

Synthesis and electrochemical performance of $\text{Co}_3\text{O}_4/\text{C}$ 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 °C, the crystallinity of the composites increases, but their reversible capacity and cycling stability decrease. Being charged/discharged at a current density of 0.1C rate, the optimized $\text{Co}_3\text{O}_4/\text{C}$ 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 °C. The filtrated precipitate was dried in an oven at 120 °C for 4 h and the composite precursor of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and acetylene black was obtained. The $\text{Co}_3\text{O}_4/\text{C}$ composite anode powders were obtained by pyrolysis of the precursor at different temperatures for 2 h in air.

Thermogravimetry/differential thermal analysis (TG/DTA) was performed on METTLER TOLEDO TGA/SDTA851e thermal analyzer at a heating rate of 10 °C/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 $\text{Co}_3\text{O}_4/\text{C}$ composite was mixed with poly(vinylidene difluoride) (PVDF) as binder in a mass ratio of 90:10. The $\text{Co}_3\text{O}_4/\text{C}$ composite electrode was prepared by spreading the above mixture on copper foil. Charge–discharge measurements of the $\text{Co}_3\text{O}_4/\text{C}$ composites were performed in the coin cells with the $\text{Co}_3\text{O}_4/\text{C}$ 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 °C on the DTA curve is endothermic and corresponds to a sample mass loss of 18.1% in the range of 148–193 °C on the TG curve. This is due to the dehydration of chemically bonded water in the $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ sample. A sharp exothermic peak observed at 282.5 °C on the DTA curve indicates the decomposition and oxidation reaction as follows:

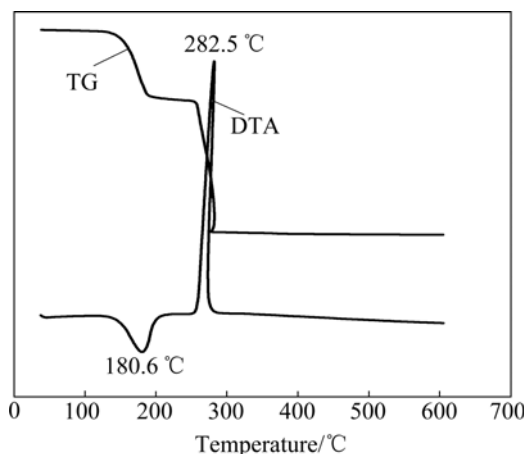


Fig.1 TG and DTA curves of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in air

Pure Co_3O_4 and $\text{Co}_3\text{O}_4/\text{C}$ composite were prepared by calcining the precursors at 300 °C for 2 h, where the precursor of pure Co_3O_4 was $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and that of $\text{Co}_3\text{O}_4/\text{C}$ composite was the mixture of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and acetylene black with a molar ratio of 2:1. Fig.2 shows the SEM images of pure Co_3O_4 and the $\text{Co}_3\text{O}_4/\text{C}$ 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 $\text{Co}_3\text{O}_4/\text{C}$ 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.

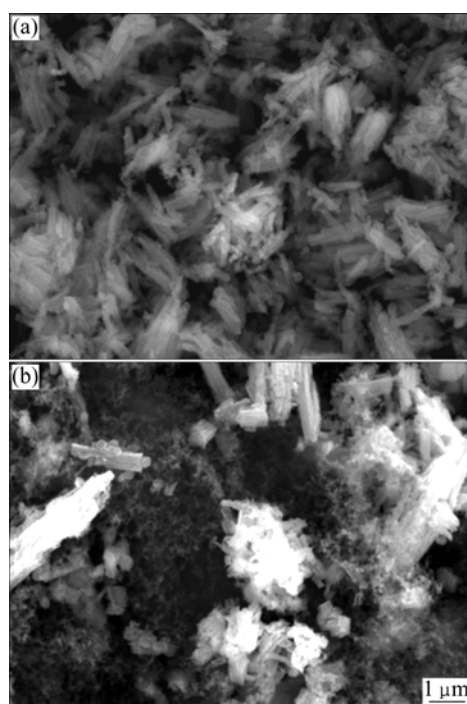


Fig.2 SEM images of pure Co_3O_4 (a) and $\text{Co}_3\text{O}_4/\text{C}$ composite(b)

The electrochemical performances of the pure Co_3O_4 and $\text{Co}_3\text{O}_4/\text{C}$ 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 $\text{Co}_3\text{O}_4/\text{C}$ 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 $\text{Co}_3\text{O}_4/\text{C}$ 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

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