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Synthesis and electrochemical performance of Co_3O_4/C composite anode for lithium ion batteries

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Abstract: The Co_3O_4/acetylene black composite anodes were successfully prepared by combination of oxalate precipitation and pyrolysis of the precipitate. The composite and its precursor were characterized by thermo-gravimetric analysis(TGA), differential thermal analysis(DTA), X-ray diffractometry(XRD), scanning electronic microscopy(SEM) and electrochemical measurements. The effects of carbon content and calcination temperature on properties of the composite were investigated in detail. The cycling performance of the Co_3O_4 anode is improved remarkably by the addition of carbon. As the calcination temperature rises in the range of 300−450 ℃, the crystallinity of the composites increases, but their reversible capacity and cycling stability decrease. Being charged/discharged at a current density of 0.1*C* rate, the optimized Co_3O_4/C composite anode shows a large initial reversible capacity of 757 mA·h/g, and a capacity of 743 mA·h/g is observed after 10 cycles.

Key words: lithium ion batteries; anode; Co_3O_4; composite

1 Introduction

Lithium ion insertion materials have received considerable attention and have been widely used as active electrodes in lithium ion batteries, which have potential applications in portable electronic devices and electric vehicles. Negative electrodes in commercial lithium ion batteries employ different forms of carbon materials. However, with the growing demand for high capacity secondary batteries, the low capacity of carbon (theoretical capacity of 372 mA·h/g) has become a limiting factor. High capacity alternatives to carbonaceous materials have been sought for and much achievement has been made[1−4].

Recently, new anode materials, namely, transition metal oxides such as nickel oxides, cobalt oxides and tin oxides have been proposed for anodes of lithium ion batteries[1,5−8]. Among them, cobalt oxides have excellent electrochemical properties as lithium storage materials in lithium ion batteries because of their large reversible capacity[9−11]. A variety of methods, such as chemical spray pyrolysis, liquid-control-precipitation and oxidation of metal particles have been used in the preparation of cobalt oxides[12−15].

In this work, the Co_3O_4/acetylene black composite anodes were prepared by combination of oxalate precipitation and pyrolysis of the precipitate. The effects of carbon content and calcination temperature on properties of the composite were investigated in detail.

2 Experimental

The cobalt chloride hexahydrate was dissolved in distilled water, and polyglycol was used as dispersant with a concentration of 50 g/L. Then a certain amount of acetylene black was introduced into the solution. Finally, diammonium oxalate monohydrate was added and precipitation of cobalt oxalate occurred, and the molar ratio of cobalt chloride hexahydrate to diammonium oxalate monohydrate was 1.0:1.2. Agitation was employed during the precipitation and the mixture was kept at 40 ℃. The filtrated precipitate was dried in an oven at 120 ℃ for 4 h and the composite precursor of $CoC_2O_4·2H_2O$ and acetylene black was obtained. The Co_3O_4/C composite anode powders were obtained by pyrolysis of the precursor at different temperatures for 2 h in air.

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Thermogravimetry/differential thermal analysis (TG/DTA) was performed on METTLER TOLEDO TGA/SDTA851e thermal analyzer at a heating rate of 10 ℃/min. Powder X-ray diffraction(XRD) measurements were made with a Rigaku diffractometer. Scanning electron micrographs(SEM) were obtained with a JEOL JSM−5600LV spectrometer.

The Co_3O_4/C composite was mixed with poly(vinylidene difluoride) (PVDF) as binder in a mass ratio of 90:10. The Co_3O_4/C composite electrode was prepared by spreading the above mixture on copper foil. Charge−discharge measurements of the Co_3O_4/C composites were performed in the coin cells with the Co_3O_4/C composite as working electrode and lithium metal as counter electrode. A UP 3025 porous membrane of 25 μm in thickness was used as separator, and the electrolyte was 1 mol/L $LiPF_6$ dissolved in a mixture of ethylene carbonate(EC), dimethyl carbonate(DMC) and methyl-ethyl carbonate(EMC) with a volume ratio of 1:1:1. The cells were discharged and charged between 3.0 and 0.01 V at a current density of 60 mA/g. AC impedance measurements were performed using a SHANGHAI CHENHUA CHI660A electrochemistry station in the frequency range from 100 kHz to 10 mHz with the amplitude of 5 mV.

3 Results and discussion

The TG and DTA curves for the prepared precursor are shown in Fig.1. The broad peak located at 180.6 ℃ on the DTA curve is endothermic and corresponds to a sample mass loss of 18.1% in the range of 148−193 ℃ on the TG curve. This is due to the dehydration of chemically bonded water in the $CoC_2O_4·2H_2O$ sample. A sharp exothermic peak observed at 282.5 ℃ on the DTA curve indicates the decomposition and oxidation reaction as follows:

$$3CoC_2O_4+2O_2 \rightarrow Co_3O_4+6CO_2 \qquad (1)$$

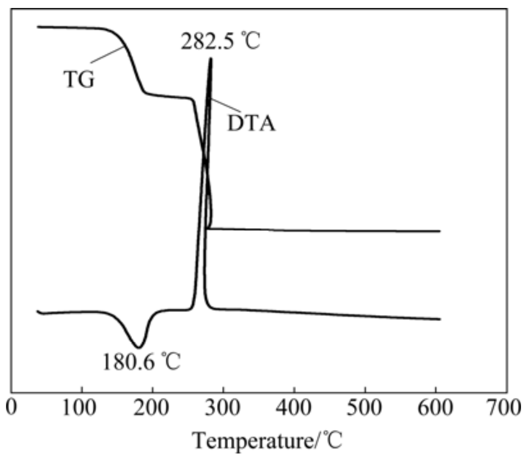

Fig.1 TG and DTA curves of $CoC_2O_4·2H_2O$ in air

Pure Co_3O_4 and Co_3O_4/C composite were prepared by calcining the precursors at 300 ℃ for 2 h, where the precursor of pure Co_3O_4 was $CoC_2O_4·2H_2O$ and that of Co_3O_4/C composite was the mixture of $CoC_2O_4·2H_2O$ and acetylene black with a molar ratio of 2:1. Fig.2 shows the SEM images of pure Co_3O_4 and the Co_3O_4/C composite. In both samples, the grains of Co_3O_4 present short strip appearance. Compared with the pure Co_3O_4 sample, a lot of tiny acetylene black particles are observed in the Co_3O_4/C composite sample and they are well distributed among the Co_3O_4 grains. The acetylene black on the surface of Co_3O_4 particles can not only increase the electric conductivity but also decrease the probability of agglomeration.

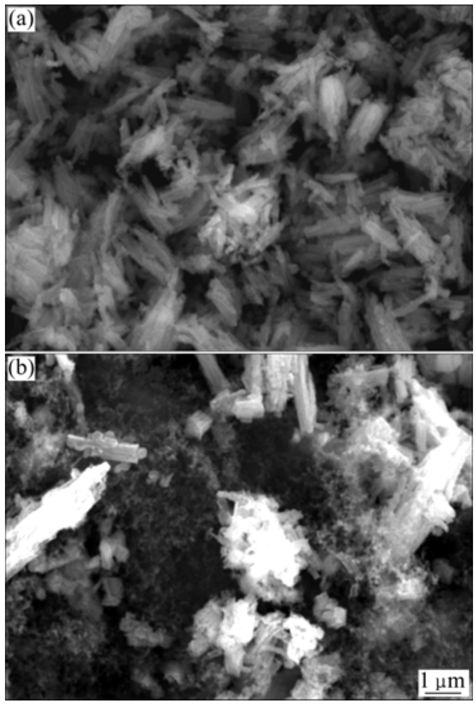

Fig.2 SEM images of pure Co_3O_4(a) and Co_3O_4/C composite(b)

The electrochemical performances of the pure Co_3O_4 and Co_3O_4/C composite were evaluated by galvanostatic charge−discharge in the voltage range of 0.01−3 V versus Li/Li^+ at a constant current density of 60 mA/g. Fig.3 shows the initial charge−discharge curves of pure Co_3O_4 and Co_3O_4/C composite. During the first discharge, the profiles of both samples present a long voltage plateau around 1.2 V and then a sloping voltage profile from 1.2 V to the cut-off voltage of 0.01 V. The Co_3O_4/C composite shows an initial discharge capacity of 974 mA·h/g and a charge capacity (reversible capacity) of 757 mA·h/g, while the pure Co_3O_4 anode has an initial discharge capacity of 797 mA·h/g and a reversible capacity of 659 mA·h/g. The results indicate that the addition of acetylene black can obviously improve the charge−discharge performance of Co_3O_4 compound, and this can be attributed to the enhancement of conductivity

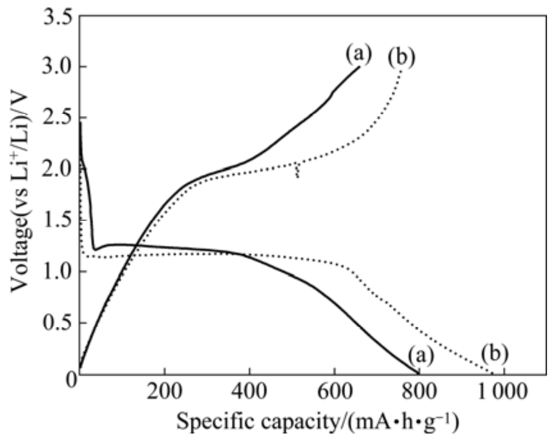

Fig.3 Charge−discharge curves of pure Co_3O_4(a) and Co_3O_4/C composite(b)

of the Co_3O_4/C composite.

Fig.4 shows the cycling performance of pure Co_3O_4 anode and Co_3O_4/C composite anode. The reversible capacity of the pure Co_3O_4 declines drastically with the increase of cycle number. While the Co_3O_4/C composite anode shows good cycling stability with a capacity retention ratio of 98.15% after 10 cycles. This indicates that acetylene black in the composite plays an important role in the improvement of the cycling performance of Co_3O_4 anode.

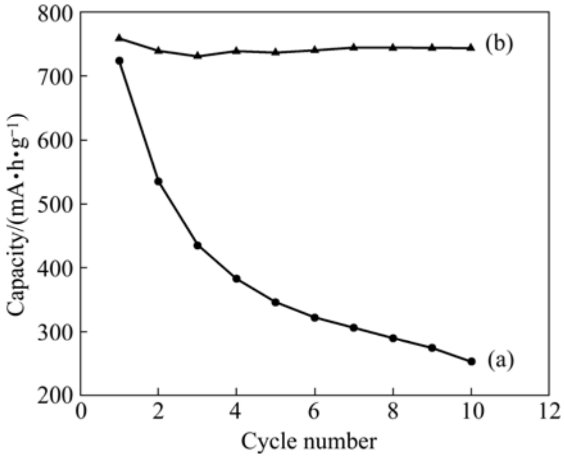

Fig.4 Cycling performance of pure Co_3O_4(a) and Co_3O_4/C composite(b)

Fig.5 shows the impedance spectra for the pure Co_3O_4 and Co_3O_4/C composite at half charged state. The impedance spectra consist of a semicircle in high-frequency range and a line inclined at a constant angle to the real axis in low-frequency range. The semicircle in high-frequency range is due to the contact resistance at the anode and the charge transfer reaction at the interface of the anode/electrolyte. The inclined line in low-frequency range is attributed to Warburg impedance that is associated with lithium ion diffusion through the anode. As observed in Fig.5, the resistance of Co_3O_4/C composite is much smaller than that of the pure Co_3O_4. This indicates that the addition of carbon black decreases the contact resistance at the anode and the impedance for charge transfer reaction at the interface of the anode/electrolyte, then improves the charge−discharge performance of the Co_3O_4/C composite.

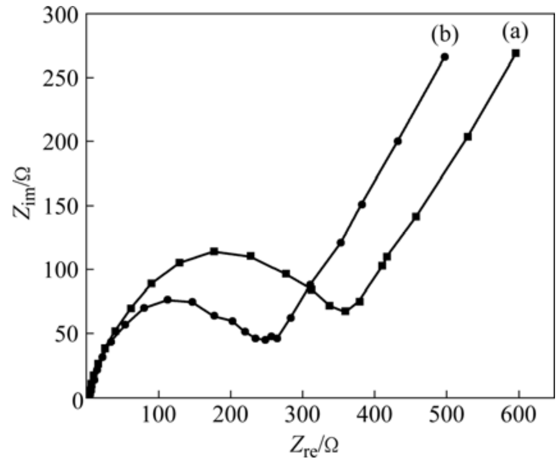

Fig.5 Impedance spectra of pure Co_3O_4(a) and Co_3O_4/C composite(b)

The effects of calcination temperature on the structure and properties of the Co_3O_4/C composites were investigated by calcining the precursor at different temperatures for 2 h, where the precursor was the mixture of $CoC_2O_4 \cdot 2H_2O$ and acetylene black with a molar ratio of 2:1. Fig.6 shows the XRD patterns of the composite samples calcined at different temperatures for 2 h. The diffraction peaks can be indexed to the Co_3O_4 with spinel structure. As the temperature rises from 300 ℃ to 450 ℃, the intensity of the diffraction peaks increases slightly, which suggests that the crystallinity of the Co_3O_4 compound rises.

Fig.7 shows SEM micrographs of the Co_3O_4/C samples calcined at different temperatures for 2 h. The

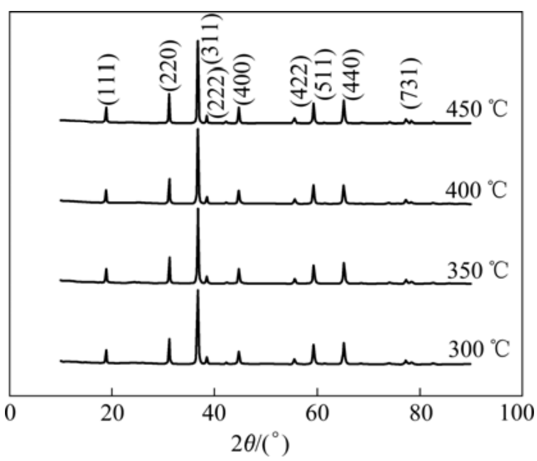

Fig.6 XRD patterns of Co_3O_4 calcined at different temperatures for 2 h

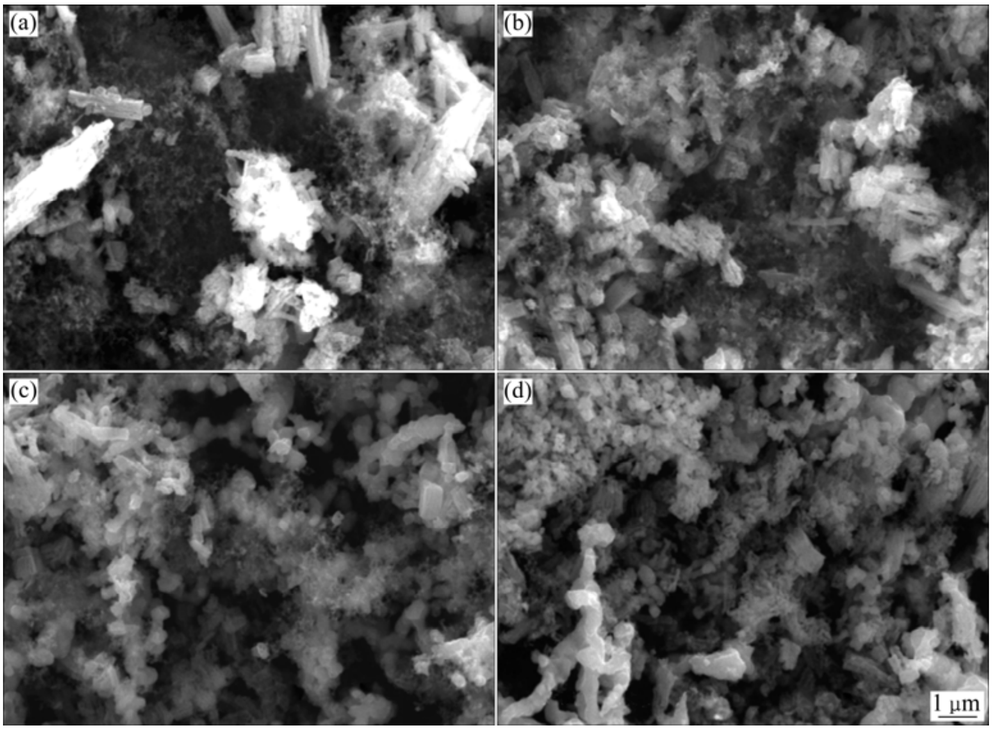

Fig.7 SEM images of Co_3O_4/C composites calcined at different temperatures for 2 h: (a) 300 ℃; (b) 350 ℃; (c) 400 ℃; (d) 450 ℃

Co_3O_4/C samples exhibit loose surface and the grains of Co_3O_4 are less than 1 μm. The grain size of Co_3O_4 increases with the increase of calcination temperature. This can be attributed to the better development of Co_3O_4 grains and more serious agglomeration of the small particles into large ones at higher temperature. In addition, large amount of disordered acetylene black is observed in the Co_3O_4/C sample prepared at 300 ℃. The acetylene black distributes on the surface of Co_3O_4 particles and surrounds the Co_3O_4 particles. With the increase of calcination temperature, the amount of acetylene black reduces greatly, and the acetylene black can hardly be seen in the SEM image of Co_3O_4 obtained at 450 ℃. This results from the oxidation and burning of the acetylene black at higher temperature.

The initial charge−discharge curves of Co_3O_4/C composite calcined at different temperatures are shown in Fig.8. All Co_3O_4/C composites display large charge capacity (reversible capacity) above 700 mA·h/g, and large irreversible capacity occurs in the first charge−discharge cycle, which is the difference between the discharge capacity and charge capacity. This is related to the formation/decomposition of Li_2O as well as solid electrolyte interface(SEI) film formation[16]. Lithium reacts with Co_3O_4 during the first discharge and forms Li_2O and cobalt metal. Li_2O is known to be electrochemically inactive and the incomplete decomposition of Li_2O is responsible for the large irreversible capacity loss during cycling. The Co_3O_4/C composite prepared at 300 ℃ has the best initial charge−discharge performance with the highest reversible capacity of 757 mA·h/g, the lowest irreversible capacity of 169.2 mA·h/g and the largest initial coulombic efficiency of 81.75%.

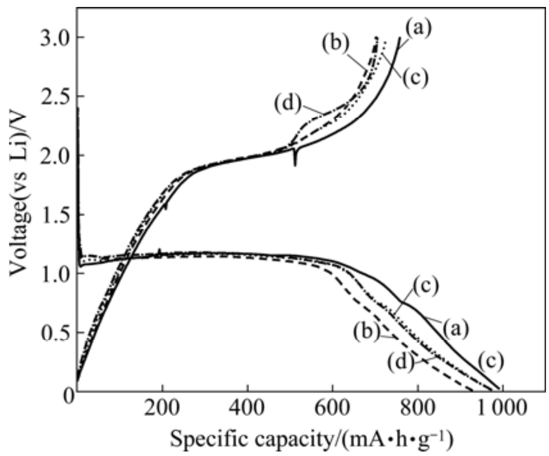

Fig.8 Initial charge−discharge curves of Co_3O_4/C composites calcined at different temperatures: (a) 300 ℃; (b) 350 ℃; (c) 400 ℃; (d) 450 ℃

Fig.9 shows the cycling performance of Co_3O_4/C composites prepared at different calcination temperatures. The cycling performance of Co_3O_4/C composites is improved with decreasing the calcination temperature. The Co_3O_4/C electrodes prepared at 450 ℃ display a fast capacity fading, while the Co_3O_4/C electrode prepared at 300 ℃ exhibits good cycling performance with a capacity of 743 mA·h/g and a capacity retention ratio of

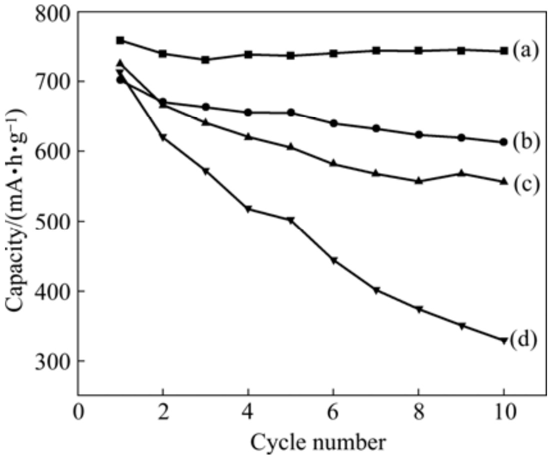

Fig.9 Cycling performance of Co_3O_4/C composites calcined at different temperatures: (a) 300 ℃; (b) 350 ℃; (c) 400 ℃; (d) 450 ℃

98.15% at the 10th cycle.

4 Conclusions

1) The Co_3O_4/C composite anode was synthesized by pyrolysis of the oxalate precursor. The Co_3O_4/C composite electrodes have high reversible capacity, which is above 700 mA·h/g and is twice as high as the commercial graphite anode material. The cycling performance of the Co_3O_4 anode is improved remarkably by the addition of carbon.

2) As the calcination temperature rises in the range of 300−450 ℃, the composites exhibit better crystalline structure, but their reversible capacity and cycling stability decrease. The optimized Co_3O_4/C composite anode shows a large initial reversible capacity of 757 mA·h/g, and a capacity retention ratio of 98.15% is observed after 10 cycles.

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