

Preparation and electrochemical performance of nanosized Co_3O_4 via hydrothermal method

YANG You-ping(杨幼平), LIU Ren-sheng(刘人生), HUANG Ke-long(黄可龙),
WANG Li-ping(王丽平), LIU Su-qin(刘素琴), ZENG Wen-wen(曾雯雯)

School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

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Abstract: The hydrotalcite-type cobalt compounds were prepared through oxidation of $\text{Co}(\text{OH})_2$ gel using NH_4OH as precipitating agent and H_2O_2 as oxidant. These hydrotalcite-type cobalt compounds were transformed into Co_3O_4 through hydrothermal decomposition with nanostructural deformation. The precursor and product were characterized by Fourier-transform infrared(FT-IR) spectrum, X-ray diffractometry(XRD) and transmission electron microscopy(TEM). The electrochemical performances of as-prepared nanosized Co_3O_4 as anode materials in lithium-ion batteries were tested by charge-discharge test in the voltage range of 0–3.0 V. The influence of morphology of Co_3O_4 particle on the capacity and cycling performance was studied. The results show that the shape and size of the final product can be controlled by altering cobalt sources. The irregular cubic Co_3O_4 with the average particle size of about 10 nm shows the best electrochemical performance. After 10 charge-discharge cycles, the specific charge capacity retains 555 $\text{mA}\cdot\text{h/g}$.

Key words: hydrotalcite-type cobalt compounds; nanosized Co_3O_4 ; hydrothermal method; anode materials

1 Introduction

In recent years, Co_3O_4 has attracted increasingly attention due to its wide applications in catalysts, gas sensors, magnetic semiconductors, negative electrodes in rechargeable lithium-ion batteries[1–6]. The performance of Co_3O_4 in its applications such as catalysts and magnetic materials can be promising owing to the high surface area and narrow size distribution. Therefore, the synthesis of uniform Co_3O_4 nanocrystal has been the target of material chemists. In this field, various synthesis methods have been reported, such as thermal decomposition of solid phase[7], chemical spray pyrolysis[8], and sol-gel method[9]. However, the size distribution of Co_3O_4 nanocrystal made by the above methods is wide. Hydrothermal method[10] is an efficient technique for preparing fine oxide powers by reaction with high temperature and high pressure in solution.

In this work, the hydrotalcite-type cobalt compounds were prepared using NH_4OH as precipitating

agent and H_2O_2 as oxidant, and then were transformed to Co_3O_4 under hydrothermal condition. The electrochemical performances of as-prepared nanosized Co_3O_4 as anode materials in lithium-ion batteries were tested.

2 Experimental

2.1 Samples preparation

All of the starting materials were in analytical grade. 15 mmol cobalt salt ($\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$, $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$, or $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$) was dissolved into deionized water containing dispersant polyethylene glycol(PEG) with relative molecular mass of about 20 000, then excessive amount NH_4OH was added with electromagnetic stirring at 30 °C to form $\text{Co}(\text{OH})_2$ gel. The pH value was monitored to 8–9. A certain volume of 30% (mass fraction) H_2O_2 was dropped into the above suspension. Finally, all of them were transferred into a Teflon-lined stainless steel autoclave with the volume of 100 mL, and the autoclave was filled with deionized water up to 70% of the total capacity. The sealed autoclave was heated to 160 °C in 1 h and maintained for 16 h, then cooled to

room temperature in air naturally. The black products were centrifuged and washed with deionized water and absolute ethanol for three times, respectively, then dried in a vacuum oven at 80 °C for 6 h.

2.2 Samples characterization

The crystal structures of samples were identified by X-ray diffraction(XRD) in the 2θ range of 10° – 80° using a Japan Rigaku D/Max–2500 X-ray diffractometer with graphite monochromatic Cu K_α radiation ($\lambda=0.154\ 056$ nm). Fourier transform infrared(FT-IR) spectra were measured with Avatar 360 FT-IR spectrophotometer within a wavelength range from $4\ 000\ \text{cm}^{-1}$ to $400\ \text{cm}^{-1}$. The morphology and size of the as-prepared Co_3O_4 were observed with Model JEM–1230 transmission electron microscope(TEM).

2.3 Electrode preparation and electrochemical performance test

The electrode was prepared by coating the mixture of Co_3O_4 (80%, mass fraction), acetylene black (10%) and polytetrafluoroethylene(PTFE) binder (10%) onto a $1\ \text{cm}^2$ stainless steel current collector. The electrode was dried in a vacuum oven at 80 °C and then pressed at 20 MPa. The electrochemical cell consisted of a Co_3O_4 working electrode and a lithium foil counter electrode. They were assembled in a MBRAUN glove box under argon atmosphere with H_2O and O_2 , in which the volume fraction of H_2O and O_2 was less than 10^{-6} . 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 cell was discharged and charged between 0.01 and 3.0 V versus Li^+/Li at a rate of 0.1C.

3 Results and discussion

Fig.1 shows the XRD patterns for the precursors, hydrotalcite-type cobalt compounds, obtained using different cobalt sources without hydrothermal treatment. All peaks shown in Fig.1 can be indexed to hydrotalcite-type cobalt compound, which is consistent with the reported data[11–14]. $d(003)=2d(006)=3d(009)$. When excessive amount NH_4OH is added to the solution of cobalt salt, there forms $\text{Co}(\text{OH})_2$ gel. After H_2O_2 is dropped into the above suspension, some divalent cobalt cations are substituted by trivalent cobalt cations, and anion species in suspension are intercalated into the interlayer space to compensate the extra position charge possessed by the trivalent cobalt cations. This structural alternation leads to the formation of hydrotalcite-like structures.

Fig.2 shows FT-IR spectra of the precursors prepared using different cobalt sources. The broad peaks

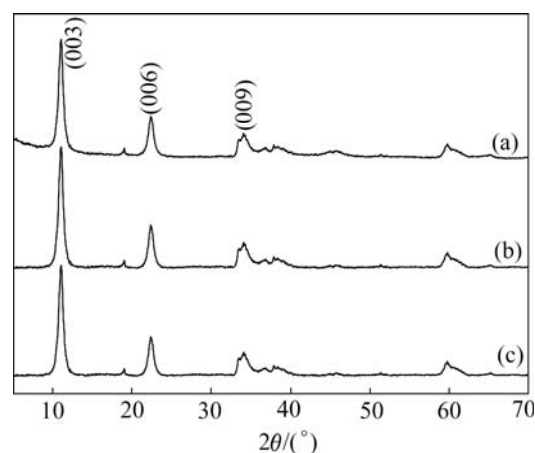


Fig.1 XRD patterns of hydrotalcite-type cobalt compounds using different cobalt sources: (a) $\text{Co}(\text{CH}_3\text{COO})_2$; (b) CoSO_4 ; (c) $\text{Co}(\text{NO}_3)_2$

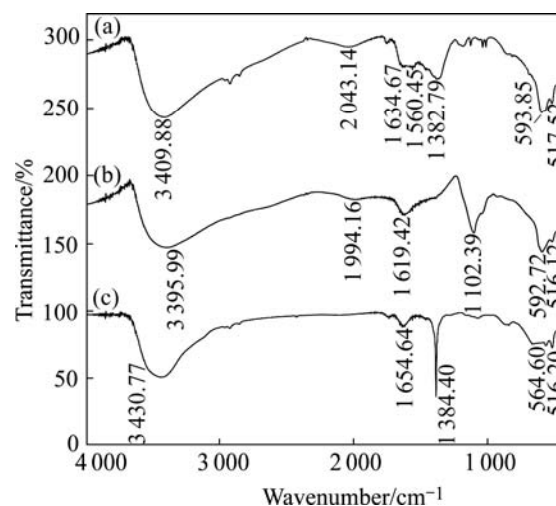


Fig.2 FT-IR spectra of precursors obtained using different cobalt sources: (a) $\text{Co}(\text{CH}_3\text{COO})_2$; (b) CoSO_4 ; (c) $\text{Co}(\text{NO}_3)_2$

at $3\ 395.99$ – $3\ 430.77\ \text{cm}^{-1}$ are assigned to the stretching vibration of the O–H bond, ν_{OH} , which indicates the presence of hydroxyl ions due to the metal-OH layer and/or water in the crystal, and the peaks at $1\ 619.42$ – $1\ 654.64\ \text{cm}^{-1}$ are assigned to the bending modes of water. The peaks at 516.12 – $517.52\ \text{cm}^{-1}$ and 564.60 – $593.85\ \text{cm}^{-1}$ can correspond to the presence of Co–O species.

In Fig.2(a), the peaks, at around $1\ 560.45\ \text{cm}^{-1}$ and $1\ 382.79\ \text{cm}^{-1}$, result from the asymmetric stretching and symmetric stretching mode of CH_3COO^- , respectively. In Fig.2(b), the peak at $1\ 102.39\ \text{cm}^{-1}$ is assigned to the asymmetric stretching mode of SO_4^{2-} in the precursor. In Fig.2(c), the peak, at around $1\ 384.40\ \text{cm}^{-1}$, belongs to the ν_3 vibrational mode of NO_3^- . Based on FT-IR spectra, the hydrotalcite-type cobalt compounds formed are indicated as $\text{Co}_{1-x}^{\text{II}}\text{Co}_x^{\text{III}}(\text{OH})_{2-y}(\text{CH}_3\text{COO})_{x+y}$, $\text{Co}_{1-x}^{\text{II}}\text{Co}_x^{\text{III}}(\text{OH})_{2-y}(\text{SO}_4)_{x+y}$ and $\text{Co}_{1-x}^{\text{II}}\text{Co}_x^{\text{III}}(\text{OH})_{2-y}$ -

$(\text{NO}_3)_{x+y}$ using $\text{Co}(\text{CH}_3\text{COO})_2$, CoSO_4 and $\text{Co}(\text{NO}_3)_2$ as cobalt sources, respectively.

Generally speaking, divalent metal cation hydroxides have a layered structure, while metal hydroxides having a formula of $[\text{M}(\text{OH})]^{x+}(\text{A}^{n-})_{x/n} \cdot y\text{H}_2\text{O}$ are known as layered double hydroxides (LDH)[15]. When adding oxidant H_2O_2 to the LDH suspension, the oxidation of Co^{2+} into Co^{3+} yields positively charged hydroxide layers $[\text{Co}_{1-x}^{II}\text{Co}_x^{III}(\text{OH})_2]^{x+}$. According to charge equilibrium, the anions such as CH_3COO^- , SO_4^{2-} and NO_3^- are then intercalated into the interlamellar spaces. Then the hydrotalcite-type cobalt compounds are formed. Upon the hydrothermal treatment of the hydrotalcite-type hydroxide at 160°C in the autoclave for 16 h, all the hydrotalcite-type cobalt compounds are converted into Co_3O_4 nanoparticles.

Fig.3 shows the XRD patterns of the products obtained by the hydrothermal method. All the diffraction peaks can be indexed to a pure cubic phase of spinel Co_3O_4 . Evaluated from Scherrer formula, the average particle sizes prepared with the hydrothermal method using $\text{Co}(\text{CH}_3\text{COO})_2$, CoSO_4 , $\text{Co}(\text{NO}_3)_2$ as cobalt sources are about 18, 27 and 10 nm, respectively. No other peaks for impurities are detected.

The TEM morphologies of crystallized powders are very homogeneous with respect to particles size and shape. Fig.4(a) shows the TEM image of hydrotalcite-

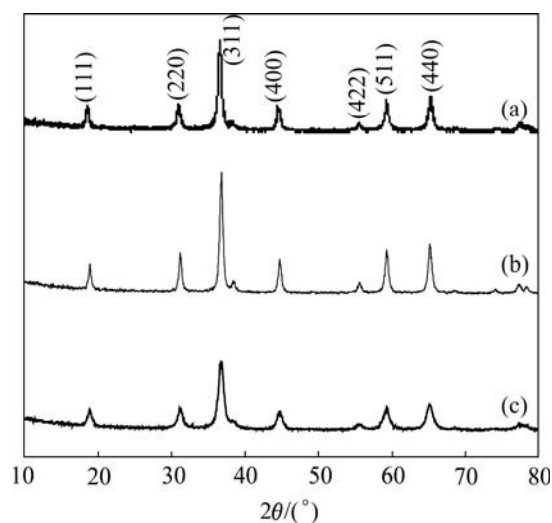


Fig.3 XRD patterns of products prepared by hydrothermal method using different cobalt sources: (a) $\text{Co}(\text{CH}_3\text{COO})_2$; (b) CoSO_4 ; (c) $\text{Co}(\text{NO}_3)_2$

type cobalt compound deposited using $\text{Co}(\text{CH}_3\text{COO})_2$ as cobalt source and H_2O_2 as oxidant. The TEM images (Figs.4(b)–(d)) show that the converted products of hydrotalcite-type cobalt compounds by hydrothermal method, Co_3O_4 powders, consist of monodispersive nanoparticles using $\text{Co}(\text{CH}_3\text{COO})_2$, CoSO_4 and $\text{Co}(\text{NO}_3)_2$

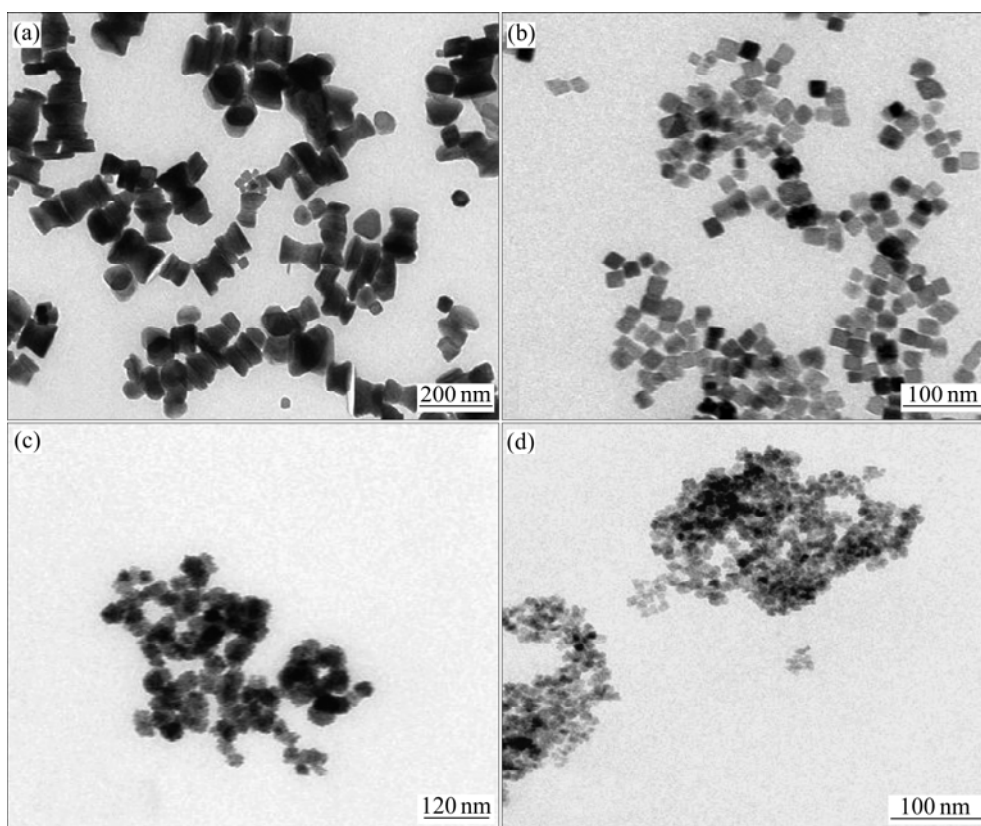


Fig.4 TEM images of hydrotalcite-type cobalt compound (a) and nanocrystalline Co_3O_4 prepared by hydrothermal method using different cobalt sources: (b) $\text{Co}(\text{CH}_3\text{COO})_2$; (c) CoSO_4 ; (d) $\text{Co}(\text{NO}_3)_2$

as cobalt sources, respectively. Fig.4(b) shows the cubic grains with an average edge length of 20 nm. The nanocubes are perfect and the particle size distribution is narrow. This result suggests that the spinel cobalt oxide nanocubes may be formed through a decomposing and redepositing process under hydrothermal conditions (Figs.4(a) and (b)). Fig.4(c) shows spherical morphology, with a diameter of around 30 nm. Fig.4(d) demonstrates that the average particle size is about 10 nm. The most of the nanocubes are imperfect, and their shapes become more spherical. The size of the Co_3O_4 powders is generally consistent with that of the XRD analysis.

In order to obtain a discharge-charge profile of nanosized Co_3O_4 , the cell was subjected to 10 cycles at 0.1C rate. The first discharge-charge curves for the regular cubic sample are shown in Fig.5. During the first discharge, the potential rapidly drops to a large plateau at 1.1 V, and then slowly drops to a plateau at 0.7 V. The specific discharge capacity (lithium-inserted process) in the first discharge reaches 1 380 $\text{mA}\cdot\text{h/g}$ and the first charge capacity(lithium-deserted process) amounts 927 $\text{mA}\cdot\text{h/g}$. The irreversible capacity loss is 33% in the first cycle. The discharge-charge profiles of nanosized Co_3O_4 with various shapes are uniform, but their capacity and the cycling performance are different.

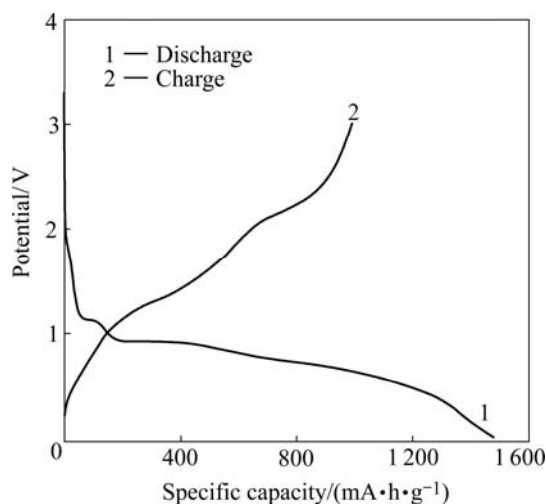


Fig.5 First discharge-charge profiles of cubic Co_3O_4 at 0.1C rate

The cycling performances of nanosized Co_3O_4 samples with different particle morphologies are shown in Fig.6. The as-prepared Co_3O_4 with regular cubic shape (see Fig.4(b)) has obvious decline in electrochemical capacity. After 10 discharge-charge cycles, the specific charge capacity decreases from 927 $\text{mA}\cdot\text{h/g}$ to 446 $\text{mA}\cdot\text{h/g}$ in the first charge process. The first and the tenth charge capacities of spherical Co_3O_4 (see Fig.4(c)) are 894 $\text{mA}\cdot\text{h/g}$ and 378 $\text{mA}\cdot\text{h/g}$, respectively. The first charge capacity of irregular cubic Co_3O_4 (see Fig.4(d)) is 912 $\text{mA}\cdot\text{h/g}$, and the charge capacity is retained at 555

$\text{mA}\cdot\text{h/g}$ after 10 cycles. It can be concluded that the electrochemical properties of Co_3O_4 as anode material for lithium-ion batteries are sensitive to their particle shape, and the irregular cubic Co_3O_4 has the best electrochemical property in all the as-prepared samples.

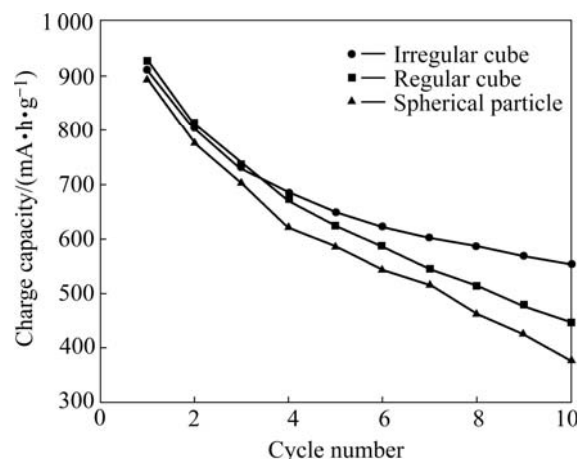


Fig.6 Cycling performance of as-prepared Co_3O_4 in charge-discharge process at 0.1C rate

4 Conclusions

1) The hydrotalcite-type cobalt compounds are synthesized through oxidation of $\text{Co}(\text{OH})_2$ gel using NH_4OH as precipitating agent and H_2O_2 as oxidant. The process that Co^{2+} is partially oxidated to Co^{3+} yields positively charged hydroxide layers, $([\text{Co}_{1-x}^{\text{II}}\text{Co}_x^{\text{III}}(\text{OH})_2]^{x+})$. According to charge equilibrium, the anions such as CH_3COO^- , SO_4^{2-} and NO_3^- are intercalated into the interlamellar spaces.

2) These hydrotalcite-type compounds are transformed into Co_3O_4 through hydrothermal decomposition with nanostructural deformation. The shape and size of the final product can be controlled by altering cobalt sources.

3) The particle shape has distinct effect on electrochemical performance of Co_3O_4 as anode material for lithium-ion batteries. The irregular cubic Co_3O_4 shows the best electrochemical performance in all the as-prepared samples. After 10 discharge-charge cycles, the specific charge capacity retains 555 $\text{mA}\cdot\text{h/g}$.

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