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# Microwave synthesis of $LiCoO_2$ cathode materials①

YU Yong-li(于永丽)[1], ZHAI Xiu-jing(翟秀静)[2],
FU Yan(符 岩)[2], YAO Guang-chun(姚广春)[2]
(1. School of Science, Northeastern University, Shenyang 110004, China;
2. School of Materials and Metallurgy, Northeastern University,
Shenyang 110004, China)

**Abstract:** $LiCoO_2$ powder used as cathode material for lithium ion battery was synthesized by microwave heating with $Co_3O_4$ and $LiOH \cdot H_2O$ as starting materials. The selection of output power and heating time of microwave can markedly affect the purity, morphology and electrochemical behaviors of the samples. X-ray diffraction (XRD) patterns display that the samples synthesized at 360 W for 10 min are pure layered $LiCoO_2$, and SEM photos show that the powders are crystalline with well-defined facets whose sizes are about 5 μm. The performance of $Co_3O_4$ and starting materials by microwave heating and conventional heating was investigated. It is indicated that $Co_3O_4$ decomposes into CoO in microwave field at 750 ℃ and the mechanism of preparing $LiCoO_2$ by microwave heating is different from that by conventional heating. The electrochemical behaviors of samples were tested. As a result, the highest specific discharge capacity is 134.3 mAh/g and the coulomb efficiency is 92.56%.

**Key words:** microwave synthesis; lithium-cobalt-oxygen compound; cathode materials; lithium ion battery
**CLC number:** TM 910.1 **Document code:** A

## 1 INTRODUCTION

$LiCoO_2$ is a commercially used cathode material for lithium ion battery. Compared with other cathode materials, such as $LiNiO_2$, $LiMn_2O_4$ and their doped compounds, $LiCoO_2$ has the advantages of high potential, excellent reversibility, long cycle life and reliable performance[1-4]. There are mainly several methods for synthesis of $LiCoO_2$, such as conventional ceramic method[5, 6], sol-gel synthesis[7], and low-temperature solution combustion[8]. Among these methods, the conventional ceramic method has been applied to industrial production, but it asks high temperature and long heating.

Microwave heating synthesis has been applied to prepare ceramic materials, nanometer sized powder, superconductors[9-11], etc, since it was invented in 1986. Recently microwave heating has been employed for the preparation of cathode materials for lithium ion battery[12-15]. Unlike the conventional ceramic method microwave heating is selective. The process of material being heated is associated closely with the polarization in molecules of the material, and the polarization in molecules leads to expending of current density in electrical field. The advantages of microwave synthesis are quick, clean, efficient and energy saving. Yan et al[14] have synthesized $LiCoO_2$ with $LiCH_3COO \cdot 2H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$ by microwave heating. Elumalap et al[15] mixed $Co(NO_3)_2$ and $LiOH_2 \cdot H_2O$ with water to prepare $LiCoO_2$. Compared with organics, $Co_3O_4$ is cheap and can absorb microwave effectively. In this paper, we use $Co_3O_4$ and $LiOH \cdot H_2O$ as starting materials to synthesize $LiCoO_2$, and then do some feasible research on industrial production of the compounds by microwave energy. Additionally the preparing mechanism of $LiCoO_2$ in microwave field was revealed.

## 2 EXPERIMENTAL

### 2.1 Preparation of $LiCoO_2$

$Co_3O_4$ and $LiOH \cdot H_2O$ (AR grade) were weighed accurately with a mole ratio of Co/Li= 1∶1 and mixed in an agate mortar thoroughly. The sample was put into a porcelain crucible, and then the crucible was placed into a microwave oven with 2.45GHz. At a proper output power the crucible was radiated for some time. After reaction, the product was cooled to room temperature in the oven. The as-prepared sample was poured into an agate mortar and ground. The final product was characterized by D/max-RB powder X-ray diffractometer and Shimadzu SSX-550 scanning electron microscope.

During the reaction, if the temperature meas-

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**Correspondence:** ZHAI Xiu-jing, Professor, PhD; Tel: +86-24-83678296; E-mail: yongli200004@163.com

urement was needed, turned off the microwave oven and put a thermocouple into the sample as soon as the crucible was taken out. Temperature reading was done by a data display temperature meter.

The preparation of $LiCoO_2$ by conventional ceramic method was carried out in a box resistant furnace.

### 2.2 Constant current charge-discharge test

The electrochemical characteristics of samples were studied using a two-electrode cell. $LiCoO_2$, carbon black and PVDF with a mass ratio of 85∶10∶5 were mixed with N-Methyl-2-ketopyrrolidine to form syrupy mixture. The mixture was repeatedly spread on to a nickel grid so as to obtain a uniform coating and finally dried at 120 ℃ for 8 h under vacuum. The electrodes thus prepared were compacted at 30 MPa pressure and then transferred into an argon filled glove box. The cell was assembled in the box with a lithium metal sheet as the counter electrode and a polypropylene film (Celgard) as the inter-electrode separator. The electrolyte consisted of 1 mol/L $LiPF_6$ in an ethylene carbonate (EC) and dimethyl carbonate (DMC) mixture (volume ratio 1∶1). The constant current charge-discharge experiment was carried out with a battery-testing instrument and the current is 0.5 $mA/cm^2$.

## 3 RESULTS AND DISCUSSION

### 3.1 Preparation of $LiCoO_2$

Firstly, the performance of $Co_3O_4$ and $LiOH \cdot H_2O$ mixture in microwave field was examined. At different output powers the mixture was irradiated for different times and the temperature was detected. The results are shown in Fig. 1. It is seen that the temperature increases sharply at the beginning of heating, and then the curves are flat. At different output powers, the temperature increases at different rates. The higher the output power is, the higher the rate is. Because microwave selectively heats the starting materials, $Co_3O_4$ can absorb microwave efficiently as cobalt is transition metal, but $LiOH \cdot H_2O$ can not. So the temperature elevation of starting materials is chiefly due to $Co_3O_4$, and $LiOH \cdot H_2O$ is heated indirectly. Generally $LiCoO_2$ is synthesized at 750 − 850 ℃. As seen in Fig. 1, the proper synthesizing time for $LiCoO_2$ at different power can be determined. At power 720, 540 and 360 W, the proper time is about 2, 6 and 10 min respectively. At power 180 W, even the heating time is 16 min, the temperature is only about 300 ℃. This indicates that the power is too low to synthesize $LiCoO_2$.

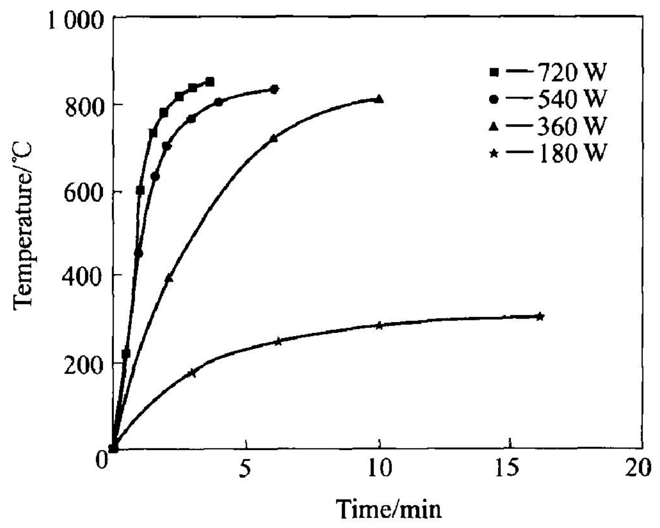

**Fig. 1** Temperature elevation of starting materials in microwave field

The performance of $LiCoO_2$ in microwave field was studied too. $LiCoO_2$ can absorb microwave efficiently, but the temperature does not increase as fast as the starting materials. The trend of temperature elevation curves is similar to that of $Co_3O_4$ and $LiOH \cdot H_2O$ mixture.

Samples prepared at different powers for different heating times were characterized by X-ray diffractometer, the results are shown in Fig. 2. It is observed that at 720 W there are impurity peaks at 2θ≈42° and 61° in the pattern, and at 540 W and 360 W the patterns are identical with reference standard's. This shows that the samples prepared at 540 W and 360 W are pure layered $LiCoO_2$.

$LiCoO_2$ can be synthesized with $Co_3O_4$ and

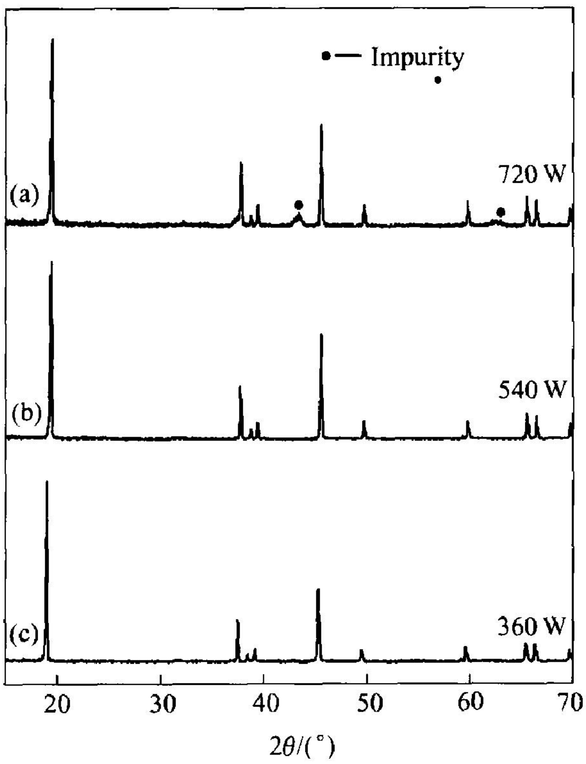

**Fig. 2** XRD patterns of samples prepared at different power

$LiOH \cdot H_2O$ at proper temperature for enough reaction time. Although the temperature of starting materials after being heated for 2 min at 720 W is about 800 ℃, at which $LiCoO_2$ can be prepared, 2 min reaction time is too short to complete the synthesis of $LiCoO_2$, which leads to the impurity in the sample. Slight sinter of samples is observed for longer heating time at such power, thus a lower power is suggested.

At 360 W power the starting materials were irradiated for 4, 6, 8, 10 min respectively and the as-prepared samples were characterized by XRD. The XRD patterns are shown in Fig. 3. For the heating time 4 or 6 min, there are impurity peaks, which are attributed to low reaction temperature. For heating time of 8 and 10 min the samples are pure layered $LiCoO_2$.

The scanning electron microscopy (SEM) photos of the above four samples are shown in Fig. 4. The particles become larger as the heating time increases. For heating time of 8 and 10 min the particles have well-defined facets.

Additionally, the crystallinity of the four samples increases with the heating time increasing, as shown in Table 1. The three strongest peaks of $LiCoO_2$ are (003), (104) and (101) peaks. The relative crystallinity of a sample is calculated as

$$R = h_{003}w_{003} + h_{104}w_{104} + h_{101}w_{101} \qquad (1)$$

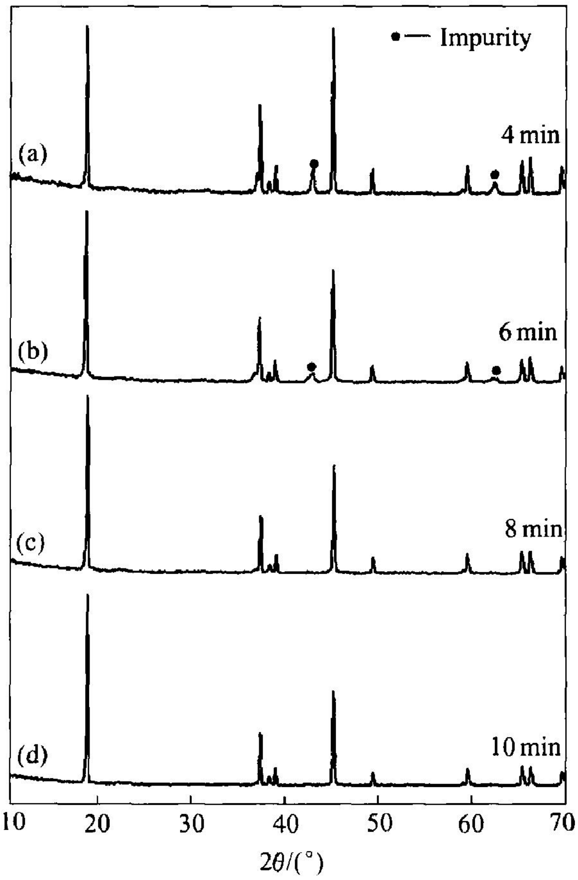

**Fig. 3** XRD patterns of samples prepared with different microwave heating times

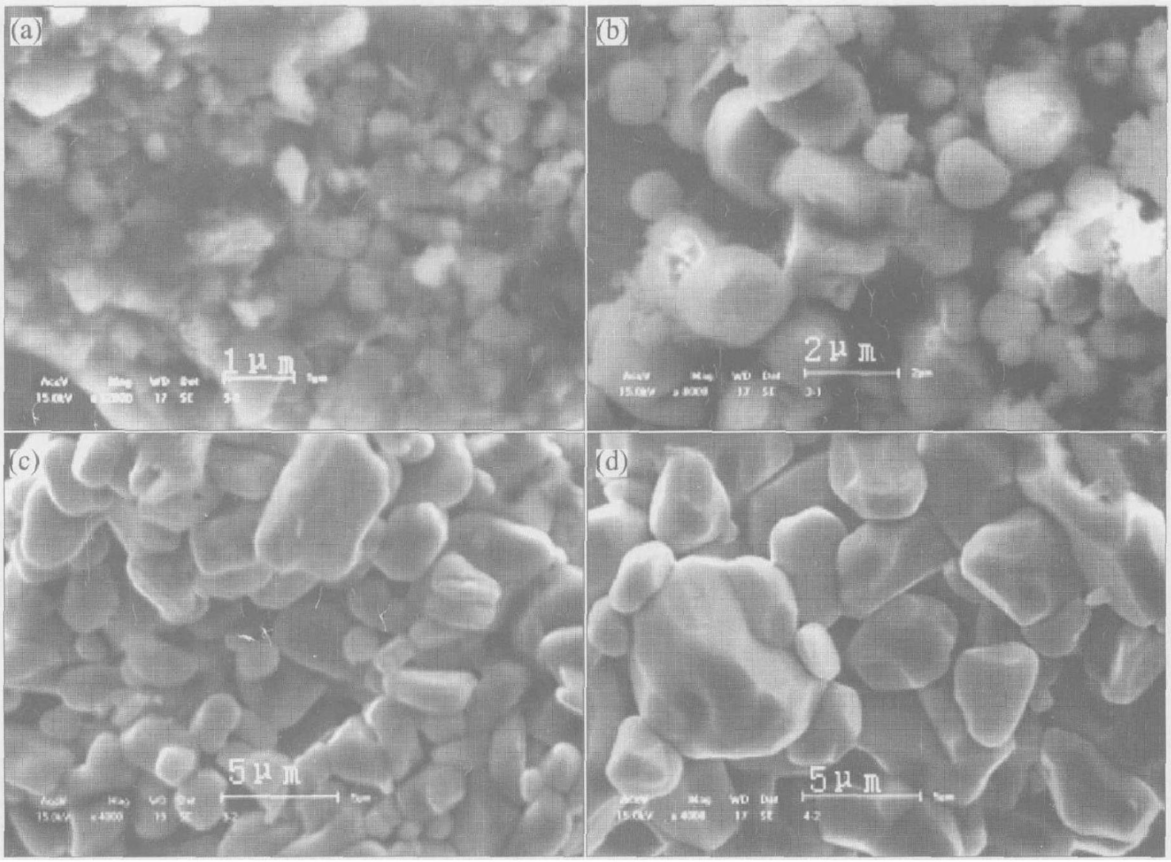

**Fig. 4** SEM photos of samples prepared with different heating times
(a) —4 min; (b) —6 min; (c) —8 min; (d) —10 min

**Table 1** Relative crystallinity of samples prepared with different heating times

| Heating time/min | 4 | 6 | 8 | 10 |
|---|---|---|---|---|
| Relative crystallinity | 403 | 806 | 1 565 | 1 604 |

where *h* is the height and *w* is the half-peak width of the peak, and *R* is relative crystallinity. The high crystallinity represents a well developed crystalline, which is beneficial to good electrochemical behaviors of $LiCoO_2$.

After the starting materials react completely, it is necessary to keep samples at proper temperature for some time in order to obtain well developed crystallinity. It is seen in Fig. 1 that, the temperature may become not suitable to synthesize $LiCoO_2$ if the heating time is too long at 720, 540 and 360 W. At 180 W the samples can absorb microwave but the temperature can retain stable. In the experiment, the synthesized $LiCoO_2$ are heated for some time at 180 W to improve their crystallinity.

The mixture of starting materials was heated for 10 min at power 360 W and irradiated for another 5 min at 180 W, then it was cooled to room temperature naturally. Using the above method the other two samples were prepared but the irradiating time at 180 W was 10 and 20 min instead. The as-prepared samples were characterized by XRD. The XRD patterns show that all samples are pure layered $LiCoO_2$, and the *d* values of (003), (104) and (101) peaks are listed in Table 2. It is seen that the *d* values decrease for heating time from 0 min to 10 min and tend to reference standard's, and the *d* values for heating 20 min are the same as those for heating 10 min.

**Table 2** Comparison of *d* values of samples for different heating times at 180 W

| Heating time/min | $d_{003}$/nm | $d_{104}$/nm | $d_{101}$/nm |
|---|---|---|---|
| 0 | 0.470 1 | 0.200 5 | 0.240 6 |
| 5 | 0.469 6 | 0.200 5 | 0.240 5 |
| 10 | 0.468 1 | 0.200 4 | 0.240 0 |
| 20 | 0.468 2 | 0.200 4 | 0.240 0 |
| Reference standard | 0.468 0 | 0.200 4 | 0.240 1 |

### 3.2 Mechanism of synthesizing $LiCoO_2$ by microwave

$Co_3O_4$ was heated by microwave at 360 W for 4 min and the detected temperature is about 750 ℃. It was observed that the color of the sample was light brown. This suggests that $Co_3O_4$ has decomposed as the color of $Co_3O_4$ is black. The sample was characterized by XRD, as shown in Fig. 5 (a). There are two other peaks at $2\theta = 42.37°$ and $61.47°$ which do not belong to $Co_3O_4$. These two peaks are indexed to peaks of CoO. This indicates that by microwave heating $Co_3O_4$ decomposes into CoO at 750 ℃. By conventional heating no change of $Co_3O_4$ is observed until 900 ℃, and its XRD pattern is identical to the reference standard of $Co_3O_4$ (as seen in Fig. 5(b)). It is suggested that the performance of $Co_3O_4$ in microwave field is different from that by conventional heating.

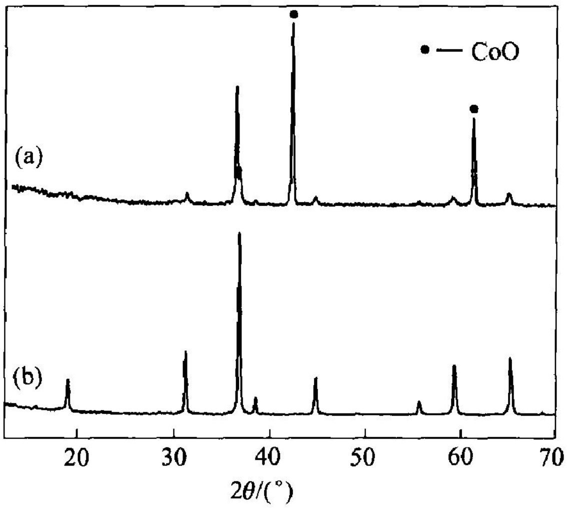

**Fig. 5** XRD patterns of $Co_3O_4$ by microwave heating at 750 ℃(a) and conventional heating at 900 ℃(b)

At 360 W the starting materials were heated for 4, 6, 8 and 10 min respectively. The color of the first two samples was light brown and the last two samples were blue-grey. The XRD patterns of the four samples are shown in Fig. 3. Certainly the impurity peaks belong to CoO. This indicates that during synthesizing $LiCoO_2$ the following reactions must occur:

$$2Co_3O_4 \longrightarrow 6CoO + O_2$$

$$4CoO + O_2 + 4LiOH \longrightarrow 4LiCoO_2 + 2H_2O$$

By conventional heating the starting materials were heated at 350, 400, 450, 500, 700, 750 ℃ respectively, and the XRD patterns are shown in Fig. 6. It is seen that there are only peaks of starting materials and $LiCoO_2$ but no CoO peaks. By conventional heating the synthesis reaction is: $4Co_3O_4 + O_2 + 12LiOH \longrightarrow 12LiCoO_2 + 6H_2O$. This indicates that the mechanism of synthesizing $LiCoO_2$ by conventional heating is different from that by microwave heating. By the conventional heating both of the samples prepared at 700 ℃ and 750 ℃ are $LiCoO_2$, but the first one is spinel-like structure (LT-$LiCoO_2$) and the other is ideal layered structure (HT-$LiCoO_2$).

The temperature elevation mechanism of material by conventional heating is different from that

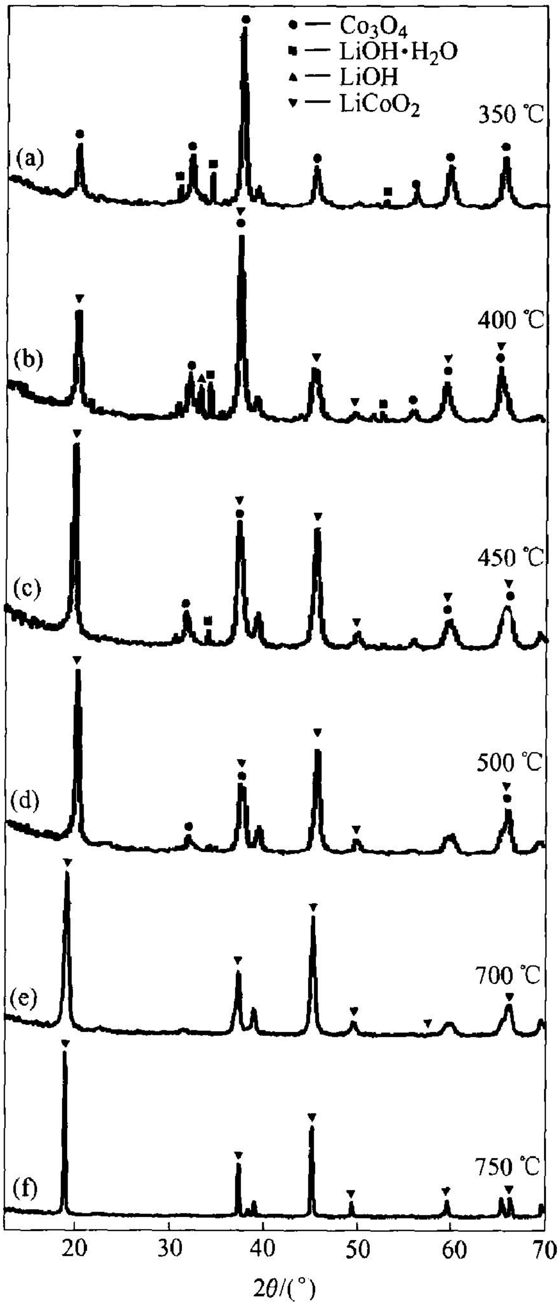

**Fig. 6** XRD patterns of samples prepared by conventional heating

in microwave field. In microwave field the material is heated from inner of molecules that are polarized by microwave. Besides temperature elevation the material could obtain microwave effect, which is different from that by conventional heating. It is a very good example of microwave effect that $Co_3O_4$ decomposes at 750 ℃ in microwave field and has no change until 900 ℃ by conventional heating.

### 3.3 Electrochemical behaviors of $LiCoO_2$

The electrochemical characterization of the four samples prepared at different powers for different heating times was carried out at 3.0−4.2 V, as seen in Fig. 7. The discharge capacity of the sample for profile a is as high as 134.3 mAh/g because the crystallinity of the sample has developed well and the charge-discharge efficiency is 92.56%. The discharge capacity of the sample for profile d is the lowest. Thus it is very important to control proper output power and heating time of microwave so as to synthesize $LiCoO_2$ with good electrochemical behaviors. After 10 cycles the discharge capacity of the sample for profile a is 118 mAh/g. There is a 12% capacity decrement at the end of 10 cycles.

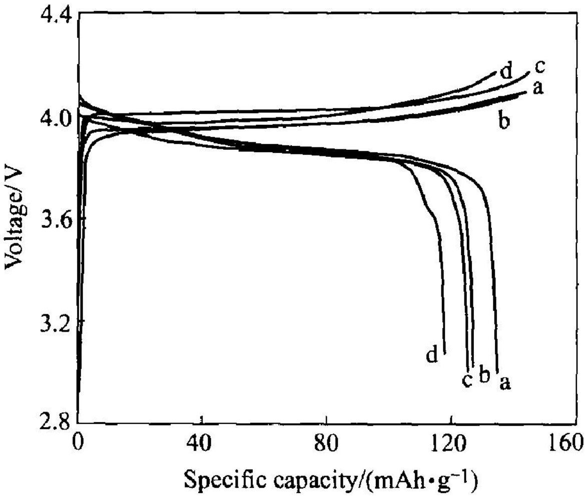

**Fig. 7** Charge and discharge curves of prepared samples

a —Heated at 360 W for 10 min and 180 W for 10 min, cooled naturally;
b —Heated at 360 W for 10 min and 180 W for 5 min, cooled naturally;
c —Heated at 360 W for 10 min, cooled naturally;
d —Heated at 540 W for 4 min, cooled naturally

## 4 CONCLUSION

By microwave heating the pure layered $LiCoO_2$ was synthesized with $Co_3O_4$ and $LiOH \cdot H_2O$ as the starting materials and the samples were characterized by X-ray diffractometer and scanning electron microscope. It is indicated that the output power and heating time of microwave have great effect on the purity, morphology and electrochemical behaviors of samples. The performance of $Co_3O_4$ and the starting materials by microwave heating and conventional heating was examined. It is found that $Co_3O_4$ decomposes into CoO in microwave field at 750 ℃ and no change occurs by conventional heating until 900 ℃, and the synthesis of $LiCoO_2$ in microwave field is two-step reaction. The electrochemical behaviors of samples were tested. The sample prepared at 360 W for 10 min and 180 W for another 10 min and then cooled naturally has the highest discharge capacity of 134.3 mAh/g and the charge-discharge efficiency of 92.56%. After 10 cycles there is a 12% discharge capacity decrement. It is shown that synthesizing $LiCoO_2$ by microwave heating is a clear, quick and energy saving method.

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