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Study on LiCoO_2 cathode materials with well performance for lithium ion batteries*

WANG Ying(王英), TANG Ren-heng(唐仁衡), XIAO Fang-ming(肖方明),
LU Qi-yun(卢其云), PENG Neng(彭能)

(Research Centre of Rare Earth Functional Materials, Guangzhou Research Institute of Non-ferrous Metals,
Guangzhou 510651, China)

Abstract: One new preparation method of Well-property LiCoO_2 , which is synthesized by caclining a good precursor obtained from aqueous solution at lower temperature for shorter time, is studied in this paper. The experimental results indicate that LiCoO_2 is pure phase layer structure with high crystallization, and excellent electrochemical properties are also proved owing to its initial charge and discharge specific capacity of 205mAh/g, 169mAh/g at the current of 0.2C respectively.

Key words: two-steps method; LiCoO_2 ; preparation process

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1 Introduction

LiCoO_2 is one of key commercial cathode materials used for lithium secondary batteries at present. It is almost synthesized by traditional high temperature solid-state reaction method. Due to not only requiring grinding and blending for a longer time, but also demanding higher caclination temperature and longer times, it is difficult to control the compositions, structure and partical size distribution of the resulting powder during the preparation process, so the identity of electrochemical performance is poor. LiCoO_2 prepared by soft chemical reaction method is advanced recently, such as sol-gel method^[1-3], spray drying method^[4], freezing drying method^[5], emulsion drying method^[6], etc., these techniques have the following advantages, lower caclination temperature, shorter caclination time, narrow partical size distribution, better electrochemical properties. The author of this paper studies the preparation process of LiCoO_2 by two-steps method. The homogeneous precursor mixtures are prepared directly from aqueous solution, and the partical size and shape of precursor are controlled by adjusting the concentration of reactors, the pH of solution and the amount of additives. Better electrochemical performance LiCoO_2 are obtained by drying and roasting without carring on liquid-solid separation. The influence of preparation technique factors responsible for solution-phase reaction on partical size and shape of precursor will be discussed later in detail, thus the preparation process of LiCoO_2 is introduced emphasisly from good precursors.

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Biography: WANG Ying(born in 1971), Female, Senior-engineer, Master.

2 Experimental

Experimental details—A stoichiometric amount of Lithium and cobalt mixture aqueous solution with the cationic ratio were mixed well at room temperature with stirring. Cobalt nitrate solution was prepared by dissolving cobalt plate electrolysed ($\text{Co} > 99.9\%$) in pure nitric acid, dispersing agent and additive were added. And lithium hydroxide solution was obtained from $\text{LiOH} \cdot \text{H}_2\text{O}$ (Analytically pure) dissolving in distilled water, and concentrated ammonium hydroxide was put into it. Then oxidizer and concentrated ammonium hydroxide were added until a pH of the solution was adjusted to 10. The resultant solution was evaporated at $80\text{--}100^\circ\text{C}$ for a few hours until water was removed, the precursor was dried at 120°C , and decomposed first at $400\text{--}600^\circ\text{C}$ for 6–10 h, then further heated to 800°C for 4–24 h. LiCoO_2 was achieved by cooling to 150°C after grinding and sieving.

Physicochemical characterization—X-ray diffraction with $\text{Cu K}\alpha$ radiation was used to identify the crystalline phase of LiCoO_2 by X-ray diffractometer (D/MAX-1200X, Rigaku, Japan). The partical size and shape of LiCoO_2 were also examined using scanning electron microscopy (JSM-5910, JEOL, Japan) and laser size analyzer (JL-1166, china).

Electrochemical characterization—The test electrodes were prepared by mixing the active material, carbon black, PTFE in a weight ratio of 80:10:10 and then cold pressing the mixture into a pellet with diameter of 15.0–15.4 mm and thickness less than $500\mu\text{m}$ under a pressure of 30 MPa. The electrochemical studies were carried out in a experimental cell consisting of a working electrode and metal lithium plate reference electrode. Cell test instrument BTS-52A (5V/2A) was used at the current of 5mA.

3 Results and discussion

3.1 Thermal analyses

Optimum heat-treatment temperatures for preparing LiCoO_2 powders are determined with thermal analysis techniques. Fig. 1 shows the TG and DTG results of the precursor prepared with solution-phase reaction method, and Fig. 2 shows the DSC result. There are five steps of weight loss in the TG-DTG plots and three main endothermic peaks in the DSC plot. Firstly, the weight loss of about 2.92% starts at around 56°C , compared with it, a small endothermic peak is observed. This reaction corresponds to the volatilization of water in the precursor and the removal of part of crystalline water in cobalt nitrate. Secondly, the weight loss is observed to be about 1.09% between 56°C and 158°C , the obvious endothermic peak at 86°C indicates the removal of crystalline water in cobalt nitrate further. Third, the weight loss is 3.34% from 158°C to 345°C , and an endothermic peak appears at 245°C . This is because $\text{Co}(\text{OH})_2$ is oxidized and CoOOH is obtained around 260°C with the weight loss of 1%, besides, two side outcomes such as LiNO_2 , NH_4NO_3 , and cobalt nitrate, dispersing agent, additives, which are also decomposed. Fourth, the weight loss of 18.88% started at 345°C and was completed at 500°C . The endothermic peak at 360°C was due to formation of LT- LiCoO_2 . Finally, LT- LiCoO_2 is transformed to HT- LiCoO_2 starting between 600°C and 800°C . The total weight loss is about 36.91%. From thermal analyses, it is found that the crystallization of the hexagonal phase takes place above 600°C , and is prepared completely at 800°C , this is confirmed by XRD phase analysis. The decomposed temperature of pretreatment is controlled at $400\text{--}600^\circ\text{C}$.

3.2 XRD analyses

Fig. 3 shows the XRD patterns of LiCoO_2 obtained at various temperature from the precursor pretrea-

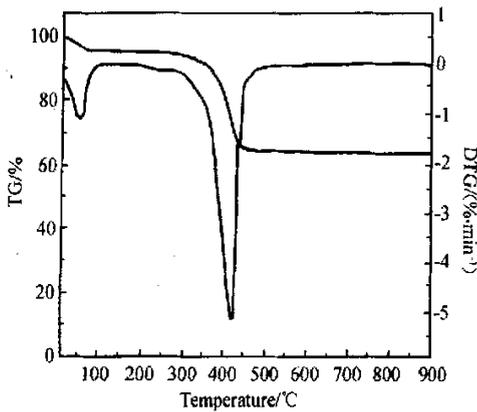


Fig. 1 TG-DTG curves of as-prepared precursor

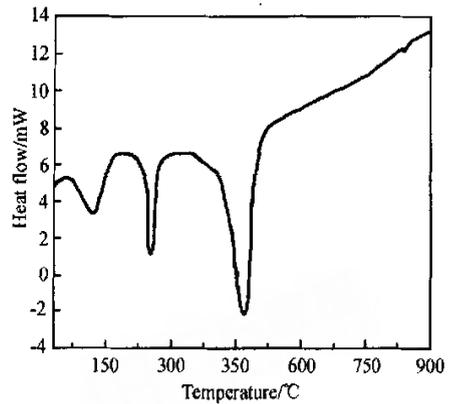


Fig. 2 DSC curve of as-prepared precursor

ted. It can be seen that HT-LiCoO₂ is synthesized by all the precursor calcined at 600–900°C, its main characteristic peaks are (003), (101), (006), (012), (104), (015), (107), (108), (110) successively. When a material is calcined at 600°C, a significant amount of LiCoO₂ phase and a small number of cobalt oxide phase are detected. Moreover, the bottom of (101) peak is more broad, and that of (006)/(012); (108)/(110) peaks are jointed with unclear splitting respectively, so it is possible that cations are located without ordering. As the temperature increases to 700°C, (101) peak is divided obviously into two peaks. The peak of Co₃O₄ phase appears at 36.9°. The splitting of (006)/(012) peaks are uncomplete, but that of (108)/(110) peaks are not so. As the temperature increased to 800°C, (006)/(012), (108)/(110) peaks are separated thoroughly, and there were negligible peak at 36.9°. High crystallization layer structure LiCoO₂ is synthesized because the pattern of it is the same as that given by the JCPDS card at 900°C. As the temperature increases, the intensity of the diffraction peaks of LiCoO₂ increases, although there are small traces of Co₃O₄ phase. Meanwhile, the location of every peak is changed, (003) peak shifts slightly to a lower Bragg angle, and the more sharp peak means the lattice rearrangement of crystal.

Fig. 4 shows the XRD patterns of the precursor fired at 900°C for various times. The clear splitting between (006)/(012) and (108)/(110) proves that cations are well located their sites without intersection. The well-ordered LiCoO₂ phase is synthesized even after 4h at 900°C, but the Co₃O₄ phase persists up to 12h. After firing for 16h, the peak of Co₃O₄ diminishes completely, and well-crystallized single phase LiCoO₂ can be obtained. When the time continues, the crystal structure will be integrated further, and (003) peak shifts slightly to a lower Bragg angle.

It is revealed that the structural changes of LiCoO₂ are affected by calcination temperature and times, then pure phase LiCoO₂ is prepared at 800°C for 16h combined with above-mentioned thermal analysis.

3.3 SEM analyses

Fig. 5 illustrates the microstructure of precursor and LiCoO₂. From Fig. 5(a), a few agglomerates consisting of the precursor particles are less than 5 μm in size, and particles were spherical, the average particle size of particle is 1.12 μm. From the LiCoO₂ picture of Fig. 5(b), the surface of particle is smooth without absorption and contains well monodispersed spherical fine particle size distribution with an average particle size of about 9.11 μm.

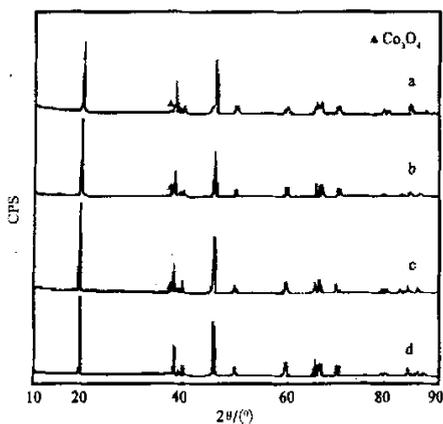


Fig. 3 XRD patterns of LiCoO_2 caclined at vari-
ous temperature for 16h

(a)— 600°C ; (b)— 700°C ; (c)— 800°C ; (d)— 900°C

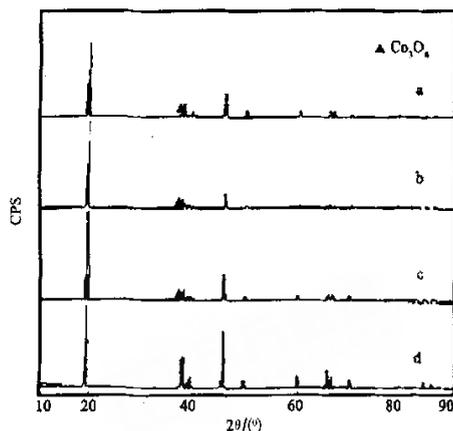


Fig. 4 XRD patterns of LiCoO_2 caclined at vari-
ous time at 900°C

(a)—4 h; (b)—8 h; (c)—12 h; (d)—16 h

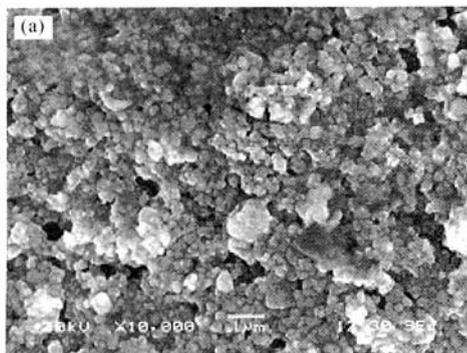


Fig. 5 SEM images

(a)—the precursor; (b)— LiCoO_2

3.4 Electrochemical properties

Fig. 6 shows the initial charge and discharge curve of LiCoO_2 . The charge capacities are 41.2 mAh by constant-current charging with cut-off voltage of 4.35 V, then charging with cut-off current of 1mA by constant-voltage charging, total charge capacities reach up to 45.9 mAh. The discharge capacities are 37.9 mAh, measured by discharging with cut-off voltage of 3.0 V. The initial discharge efficiency are 84.8%, discharge midpoint-voltage is 3.86 V, and discharge capacity is 95.3% above 3.6 V. the charge curve has a flatform at voltage between 4.0 V and 4.3 V, its charge specific capacity is 205 mAh/g, and discharge curve also exsits a flatform between 3.6 V and 4.3 V, its discharge specific capacity is 169 mAh/g.

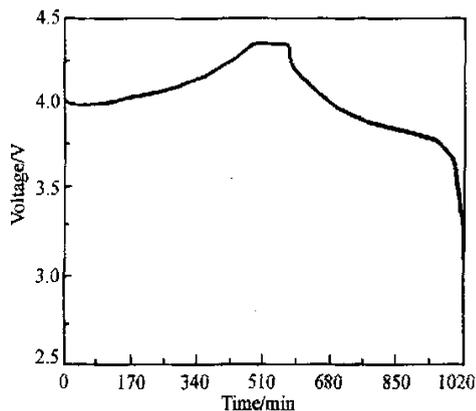


Fig. 6 The initial charge-discharge curve of LiCoO_2

4 Conclusions

Layer structure LiCoO₂ is synthesized by two steps method at lower calcination temperature for shorter calcination time, and it will be high crystallization without impure phase. Moreover, the different crystal phase of prepared LiCoO₂ varies from different calcination temperature and time, and then the best technique conditions of pure LiCoO₂ obtained are determined. The particle shape of LiCoO₂ is better and be similar to ball, the surface of particle is smooth without absorption, and particle size distribution is narrow, and it has well electrochemical performance, which charge and discharge specific capacity reaches up to 205 mAh/g, 169 mAh/g, respectively.

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