and high specific surface area have been shown to have high capacity [5].

In this paper, we report the facile synthesis of Co_3O_4 micro-cubes morphology with micro/nano-structure. The electrochemical analysis shows that the Co_3O_4 electrodes exhibit low initial irreversible capacities, high capacities at different densities and superior cycling performance. We find that the micro/nano-structure plays important roles in improving the electrochemical performance of the electrodes for LIBs.

Experimental

Synthesis and characterization of the samples

All chemicals were of analytical grade and were used without further purification. In a typical synthesis, $CoAc_2 \cdot 4H_2O$ and Urea were dissolved in 30 mL of solution of H_2O, ethylene glycol and glycerinum (2:2:1 by volume). The mixture solution was stirred for 30 min and then transferred into a 100 mL of Teflon-lined autoclave. The mixed reactants were heated at 180 ℃ for 20 h and then cooled down to room temperature. The obtained pink products were washed with distilled water and

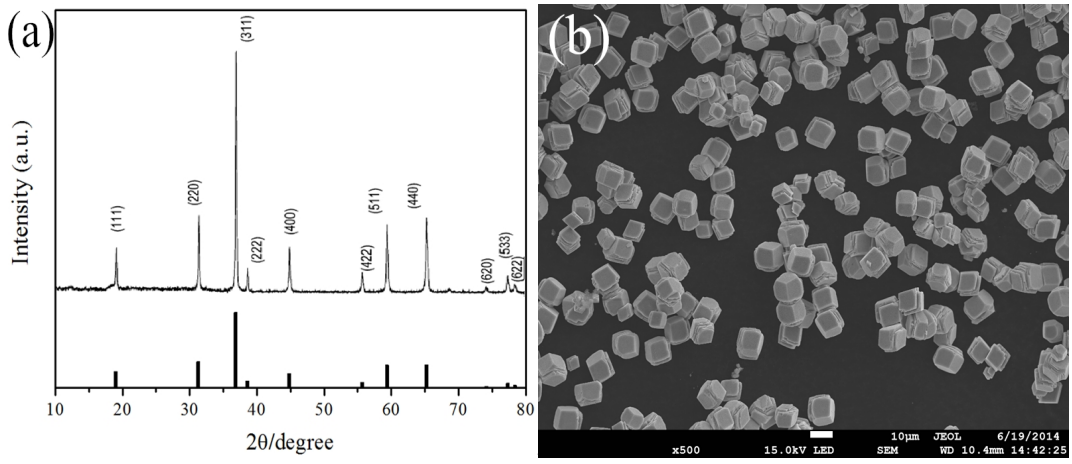
ethanol for several times, and dried under vacuum at 60 ℃ for 10 h. And then the products were calcined at 500 ℃ for 5 h.

The crystallinity and structure of the samples were characterized by X-ray diffraction (XRD), using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.5405Å). The morphologies of the samples were observed using a scan electron microscopy (SEM) images and EDS were carried out with a LEO 1530VP (LEO, Germany) electron microscopy.

The electrochemical characterization was performed using CR2032 coin-type test cells. The cell consisted of a cathode with the composition of 70 wt.% active materials, 20 wt.% carbon black, and 10 wt.% PVDF, a lithium metal anode separated by a Celguard 2400 microporous film. The electrolyte was l $molL^{-1}$ $LiPF_6$/ (EC) and (DEC) (1:1). The charge–discharge tests were galvanostatically performed over 0.01 to 3.0 V at different current densities. Cyclic voltammetry (CV) tests were carried out in the potential window of 0.01 to 3.0 V on an electrochemical workstation (CHI 660).

Results and discussion

Fig. 1(a) depicts the XRD pattern of the porous Co_3O_4 irregular micro-cubes. All the reflection peaks could be indexed to standard Co_3O_4. which is in good agreement with the literature values (JCPDS file Card No. 74–212). No other impurity peak is detected. Fig. 1(b-d) shows the SEM images of the porous Co_3O_4 irregular micro-cubes. The overall morphology of the samples, as shown in Fig. 2a, indicates that large scale micro-cubes were achieved by using this simple hydrothermal approach. The high magnification SEM image (Fig. 2b and c) shows that the micro-cubes have diameters ranging of 10 μm, and each of the size of the Co_3O_4 nanoparticles (in Fig. 1(d) is about 100 nm) consists of a large number of primary grains with submicron size.



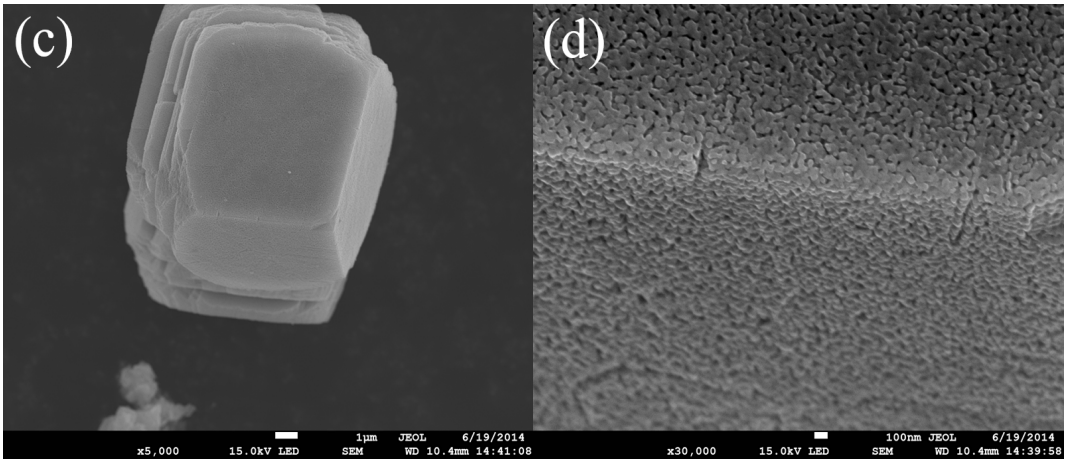


Fig. 1. XRD patterns (a) and SEM patterns (b, c, and d) of the porous Co_3O_4 irregular microcubes.

The electrochemical performances of the porous Co_3O_4 irregular micro-cubes were measured via coin cell testing. In cyclic voltammetry experiment a wider voltage range between the potential limits 0.0 and 3.0 V versus Li/Li^+ was chosen and the series of scans was performed at a slow scan rate of 0.1 mV/s. Comparing the curves shown in Fig. 2a, one can see immediately the difference between the first and following cycles. The broad peak at 1.1V was observed at the first potential sweep in the cathodic direction. In the other cycle, the main reduction peaks is shifted to 1.0 V vs Li/Li^+ for anodes, The oxidation peaks for both anodes remind at the same potential (ca. 2.2 V), indicating that Co oxide is electroactive for Li storage. Fig.3(b, c) showed the typical discharge/charge cycles of the as-prepared the porous Co_3O_4 irregular micro-cubes electrodes cycled between 0.01 and 3.0 V with a current density of 200 mA/g at room temperature, respectively. The initial discharge capacity of the porous Co_3O_4 irregular micro-cubes was 1174 mAh/g and shows a high reversible capacity of 889 mAh/g for the second cycle. It still retains a high capacity of 796 mAh/g, even after 100 cycles.

To good understand the electrochemical behavior of the porous Co_3O_4 irregular micro-cubes, we also investigated its rate performance, as shown in Fig 2(d). The porous Co_3O_4 irregular micro-cubes electrode is cycled at various current densities (200 to 4000 mA/g). The cell shows good rate capability with average discharge capacity of 1113, 754, 653, 515, and 434 mAh/g when the current densities are200, 500, 1000, 2000, and 5000 mA/g, respectively. Upon altering the current density back to 200 mA/g after the rate performance testing, an average discharge capacity as high as 791 mAh/g could be recovered. Large surface area and the short diffusion length of spherical porous structured electrode can improve the kinetic properties of the lithium-ion during intercalation and easily delivers high discharge capacity even under extremely high currents. These results demonstrate that the porous Co_3O_4 irregular micro-cubes have great potential as high-rate anode material in LIBs.

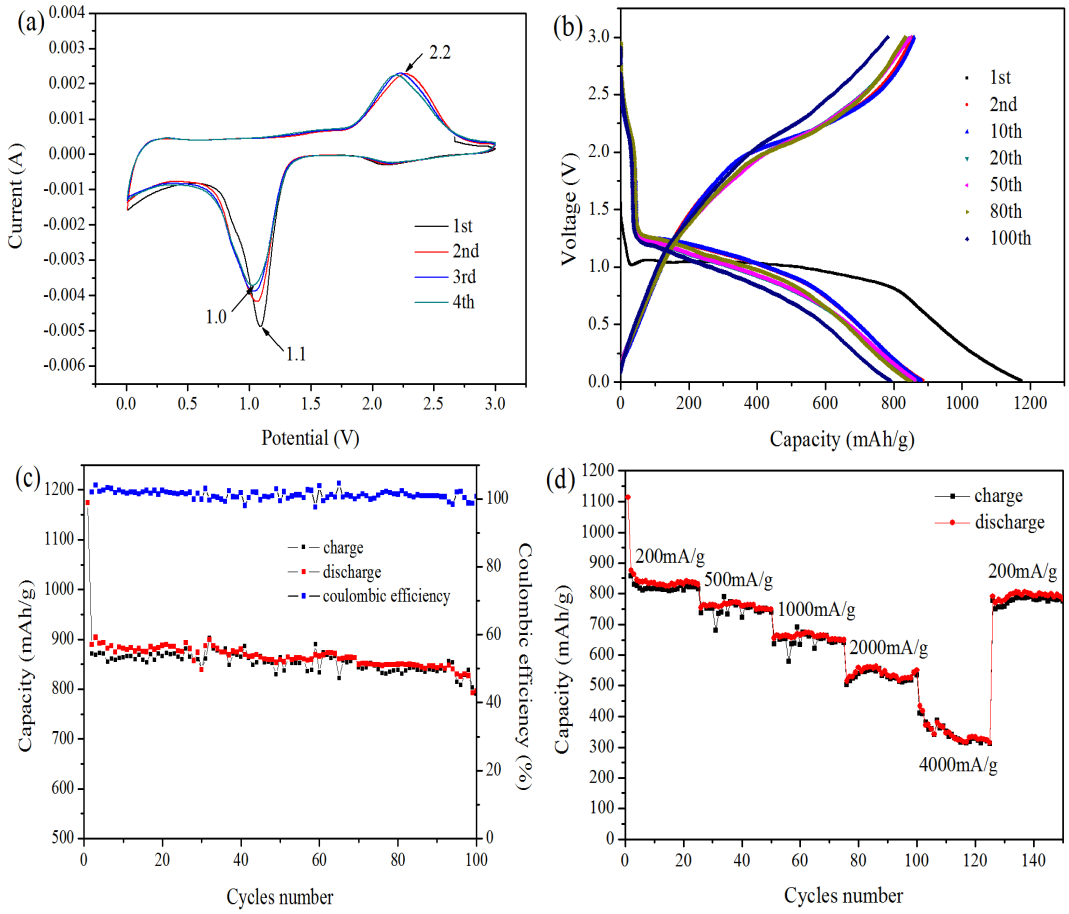


Fig. 3. Cyclic voltammetry (a), Typical discharge/charge curves (b), and Cycling performance (c) of the porous Co_3O_4 irregular micro-cubes; cycling performance(d) of the Co_3O_4 electrode at various current densities

Summary

In summary, we have shown that the porous Co_3O_4 irregular micro-cubes electrodes can be produced with synthesized via a hydrothermal process. These materials exhibit enhanced lithium ion storage capabilities, the discharge capacity of porous Co_3O_4 irregular micro-cubes show a larger initial capacity of 1174 mAh/g and still retains a high capacity of 796 mAh/g, even after 100 cycles,because the combination of nanoscale porosity and nanocrystallinity seems to provide a beneficial microstructure for battery applications.

Acknowledgments

This work was financially supported by the joint science and technology funds of Guizhou Science and Technology Department, Anshun city people's government and Anshun university (grant No. LH [2014] 7505, LKA [2013]17, and LH [2015] 7695).

References

[1] V. Etacheri, R. Marom, R. Elazari, G. Salitra and D. Aurbach: Energy Environ. Sci. 4 (2011) 3243.

[2] S. Xin, Y.G. Guo and L.J. Wan: Acc. Chem. Res. 45 (2012) 1759.

[3] C. Yuan, L. Yang, L. Hou, L. Shen, X. Zhang and X.W. Lou: Energy Environ. Sci. 5 (2012) 7883.

[4]L. Hu and Q. Chen: Nanoscale 6 (2014) 1236.
[5]Y. Fu, X. Li, X. Sun, X. Wang, D. Liu and D. He: J. Mater. Chem. 22 (2012) 17429.